



Desalination of chromium tannery wastewater by nanofiltration with different diafiltration mode

Paweł Religa^a, Bernadetta Kaźmierczak^{b,*}

^a*Department of Environmental Protection, Kazimierz Pulaski University of Technology and Humanities in Radom, Chrobrego 27, Radom, Poland, Tel. +48 48 3617583; Fax: +48 48 3617598; email: p.religa@uthrad.pl*

^b*Faculty of Building Services, Hydro and Environmental Engineering, Warsaw University of Technology, Nowowiejska 20, 00-653 Warsaw, Poland, email: bernadettakazmierczak@gmail.com*

Received 4 April 2016; Accepted 4 August 2016

ABSTRACT

This paper compares nanofiltration (NF) processes conducted by a constant volume diafiltration (CVD) and an intermittent volume diafiltration (IVD). The authors discuss the way the processes are executed and influences on processes of salt removal, chromium(III) rejection as well as the permeate flux. This investigation enabled the conclusion that the rate of salt elution depended on the method of washing diluent addition. The continuous dilution of the pre-concentrated feed solution, during the diafiltration step in NF in the CVD mode, enabled the maintenance of the stable salt concentration in the permeate flux, and thus made the elution of chloride ions efficient. In NF in the IVD mode, the recurring addition of high amount of a washing diluent resulted in significant decrease of the salt concentration in the solution and a lower level of chloride ions elution. The salt elution in NF in the CVD mode reached the level of ca. 62%, while in NF in the IVD mode only 54%. The authors stated that NF in the CVD mode enabled better desalination of the simulated chromium tannery wastewater than NF in the IVD mode. Moreover, chromium retention at the level of 93% and 95% for the CVD and IVD diafiltration was maintained.

Keywords: Nanofiltration; CVD diafiltration; IVD diafiltration; Chromium(III); Desalination

1. Introduction

The characteristic feature of chromium tannery wastewater is not only the presence of chromium but also its high salinity. The traditional treatment methods of chromium tannery wastewater solve only the problem of chromium separation, not the problem of salinity. Nanofiltration (NF) is proposed for salt reduction in the tannery wastewater. The composition of the tannery wastewater, characterized by mono- and multivalent ions with different charge causes the Donnan effect. This phenomenon, additionally supported by the individual membrane charge, favorably influences the decrease in retention of chloride ions. Cuartas-Uribe et al. [1] carried out NF process for simulated tannery wastewater

with different concentrations of chloride, but at constant concentration of sulfate ions. The authors of the study observed the chloride retention in the range 5%–15% for different chloride/sulfate ions ratio. In experiment conditions, the low pH (3.5) of the solution minimized the membrane effect as a result of the same value of the membrane isoelectric point and the operating pH. The negative chloride ions retention in the simulated chromium tannery wastewater was obtained by Religa et al. [2–4] for a system with a negative membrane charge and the chloride ions to sulfate ions ratio equal to 1. The new process system with partial permeate recirculation, proposed on the basis of the obtained results, allowed the increase of salt concentration in the permeate [4]. Cassano et al. [5–7] conducted a study for real chromium solutions in a pilot scale NF installation. The retention of chloride was

* Corresponding author.

equal to 20%. It is important that, in each case, regardless of both, the membrane type and the solution composition, a very high retention of chromium, in the range of 94%–99%, was achieved [1–7]. As a result, a permeate with high concentration of chlorides and a retentate characterized with a high concentration of chromium and a slightly lower salinity were obtained. The above review shows, that NF process works for salt separation, but not for real desalination of tannery wastewater.

NF process in a diafiltration mode is proposed to reduce as much salt as possible from the feed solution. This process involves washing out of low molecular weight substances, with the use of a washing diluent, added to the feed solution [8,9]. It consists of three steps: pre-concentration, where the volume of the feed solution is partially reduced; diafiltration – when a washing diluent is added in different way to the preliminary concentrated feed solution; post-concentration – which involves further reduction of the volume of the feed solution [8–14]. Xie and Xu [15] carried out NF process in the diafiltration mode in order to desalinate a glyphosate liquor. They noticed that during this process more than 75% of chloride ions were removed from a tested solution, for the volume ratio (ratio of the feed volume after the pre-concentration to the added diluent volume) of 2. Zhang et al. [16] applied NF process in a diafiltration mode in order to reduce the salt concentration in a lactulose syrup. For the volume ratio of 5, they achieved a 97% reduction of NaCl for the studied system.

