

Experimental and modelling analysis of the separation of ionic salts solution in nanofiltration process

Anna Kowalik-Klimczak, Mariusz Zalewski, Paweł Gierycz

Warsaw University of Technology
Faculty of Chemical and Process Engineering
Waryńskiego 1, 00-645 Warsaw, Poland,
e-mail: a.kowalik@ichip.pw.edu.pl

This paper presents the possibility of the use of Donnan and Steric Partitioning Pore Model (DSPM) based on the extended Nernst-Planck equation for interpretation of the separation of chromium(III) and chloride ions from concentrated salt solution in nanofiltration process. Results of predictions obtained with the analyzed model showed the significant effect of the pore dielectric constant on separation of chromium(III) and chloride ions from concentrated salt solution on nanofiltration membranes. It was found that the increase of pore dielectric constant caused the decrease of chromium(III) and chloride ions separation. Additionally, the satisfactory agreement between experimental and predicted data was stated. The Donnan and Steric Partitioning Pore Model may be helpful for the monitoring of nanofiltration process applied for different industrial wastewater treatment.

Key words: Nanofiltration, Nernst-Planck equation, Modelling, Salts solution

Introduction

Nanofiltration is a membrane pressure technique, which allows for both high efficiency and high selectivity of a process [1]. That is why it can be successfully applied for softening of both surface and ground water [2-5] and separation of metal ions from industrial wastewaters [6-11]. According to the literature data [9-11] and our own investigations [12-14], one of the most important and interesting research area of nanofiltration is separation of chromium (III) ions from concentrated salt solutions characterized by low pH. The nanofiltration membrane in such condition becomes non-permeable for multi-charged ions and permeable for one-charged anions and cations [14-16]. That is why nanofiltration seems to be a promising process allowing for effective and efficient separation of chromium (III) ions from concentrated salts solutions at low pH. However, for prediction of the productivity and the effectiveness of the ions separation from the examined salt solutions it is necessary to elaborate the mathematical model describing this process.

Based on the results of previous investigations [13,14], it was found that the chromium (III) ions separation from concentrated salt solutions at low pH depends on the type of the used nanofiltration membrane. The functional groups present at membrane surface, granting the respective charge of the surface [15-17], are the most important for the selectivity of nanofiltration membrane. The membrane surface charge depends on pH and solution composition (concentration and kind of a salt) [15-20]. The streaming potential method is the most often applied for

the measurement of the value of the surface charge of membranes [15-22]. This method allows for appointing the streaming potential, which can be further recalculated on zeta potential by the use of Helmholtz-Smoluchowski equation [23,24].

Our previous investigations [14,25] showed also that one of the most important factor which limits an affectivity of chromium(III) ions separation from concentrated salt solutions at low pH is concentration polarization caused by the gathering of solution components near membrane surface. In the case of nanofiltration membranes this phenomenon causes additionally change of both kind and density of the surface membrane charge. In consequence the membrane selectivity is also changed [14].

In spite of many applications of the nanofiltration [1-12], the separation mechanism of the ionic salt was not still entirely clarified. Many different theories attempt to explain the ions separation mechanism on nanofiltration membranes [11,25-28]. After analysing of the literatures data [29-33] one can state that both theoretical and experimental works explaining the ions separation mechanism on nanofiltration membranes are not yet satisfactory and require further actions.

Recently the modelling of nanofiltration process of salt solution has been widely investigated [26-30]. The mass transfer through the membrane was described by different models such as Kedem-Katchalsky [28] or Spiegler-Kedem [29]. However none of the models used took into consideration a density of membrane surface charge, which, as it was mentioned, is one of the main factors in the case of

nanofiltration of concentrated salts solutions [11,26,27]. Therefore, the Donnan and Steric Partitioning Model (DSPM) based on the extended Nernst-Planck equation has been proposed for interpretation of the separation of chromium(III) and chloride ions from concentrated salt solution at low pH on nanofiltration membranes. In this model, membrane was considered as a porous medium composed of cylindrical single nanometer-size pores uniformly dispersed [11]. One of the main parameters governing retention of ions by the membrane is pore dielectric constant (ϵ_p) [11,26,27]. According to Deon et al. [26,27] the value of pore dielectric constant is lower for membrane characterized by smaller pore size. The confinement effect inside the pores is probably higher leading to a lower dielectric constant. In the present work, the effect of pore dielectric constant on chromium (III) and chloride ions retention was analyzed.

DSPM model description

Basic equations used in the DSPM model are summarized in Table 1 and the all symbols are explained at the end of the paper.

The extended Nernst-Planck equation (1) described the transport of ion inside the membrane. This equation contains three terms due to contributions from diffusion, electromigration and convection, respectively. Solving this equation requires knowing the boundary conditions at the pore inlet and outlet (2). The hindered nature of diffusion and convection of the ions inside the membrane accounted for the terms $K_{i,d}$ (3) and $K_{i,c}$ (4). $K_{i,d}$ and $K_{i,c}$ are expressed as a function of the ion radius r_i related to the pore radius r_p ratio λ_i (5) and (6). The solvent velocity within the pore (V) related to the pressure gradient through the pore is calculated using the Hagen-Poiseuille expression (7), where the osmotic pressure difference ($\Delta\pi$) is calculated by Van't Hoff equation (8). The solvation energy barrier ΔW_i (9) represented by a decrease of the effective dielectric constant of the solution in the pores is described by the Born model. The electroneutrality conditions in the bulk solution and inside the membrane are given as equations (10) and (11), respectively.

Conducting the model calculations apart from accepting process conditions such as: operating pressure (ΔP) and concentration of the ion in feed ($c_{i,w}$) it was necessary to assume the following parameters: the membrane hydraulic permeability coefficient (L_p), the mean pore radius (r_p), the membrane charge density of the membrane (X_d), diffusion coefficient of ions (D_i) and finally the pore dielectric constant (ϵ_p). The used equations (Fig. 1) allow for evaluation of ions transport through the membrane taking into account the membranes selectivity determined by the retention (R_i), as well as productivity expressed by the permeate flux (J_p).

The influence of the pore dielectric constant (ϵ_p) on chromium(III) and chloride retention during nanofiltration

Table 1. Basic equations of the DSPM model

The extended Nernst-Planck equation:	
$J_i = -K_{i,d}D_i \frac{dc_i}{dx} - \frac{z_i c_i K_{i,d} D_i}{RT} F \frac{d\psi}{dx} + K_{i,c} c_i V$	(1)
Steric, Donnan and dielectric effects:	
$\frac{c_i}{C_i} = \frac{\gamma_{i,sol}}{\gamma_{i,pore}} \phi_i \exp(-\Delta W_i) \exp\left(\frac{-z_i F}{RT} \Delta \Psi_D\right)$	(2)
Hidrance factors:	
$K_{i,d} = 1 - 2,30\lambda_i + 1,154\lambda_i^2 + 0,224\lambda_i^3$	(3)
$K_{i,c} = (2 - \phi_i)(1 + 0,054\lambda_i - 0,998\lambda_i^2 - 0,44\lambda_i^3)$	(4)
Steric partitioning:	
$\phi_i = (1 - \lambda_i)^2$	(5)
where:	
$\lambda_i = \frac{r_i}{r_p}$	(6)
Hagen-Poiseuille equation:	
$V = \frac{r^2(\Delta P - \Delta \pi)}{8\eta \Delta x}$	(7)
where:	
$\Delta \pi = RT \sum_{i=1}^n (c_{i,w} - c_{i,p})$	(8)
Born solvation energy barrier:	
$\Delta W_i = \frac{z_i^2 e^2}{8\pi \epsilon_o k_b T r_i} \left(\frac{1}{\epsilon_p} - \frac{1}{\epsilon_b} \right)$	(9)
Electroneutrality in bulk solution/within the pores:	
$\sum_{i=1}^n z_i c_i = 0$	(10)
$\sum_{i=1}^n z_i c_i + X_d = 0$	(11)

of concentrated salt solution characterized by low pH was analyzed in this work. The properties of the ionic species analyzed in this model are listed in Table 2.