Consequently, based on the literature review, we suppose that NF process in a diafiltration mode can give beneficial results as far as the desalination of chromium(III) solution is concerned. To our knowledge, there have been no reports regarding the desalination of chromium tannery wastewater by NF in the diafiltration mode.

In this paper, the authors present results of the research concerning desalination of a simulated chromium tannery wastewater for a constant volume of the diafiltration process (constant volume of diafiltration [CVD]) and the intermittent volume diafiltration (IVD) process. Additionally, the impact of the process execution in terms of permeate flux, salt removal and chromium(III) concentration was investigated.

2. Materials and methods

NF process in the diafiltration mode was carried out in the laboratory installation presented in Fig. 1.

The experiments were performed with the use of the flat sheet DL membrane with an effective surface area of 0.0155 m² provided by GE Osmonics. The characteristic of the DL membrane used in the experiments is presented in Table 1. The study was performed at TMP = 1 MPa, $Q_R = 800 \text{ L h}^{-1}$. The feed solution temperature equal to 20°C ± 1°C was maintained during the processes.

The simulated solution of chromium tannery wastewater (4 L) was pumped through a high-pressure pump from a feed/retentate tank directly to the NF membrane module. The retentate was turned back to the feed/retentate tank and the permeate was collected in the permeate tank.

The simulated solution of chromium tannery wastewater contained 2 g Cr³⁺ L⁻¹, 10 g SO₄²⁻ L⁻¹ and 20 g Cl⁻ L⁻¹, and it was characterized by pH ≈ 4. For preparation of

the simulated solution, following chemicals were used: CrCl₃·6H₂O (Chempur®), Na₂SO₄ (Chempur®) and NaCl (Chempur®). Samples of retentate and permeate collected during the process were analyzed in terms of concentration of chromium with the spectrophotometer tric method with 1.5 – diphenylcarbazide in Nanocolor UV/VIS at the wavelength $\lambda = 540 \text{ nm}$. The chloride concentration was analyzed using the Mohr method.

NF process in the diafiltration mode was conducted for an IVD and a CVD.

In the IVD mode, the pre-concentration of the feed solution was carried out until the permeate flux decreased to about 20% of its initial value. The volume of the retentate after the pre-concentration step amounted to 2.7 L. During the diafiltration step the washing diluent was added to the retentate by portions. Each portion of the added washing diluent (1.35 L) was equal to the volume of the permeate collected during the pre-concentration step. This activity was repeated twice. The total volume of the added washing diluent corresponded to the volume of the retentate after the pre-concentration step. After adding the second portion of the washing diluent, the filtration step was considered as the post-concentration step. The process was finished when the permeate flux decreased to about 60% of its initial value.

In the CVD mode, the washing diluent was added to the retentate when the permeate flux decreased to about 20% of its initial value. The volume of the retentate after the pre-concentration was equal to 2.7 L. During the diafiltration

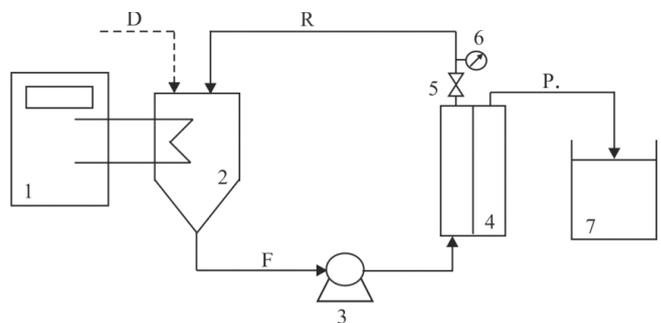


Fig. 1. Scheme of a laboratory installation for nanofiltration in the diafiltration mode: 1 – thermostat, 2 – feed/retentate tank, 3 – high pressure pump, 4 – NF module, 5 – valve, 6 – manometer, 7 – permeate tank, F – feed, R – retentate, P – permeate, D – washing diluent (RO water).

Table 1
Characteristic of DL membrane used in the experiments [2,17–19]

	The DL membrane
Surface material	Polyamide
Support material	Polysulfone
Type of membrane	Thin film
Cut-off (Da)	150–300
Max pressure (MPa)	4.0
Max temperature (°C)	90
pH range	2–11
Isoelectric point (pH)	3.0
Zeta potential (mV) (pH = 4)	–14.0

step, the washing diluent was constantly added with an equal rate as the permeate was collected and the volume of the retentate during the diafiltration step was constant. The total volume of the washing diluent corresponded to the volume of the retentate after the pre-concentration step. The post-concentration was carried out as the permeate flux decreased to about 60% of its initial value.