Experimental

The experiments were carried out at laboratory scale in cross flow cell made of stainless steel operated in batch mode with circulation (Fig. 2). The nanofiltration of concentrated salt solutions containing 2 g dm⁻³ Cr³⁺, 10/14 g dm⁻³ Cl⁻, 10 g dm⁻³ SO₄²⁻ and characterized by pH≈4 was conducted for $\Delta P = 14$ bar.

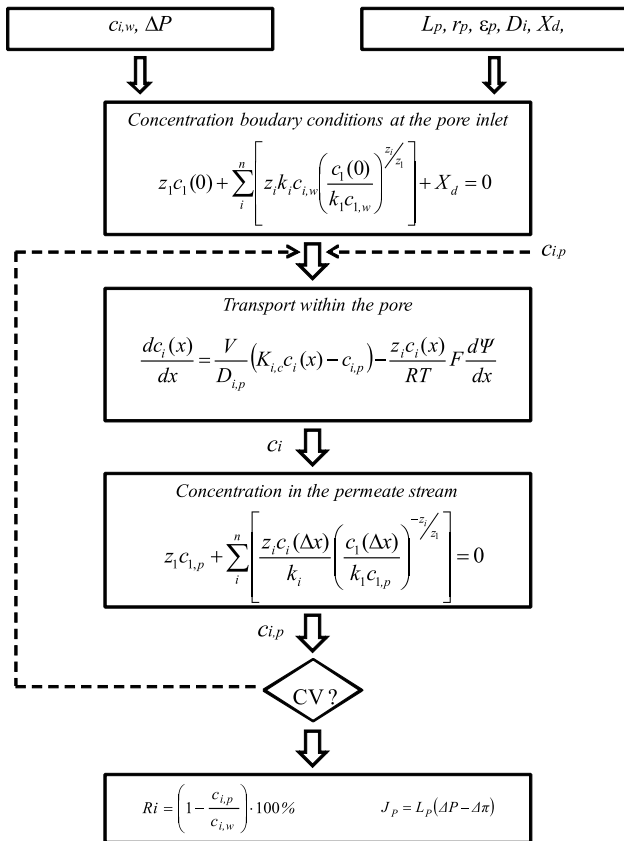


Figure 1. Numerical procedure diagram

Table 2. Properties of ionic species

Parametr	Cr ³⁺	Cl ⁻
M _i [g mol ⁻¹]	52.00	35.45
r _i [nm]	0.400	0.121
D _i · 10 ⁻⁹ [m ² s ⁻¹]	0.062	2.031
z _i [-]	3	1

The commercial nanofiltration flat sheet membranes (under symbol DL) with effective area of 0.0155 m² provided by GE Osmonics were used in the experiments. The characteristic of tested nanofiltration membrane is presented in Table 3.

After the end of the experiment, samples of permeate and retentate have been collected for determination of the chromium(III) and chloride concentration. The samples of permeate, feed and retentate have been analyzed using the following methods:

- chromium(III) – spectrophotometer NANOCOLOR UV/VIS using 1,5-difenylokarbazyde method with wave length $\lambda = 540$ nm,
- chloride - the Mohr titration method.

The feed solution has been prepared using the following chemicals: CrCl₃·6H₂O (Sigma-Aldrich), pure NaCl (Chempur®), pure Na₂SO₄ (Chempur®) and the deionized

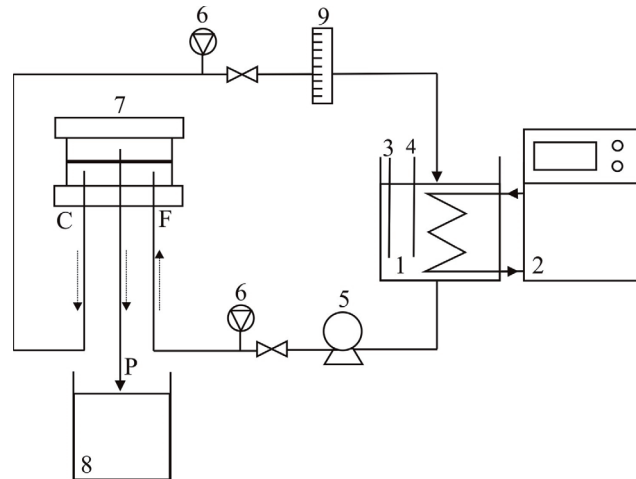


Figure 2. Schema of the laboratory plant: 1 – feed/retentate tank, 2 – thermostat, 3 – measurement of temperature, 4 – measurement of pH, 5 – high pressure pump, 6 – manometer, 7 – NF membrane module, 8 – permeate tank, 9 – flowmeter, P – permeate, F – feed, and C – retentate (concentrate)