In both options of NF, the same volume of the washing diluent (2.7 L) was used for salt elution and it corresponded to the volume of the retentate after the pre-concentration step.

Permeate flux (J_p) was determined from the Eq. (1) [20]:

$$J_p = \frac{V_p}{A \cdot t} \quad (1)$$

where J_p is permeate flux ($L \cdot m^{-2} \cdot h^{-1}$), V_p is volume of the received permeate (L), A is membrane area, (m^2), t is time (h).

Chromium(III) ions retention ratio (R) was determined from the Eq. (2) [20]:

$$R = \left(1 - \frac{C_p}{C_N}\right) \cdot 100\% \quad (2)$$

where R is chromium(III) retention ratio (%), C_N is concentration of chromium(III) ions in the feed ($g \cdot L^{-1}$), C_p is concentration of chromium(III) ions in the permeate ($g \cdot L^{-1}$).

The salt elution ratio (E) was determined from the Eq. (3) [20]:

$$E = \frac{C_K}{C_O} \cdot 100\% \quad (3)$$

where E is salt elution ratio (%), C_O is salt concentration in the feed solution after pre-concentration ($g \cdot L^{-1}$), C_K is salt concentration in the concentrate during diafiltration ($g \cdot L^{-1}$).

3. Results and discussion

3.1. Permeate flux

In both types of the diafiltration, changes in the permeate flux were observed. During the pre-concentration step, the permeate flux in both, CVD and IVD NF modes decreased (Fig. 2), which was a result of the increasing ion concentration in the retentate [19,21].

During the diafiltration step in the IVD mode, the periodical changes in the permeate flux (Fig. 2(a)) were observed. It is characteristic, when the washing diluent is added into the solution, the permeate flux increases. This phenomenon can indicate the interruption of the boundary layer formation and minimize the membrane polarization [15].

In the diafiltration step in the CVD mode, the permeate flux was constant (Fig. 2(b)). Introducing a washing diluent with an equal rate as the permeate was collected, made that the polarization layer formed near the membrane surface was not changed.

During the post-concentration step, the higher reduction in the retentate volume led to the rise in the concentration of

its particular components. The consequence of this was the permeate flux decrease. These changes were clearer for NF process in the IVD mode (Fig. 2). This phenomenon can be explained by two aspects. Firstly, an increase in membrane polarization, caused by a worse desalination level in this case (Table 2), probably influenced on the exceeding of solubility of the local retentate component. It led to the precipitation of chromium sediment, probably chromium chloride. The scaling of the membrane clearly decreased the permeate flux. In Fig. 3, the membrane after NF in the IVD mode and the NF in the CVD mode processes is shown. The intense, dark places on the membrane after NF in the IVD mode indicate the formation of a sediment layer (Fig. 3(a)). Such an effect hardly appears in the case of NF in the CVD mode, when more effective desalination of the simulated chromium solution was achieved (Fig. 3(b)). Secondly, higher chromium concentration intensifies its actions with a negative membrane fixed ions. Such conditions favor chromium adsorption on a membrane surface.

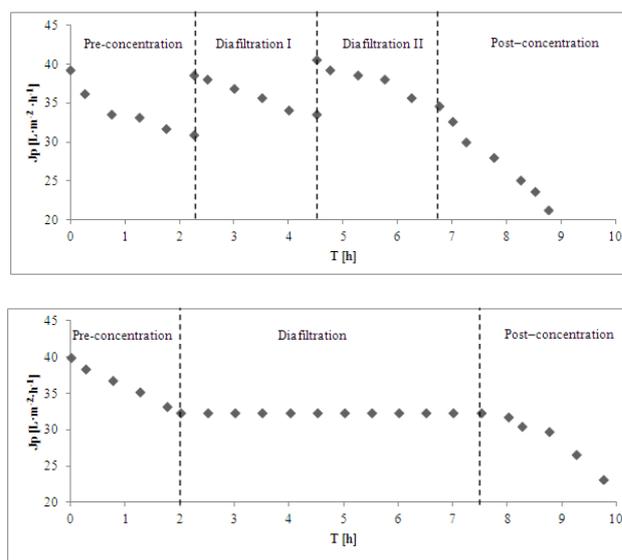


Fig. 2. Changes in the permeate flux vs. time during desalination of the simulated chromium tannery wastewater by NF in (a) IVD and (b) CVD mode.