Table 3. Characteristic of nanofiltration membrane used in the experiments

Surface material	Poly(piperazine-amide)
Support material	Polysulfone
Type of membrane	Thin film
Cut-off (g mol ⁻¹)	150-300
Permeability coefficient 10 ⁻⁶ (m ³ m ⁻² ·s ⁻¹ ·bar ⁻¹)	2.4 [13]
pH range	2-11
Max. temperature (°C)	90
Max. pressure (bar)	40
Isoelectric point (pH)	3.0 [25]
Zeta potential (mV) (pH=4, t=25°C)	-14.0 [25]

water. The feed solution was characterized by pH ≈ 4. For initial pH correction the pure HCl (Lachner) was used. The pH was measured by pH-meter (Mettler Toledo SevenEasy).

Result and discussion

The influence of pore dielectric constant (ε_p) on chromium(III) and chloride ions retention was illustrated in Fig. 3.

The decrease of chromium(III) and chloride ions retention with the increase of pore dielectric constant (ε_p) was

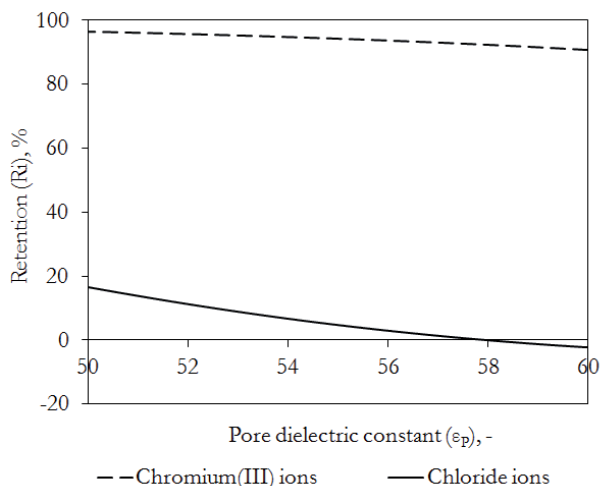


Figure 3: Retention (R_i) of chromium(III) and chloride ions vs. pore dielectric constant (ϵ_p)

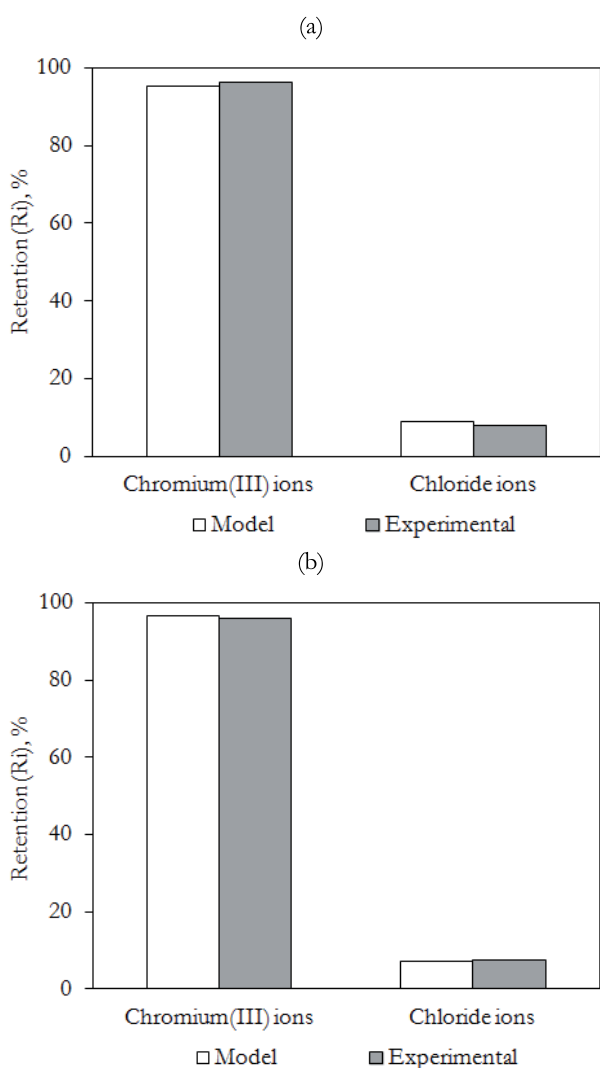


Figure 4. Comparison of model and experimental chromium (III) and chloride retention (R_i) for feed composition: (a) $2 \text{ g dm}^{-3} \text{ Cr}^{3+}$, $10 \text{ g dm}^{-3} \text{ Cl}^-$, $10 \text{ g dm}^{-3} \text{ SO}_4^{2-}$; (b) $2 \text{ g dm}^{-3} \text{ Cr}^{3+}$, $14 \text{ g dm}^{-3} \text{ Cl}^-$, $10 \text{ g dm}^{-3} \text{ SO}_4^{2-}$

observed. According to Gomes et al. [11] this phenomenon can be explained by Born solvation energy effect (Table 1 - equation 9). The difference in dielectric constant between external and internal (i.e. inside pores) solutions caused exclusion of both co-ions and counter-ions from membrane pores. Thus, if the pore dielectric constant increases, the Born effect becomes weaker and the salt retention decreases (Fig. 3).

Comparison of the results of model calculation with the experimental results for the selected dielectric constant in membrane pore ($\epsilon_p = 53$) have been performed. The obtained results of retention for chromium(III) and chloride ions were shown in Fig. 4.

The selected value of ϵ_p allowed for the satisfactory agreement between model and experimental values of the chromium(III) and chloride ions retention. The difference between experimental and modelling retention of chromium (III) and chloride ions was less than 1%. Additionally it was found that the chloride ion concentration has not influence the pore dielectric constant, because the same ϵ_p values was received for 10 and 14 g dm^{-3} . Deon et al. obtained similar results for single as well as mixing salt solution [26,27].

Conclusion

The main objective of this work was the experimental and modelling analysis of the nanofiltration process used for separation of the chromium (III) and chloride ions from concentrated salts solution at low pH. The tested mathematical model was based on extended Nernst-Planck equation. The effect of pore dielectric constant on chromium (III) and chloride ions retention was analyzed. Based on the model it was observed the reduction of the retention of chromium(III) and chloride ions with the increase of dielectric constant in pore of the membrane. Selected appropriate pore dielectric constant gave the very good agreement between experimental and model results.

Acknowledgements

“This project was financed by National Science Centre granted on the basis of the decision number DEC-2013/09/N/ST8/01784”

Nomenclature

- J_i – molar flux of species i [$\text{m}^3 \text{ m}^{-2} \text{ s}^{-1}$],
- $K_{i,d}$ – ionic hindrance factor for diffusion [-],
- $K_{i,c}$ – ionic hindrance factor for convection [-],
- D_i – diffusion coefficient of ion [$\text{m}^2 \text{ s}^{-1}$],
- c_i – concentration of ion inside pores of the membrane [mol m^{-3}],
- $c_{i,p}$ – concentration of ion in permeate [mol m^{-3}],
- $c_{i,w}$ – concentration of ion in feed [mol m^{-3}],

C_i – concentration of ion within the polarization layer [mol m⁻³],
 z_i – valence of ion [-],
 F – Faraday constant [C mol⁻¹],
 R – universal gas constant [J mol⁻¹ K⁻¹],
 T – temperature [K],
 Ψ – electrical potential of ion inside pores [V],
 J_p – permeate flux in membrane [m³ m⁻² s⁻¹],
 V – solvent velocity [m s⁻¹],
 k – mass transfer coefficient [m s⁻¹],
 Δx – membrane thickness [m],
 ΔP – applied pressure [bar],
 $\Delta \pi$ – osmotic pressure difference [bar],
 ϵ_0 – permittivity of free space [-],
 ϵ_p – pore dielectric constant [-],
 ϵ_b – bulk dielectric constant [-],
 e – electron charge [-],
 k_B – Boltzmann constant [J K⁻¹],
 η – dynamic viscosity [bar s],
 X_d – membrane charge density [mol m⁻³],
 ΔW_i – Born solvation energy barrier [J],
 $\Delta \Psi_D$ – Donnan potential [V],
 $\gamma_{i,sol}$ – activity coefficient of ion in the solution side of the interface [-],
 $\gamma_{i,pore}$ – activity coefficient of ion in the pore side of the interface [-],
 L_p – permeability coefficient of membrane [m³ m⁻² s⁻¹ bar⁻¹],
 r_p – pore radius [m],
 r_i – ionic radius [m],
 R_i – retention [%].