Table 2
Characteristics of the process parameters

Parameter	CVD	IVD
Concentrate volume, L	1.4	1.5
Final chromium concentration in the retentate, $g \cdot L^{-1}$	4.93	3.96
Final chloride concentration in the retentate, $g \cdot L^{-1}$	7.65	9.21
Water consumption, L	2.7	2.7
Average, final chromium concentration in the permeate, $g \cdot L^{-1}$	0.14	0.11
Average, final chloride concentration in the permeate, $g \cdot L^{-1}$	12.76	11.77
Process time, min	585	525

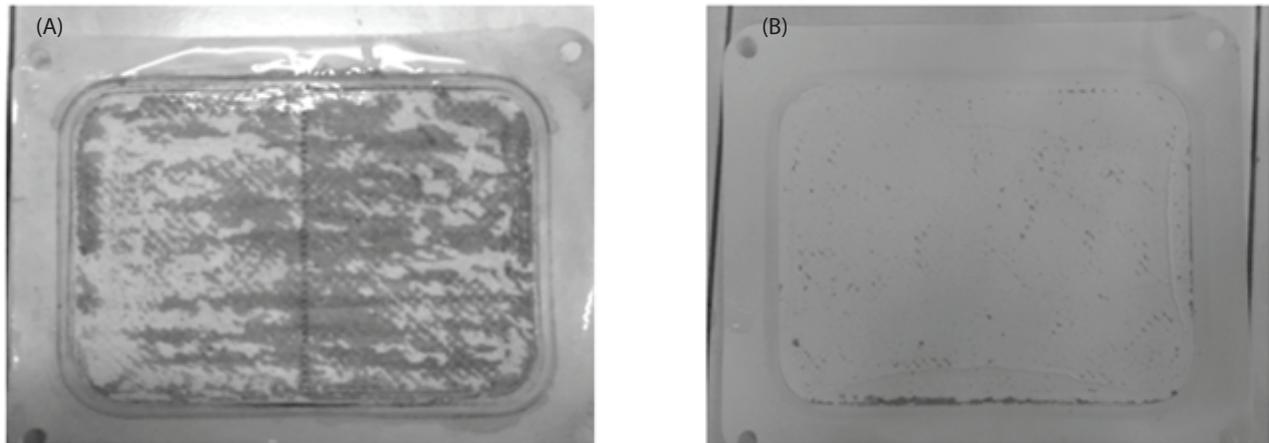


Fig. 3. Pictures of the membrane after NF process in (a) IVD mode (b) CVD mode.

It was always observed, that the way of NF conductance had an influence on the time of the process. Thanks to favorable values of the permeate flux during the diafiltration step after NF in the IVD mode, it was possible to shorten the process time. Additionally, because of the membrane scaling at post-concentration, the time of this step was also slightly shorter. As a result, the process of NF in the IVD mode took 1 h less than process of NF in the CVD mode.

3.2. Salt removal

To evaluate the feasibility of NF for chromium solution desalination, the IVD and constant volume diafiltration (CVD) were conducted at the pressure of 1.0 MPa. The salt elution in NF in the CVD mode was about 62%, while in NF in the IVD mode only 54% (Fig. 4). Differences in desalination between CVD and IVD modes were caused by differences in the case of the washing diluent added during the diafiltration step. Due to the Donnan effect, the higher the ion concentration into the solution, the higher ion concentration in the membrane and consequently in the permeate [2]. Thus, addition of washing diluent, with the same rate as the rate of permeate collection during the diafiltration step in NF in the CVD mode, prevented sudden dilution of the retentate. The authors did not observe any leap changes in salt concentration, what made the elution of chloride ion efficient.

In this case, the salt elution was like a theoretical value (63%) – the elution ratio for membrane with complete permeability in relation to chloride ions and for the volume of washing diluent equaled to volume of the retentate after pre-concentration step [20]. In NF in the IVD mode, periodic addition of high amounts of a washing diluent caused a significant decrease in salt concentration in the solution and a lower level of washed out chloride ions was obtained.