References

- [1] Koltuniewicz A.B., Drioli E.: Membrane in clean technology. Theory and practice, Vol.1-2, Wiley-VCH Verlag GmbH & Co. KGaA, 2008
- [2] Ahmad A.L., Ooi B.S., Wahab Mohammad A., Choudhury J.P.: Development of a highly hydrophilic nanofiltration membrane for desalination and water treatment, *Desalination*, 168, pp. 215-221, 2004
- [3] Ghizellaoui S., Chibani A., Ghizellaoui S.: Use of nanofiltration for partial softening of very hard water, *Desalination*, 179, pp. 315-322, 2005
- [4] Orecki A., Tomaszewska M., Karakulski K., Morawski A.W.: Surface water treatment by the nanofiltration method, *Desalination*, 162, pp. 47-54, 2004
- [5] Bellona C., Drewes J.E.: Viability of a low-pressure nanofilter in treating recycled water for water reuse applications: A pilot-scale study, *Water Research*, 41, pp. 3948-3958, 2007
- [6] Ku Y., Chen S., Wang W.: Effect of solution composition on the removal of copper ions by nanofiltration, *Sep. Purif. Technol.*, 43, pp. 135-142, 2005
- [7] Ortega L.M., Lebrun R., Blais J.F., Hausler R.: Removal of metal ions from an acidic leachate solution by nanofiltration membranes, *Desalination*, 227, pp. 204-216, 2008
- [8] Wang Z., Liu G., Fan Z., Yang X., Wang J., Wang S.: Experimental study on treatment of electroplating wastewater by nanofiltration, *J. Membr. Sci.*, 305, pp. 185-195, 2007
- [9] Ortega L.M., Lebrun R., Noël I.M., Hausler R.: Application of nanofiltration in the recovery of chromium(III) from tannery effluents, *Sep. Purif. Technol.*, 44, pp. 45-52, 2005
- [10] Das C., Patel P., De S., DasGupta S.: Treatment of tanning effluent using nanofiltration followed by reverse osmosis, *Sep. Purif. Technol.*, 50, pp. 291-299, 2006
- [11] Gomes S., Cavaco S.A., Quina M.J., Gando-Ferreira L.M.: Nanofiltration process for separating Cr(III) from acid solutions: Experimental and modelling analysis, *Desalination*, 254, pp. 80-89, 2010
- [12] Religa P., Kowalik A., Gierycz P.: Application of nanofiltration for chromium concentration in the tannery wastewater, *J. Hazard. Mater.*, 186, pp. 288-292, 2011
- [13] Religa P., Kowalik A., Gierycz P.: Effect of membrane properties on chromium(III) recirculation from concentrate salt mixture solution by nanofiltration, *Desalination*, 274, pp. 164-170, 2011
- [14] Religa P., Kowalik A., Gierycz P.: A new approach to chromium concentration from salt mixture solution using nanofiltration, *Sep. Purif. Technol.*, 82, pp. 114-120, 2011
- [15] Tanninen J., Mänttari M., Nyström M.: Effect of salt mixture concentration on fractionation with NF membranes, *J. Membr. Sci.*, 283, pp. 57-64, 2006
- [16] Sharna R.R., Chellam S.: Solute rejection by porous thin film composite nanofiltration membranes AT high feed water recoveries, *J. Colloid Interface Sci.*, 328, pp. 353-366, 2008
- [17] Childress A.E., Elimelech M.: Relating nanofiltration membrane performance to membrane charge (electrokinetic) characteristic, *Environ. Sci. Technol.*, 34, pp. 3710-3716, 2000
- [18] Afonso M.D., Hagemeyer G., Gimbel R.: Streaming potential measurements to assess the variation of nanofiltration membranes surface charge with the concentration of salt solutions, *Sep. Purif. Technol.*, 22-23, pp. 529-541, 2001
- [19] Rice G., Barber A.R., O'Connor A.J., Pihlajamaki A., Nyström M., Stevens G.W., Kentish S.E.: The influence of dairy salts on nanofiltration membrane charge, *J. Food Eng.*, 107, pp. 164-172, 2011
- [20] Teixeira M.R., Rosa M.J., Nyström M.: The role of membrane charge on nanofiltration performance, *J. Membr. Sci.*, 265, pp. 160-166, 2005
- [21] Ernst M., Bismarck A., Springer J., Jekel M.: Zeta-potential and rejection rates of a polyethersulfone nanofiltration membrane in single salt solutions, *J. Membr. Sci.*, 165, pp. 251-259, 2000
- [22] Weber R., Chmiel H., Mavrov V.: Characteristics and application of new ceramic nanofiltration membranes, *Desalination*, 157, pp. 113-125, 2003
- [23] Al-Amoudi A., Williams P., Mandale S., Lovitt R.W.: Cleaning results of new and fouled nanofiltration membrane characterized by zeta potential and permeability, *Sep. Purif. Technol.*, 54, pp. 234-240, 2007
- [24] Petrinic I., Pusic T., Mijatovic I., Simoncic B., Sostar Turk S.: Characterization of polymeric nanofiltration membranes, *Kem. Ind.*, 56, pp. 561-567, 2007
- [25] Religa P., Kowalik-Klimczak A., Gierycz P.: Study on the behavior of nanofiltration membranes using for chromium(III) recovery from salt mixture solution, *Desalination*, 315, pp. 115-123, 2013
- [26] Deon S., Escoda A., Fievet P.: A transport model considering charge adsorption inside pores to describe salts rejection by nanofiltration membranes, *Chem. Eng. Sci.*, 66, pp. 2823-2832, 2011
- [27] Deon S., Dutournie P., Limousy L., Bourseau P.: Transport of salt mixture through nanofiltration membranes: Numerical

- identification of electric and dielectric contributions, Sep. Purif. Technol., 69, pp. 225-233, 2009
- [28] Chaudhari L.B., Murthy Z.V.P.: Separation of Cd and Ni from multicomponent aqueous solutions by nanofiltration and characterization of membrane using IT model, J. Hazard. Mater., 180, pp. 309-315, 2010
- [29] Kelewou H., Lhassani A., Merzouki M., Drogui P., Sellamuthu B.: Salts retention by nanofiltration membranes: Physicochemical and hydrodynamic approaches and modeling, Desalination, 277, pp. 106-112, 2011
- [30] Zhua H., Szymczyk A., Balanec B.: On the salt rejection properties of nanofiltration polyamide membranes formed by interfacial polymerization, J. Membr. Sci., 379, pp. 215-223, 2011
- [31] Schaep J., Vandecasteele C., Mohammad A.W., Bowen W.R.: Modelling the retention of ionic components for different nanofiltration membranes, Sep. Purif. Technol., 22-23, pp. 169-179, 2001
- [32] Mohammad A.W., Takriff M.S.: Preciding flux and rejection of multicomponents salts mixture in nanofiltration membranes, Desalination, 157, pp. 105-111, 2003
- [33] Hagemeyer G., Gimbel R.: Modelling the salt rejection of nanofiltration membranes for ternary ion mixture and for single salts at different pH value, Desalination, 117, pp. 247-256, 1998

Author(s): MSc Eng. Anna KOWALIK-KLIMCZAK – *PhD Candidate. Her research activities are mainly focused on the applicability of membrane processes for the treatment of chromium wastewater.*

PhD Eng. Mariusz ZALEWSKI – *Assistant Professor. His research activities are mainly focused on chaos and periodic oscillations in chemical reactors and bioreactors.*

Professor Paweł GIERYCZ – *Professor. His research activities are mainly focused on thermodynamics of phase equilibria in multicomponent solutions and the applications of membranes in environmental protection.*