3.3. Chromium(III) concentration

At the experiment conditions, NF of the simulated chromium tannery wastewater allowed the salt concentration reduction from 20 to 7.65 g Cl⁻ L⁻¹ and 9.21 g Cl⁻ L⁻¹, in the case of NF in the CVD and IVD mode, respectively (Table 2).

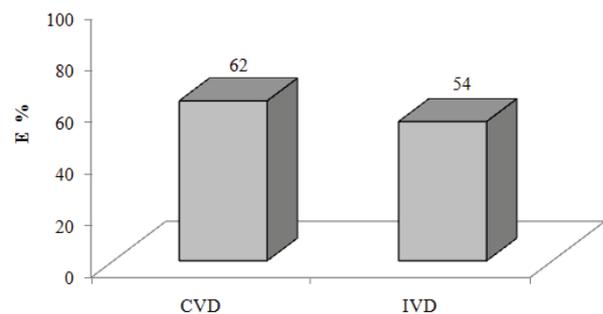


Fig. 4. Salt elution from a simulated chromium tannery wastewater by NF in CVD and IVD mode.

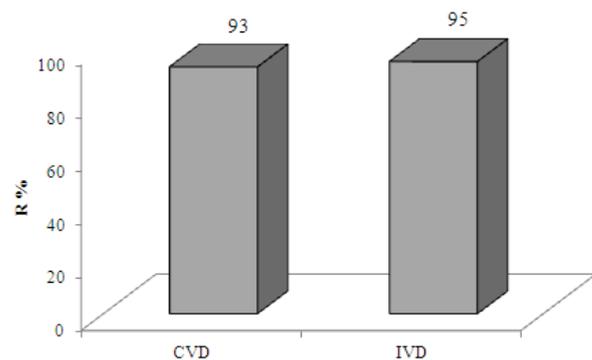


Fig. 5. Chromium(III) retention during nanofiltration of the simulated chromium tannery wastewater in CVD and IVD mode.

At the same time, in both NF options, high chromium retention was obtained (Fig. 5). Partial decrease in chromium retention for both, CVD and IVD NF was caused by chromium elution through the addition of the washing diluent during the diafiltration step. Differences between chromium retention in each tested mode were the result of different way of the process execution.

Both, high chromium retention and high feed solution volume reduction allowed achieving the high chromium concentration of the retentate (Table 2). For NF in the IVD mode,

chromium concentration in the retentate increased nearly twice. For NF in the CVD mode, the obtained final chromium concentration was almost 2.5 times higher than its initial concentration. It was possible, because of better salt removal during the diafiltration step in NF in the CVD mode, which decreased membrane polarization and allowed to receive a higher amount of permeate during the post-concentration step.

4. Conclusion

The aim of this work was to define the impact of NF conductance method on the chromium solutions desalination efficiency. Two different NF methods were examined: NF as a CVD mode and NF as an IVD mode. The analysis of the results confirmed, that NF in the CVD mode enables better desalination of the simulated chromium tannery wastewater than the NF in IVD mode. The continuous dilution of the pre-concentrated feed solution during the diafiltration step facilitated high level of salt removal. Such conditions enabled the maintenance of stable salt concentration in the permeate flux, what made chloride ion elution efficient. Moreover, the membrane polarization decreased and the better volume reduction of the solution was possible. Additionally, better retention of chromium was received during NF in the CVD mode than for NF in the IVD mode. As a result, concentrated chromium solution with a low salt content was obtained.

Symbols

A	—	Membrane area, m^2
C_O	—	Salt concentration in the feed solution after pre-concentration, $g L^{-1}$
C_K	—	Salt concentration in the concentrate during diafiltration, $g L^{-1}$
C_N	—	Concentration of chromium(III) ions in the feed, $g L^{-1}$
C_p	—	Concentration of chromium(III) ions in the permeate, $g L^{-1}$
E	—	Salt elution ratio, %
J_p	—	Permeate flux, $L m^2 \cdot h^{-1}$
R	—	Chromium(III) retention ratio, %
t	—	Time, h
V_p	—	Volume of the received permeate, L

References

- [1] B. Cuartas-Urbe, A. Iborra-Clar, A. Bes-Piá, J.A. Mendoza-Roca, M.V. Galiana-Aleixandre, M.I. Iborra-Clar, Nanofiltration of a simulated tannery wastewater: influence of chlorides concentration, *Desalination*, 191 (2006) 132–136.
- [2] P. Religa, A. Kowalik, P. Gierycz, Effect of membrane properties on chromium(III) recirculation from concentrate salt mixture solution by nanofiltration, *Desalination*, 274 (2011) 164–170.
- [3] P. Religa, A. Kowalik, P. Gierycz, Application of nanofiltration for chromium concentration in the tannery wastewater, *J. Hazard. Mater.*, 186 (2011) 288–292.
- [4] P. Religa, A. Kowalik, P. Gierycz, A new approach to chromium concentration from salt mixture solution using nanofiltration, *Sep. Purif. Technol.*, 82 (2011) 114–120.
- [5] A. Cassano, L. Della Pietra, E. Drioli, Integrated membrane process for the recovery of chromium salts from tannery effluents, *Ind. Eng. Chem. Res.*, 46 (2007) 6825–6830.
- [6] A. Cassano, R. Molinari, M. Romano, E. Drioli, Treatment of aqueous effluents of the leather industry by membrane processes a review, *J. Membr. Sci.*, 181 (2001) 111–126.
- [7] A. Cassano, J. Adzet, R. Molinari, M.G. Buonomenna, J. Roig, E. Drioli, Membrane treatment by nanofiltration of exhausted vegetable tannin liquors from the leather industry, *Water Res.*, 37 (2003) 2426–2434.
- [8] L. Wang, Z. Yang, L. Wang, R. Zhu, Minimizing the operation time for continuous feed diafiltration processes under constant concentration ratio, *Desalination*, 346 (2014) 100–106.
- [9] M. Jelemenský, R. Paulen, M. Fikar, Z. Kovács, Time-optimal operation of multi-component batch diafiltration, *Comp. Chem. Eng.*, 83 (2015) 131–138.
- [10] L. Wang, G. Yang, W. Xing, N. Xu, Mathematic model of the yield for diafiltration processes, *Sep. Purif. Technol.*, 59 (2008) 206–213.
- [11] M. Fikar, Z. Kovacs, P. Czermak, Dynamic optimization of batch diafiltration processes, *J. Membr. Sci.*, 355 (2010) 168–174.
- [12] R. Paulen, M. Fikar, G. Foley, Z. Kovács, P. Czermak, Optimal feeding strategy of diafiltration buffer in batch membrane processes, *J. Membr. Sci.*, 411–412 (2012) 160–172.
- [13] Z. Kovács, M. Fikar, P. Czermak, Mathematical modeling of diafiltration, *Hung. J. Indus. Chem.*, 37 (2009) 159–164.
- [14] R. Paulen, M. Jelemenský, Z. Kovács, M. Fikar, Economically optimal batch diafiltration via analytical multi-objective optimal control, *J. Process Control.*, 28 (2015) 73–82.
- [15] M. Xie, Y. Xu, Partial desalination and concentration of glyphosate liquor by nanofiltration, *J. Hazard. Mater.*, 186 (2011) 960–964.
- [16] Z. Zhang, R. Yang, S. Zhang, H. Zhao, X. Hua, Purification of lactulose syrup by using nanofiltration in a diafiltration mode, *J. Food Eng.*, 105 (2011) 112–118.
- [17] A. Al-Amoudi, P. Williams, S. Mandale, R.W. Lovitt, Cleaning results of new and fouled nanofiltration membrane characterized by zeta potential and permeability, *Sep. Purif. Technol.*, 54 (2007) 234–240.
- [18] M. Mänttari, A. Pihlajamäki, M. Nyström, Effect of pH on hydrophilicity and charge and their effect on the filtration efficiency of NF membranes at different pH, *J. Membr. Sci.*, 280 (2006) 311–320.
- [19] A.W. Mohamad, Y.H. Teow, W.L. Ang, Y.T. Chung, D.L. Oatley-Radcliffe, N. Hilal, Nanofiltration membranes review: Recent advances and future prospects, *Desalination*, 356 (2015) 226–254.
- [20] M. Bodzek, J. Bohdziewicz, K. Konieczny, *Membrane Techniques in Environmental Protection*, Publisher the Silesian Technical University, Gliwice, 1997.
- [21] S. Gomes, S.A. Cavaco, M.J. Quina, L.M. Gando-Ferreira, Nanofiltration process for separating Cr(III) from acid solutions: experimental and modelling analysis, *Desalination*, 254 (2010) 80–89.