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Removal of emerging contaminants of industrial origin by NF/RO – A pilot scale study

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ABSTRACT

In this study a recently built NF/RO pilot unit for removal of emerging contaminants from a plant producing veterinary pharmaceuticals was tested. A wastewater stream of the plant, containing residuals of antibiotics and other organics was treated by three different types of reverse osmosis (RO) and nanofiltration membranes: XLE, NF90 and HL. Target compounds selected for this study included three different classes of antibiotics: sulphonamides, diaminopyrimidine and fluoroquinolone. A developed chromatographic method for determination of pharmaceuticals in a complex wastewater was applied. The method involved a sample pretreatment by solid-phase extraction (SPE) and analytical determination by high performance liquid chromatography (HPLC) with DAD detectors. The results showed the complete removal of all the antibiotics by the typical RO XLE membrane and by the tight nanofiltration membrane NF90. Only the loose nanofiltration membrane element HL incompletely rejected the smaller sulphonamide molecules. The satisfactory rejection of other solutes from a complex wastewater stream was also obtained.

Keywords: Emerging contaminants; Veterinary antibiotics; Wastewater; RO/NF pilot treatment; SPE-HPLC-DAD

1. Introduction

Emerging contaminants are unregulated contaminants, which may be candidates for future regulation depending on research on their potential health effects and monitoring data regarding their occurrence. An interesting group of such products used in large quantities in everyday life, comprises human and veterinary pharmaceuticals, personal care products, surfactants and surfactant residues, plasticizers, different industrial additives, dyes, etc. [1,2]. They are present in raw sewage, treated water, surface water, ground water and sometimes in drinking water. The characteristic of this group of contaminants is that they do not need to be persistent in the environment to cause negative effects since they are most often continuously introduced into environment. Of all the emerging contaminants antibiotics [3,4] are of the biggest concern since their environmental emissions can increase the occurrence of resistant bacteria in the environment, which may lead to unforeseen consequences [5,6]. Although some of these compounds occur in trace concentrations, their physicochemical properties enable their penetration through all natural filters and constructed treatment facilities thus putting drinking water supply systems at the risk. Existing technologies are not capable of reaching the new levels of cleanliness, and the international standards demand more efficient separation systems than those now in common use. In Croatia, many industrial and agriculture wastewaters are

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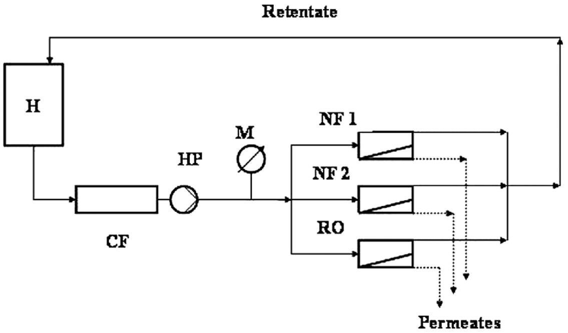


Fig. 1. Schematic representation of the pilot-plant: H-holdup tank; CF-20 μm cartidge filter; HP-high pressure pump "GRUNDFOS", type CRN 5-32; NF1-Filmtec NF90-2540 nanofiltration spiral element; NF2- Desal, Osmonics HL-2540 nanofiltration spiral element; RO, Filmtec XLE-2540 reverse osmosis spiral element; P, permeate; R, – retentate.

still discharged untreated into the rivers. Protection of surface waters and environmental sustainability, in general, through efficient treatment of wastewaters prior to their discharge are key issues in keeping the satisfactory quality of water supplies.

As conventional water treatment processes are ineffective in removal of emerging contaminants, advanced methods such as membrane processes, advanced oxidation processes (AOPs), carbon adsorption, etc., should be used for this purpose [7-16]. Unfortunately, oxidative processes with ozone and UV radiation can produce a number of harmful disinfection by products. Therefore, the ability of membrane separation processes, especially reverse osmosis (RO) and nanofiltration (NF), to remove efficiently and economically various substances makes them a natural choice for removal of the emerging contaminants from water. As the wastewaters are very complex, each wastewater makes a case for itself and its optimal treatment asks for a detailed study.

The aim of this study is to examine the efficiency of the recently built NF/RO pilot unit for removal of emerging contaminants from manufacturing plant producing veterinary pharmaceuticals, and to verify the results obtained earlier [4] on the laboratory scale.

2. Methods and materials

2.1. RO/NF pilot unit

A newly built pilot unit (Fig. 1) containing two 5 μm cartridge filters and three spiral wound membrane elements, type 2540: $L = 1000$ mm and $D = 64$ mm, was installed at Veterina, Kalinovica. The membrane elements chosen after the laboratory screening [4] were: the RO membrane element, type XLE from Dow/FilmTec, Midland MI; and two NF membrane elements: NF90 from Dow/FilmTec and HL Desal, Osmonics, GE Infrastructure Water & Process Techn., Vista, CA.

Before NF/RO experiments the wastewater was treated by a coagulation–flocculation procedure. $FeCl_3 \cdot 6H_2O$ coagulant ($c_{Fe3+} = 3$ g l^{-1}) and Magnafloc LT20 flocculant (Ciba Specialty Chemical Ltd.) (0,001 wt%) were added to 1 m^3 of wastewater in the water tank coagulant/flocculant doses were previously determined by jar test. Then the wastewater was filtrated using a filtering cloth. Turbidity of pretreated water was 6.9 NTU measured by a Hach 2100P turbidimeter. Conductivity and TOC of feed and permeates were determined by the conductometer, Schott, model Lab960 and by the carbon analyzer, Shimadzu, model TOC-V_{WS}, respectively.

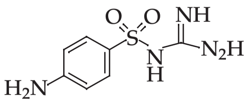
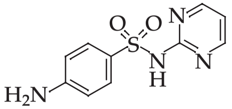
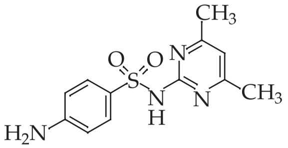
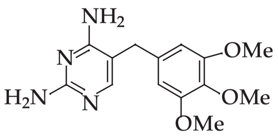
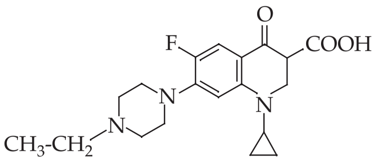
The first experiments on the pilot unit using water were performed in the continuous circulation mode to determine the water permeation rates of the membrane elements and to adjust the appropriate recovery rates. The operation conditions during the experiments were: pressure feed $P_{Feed} = 8$ bar; pressure on membrane elements P_m=7 bar; flow of retentate $Q = 600$ l h^{-1}, $T = 25$°C; recovery rate (conversion): $Y = 0.10$–0.16

Then, the pretreated wastewater stream of the manufacturing plant was treated with the same membrane elements. It was previously found that the wastewaters do not contain all the targeted antibiotics due to the sporadic character of the antibiotics production in the pharmaceutical works. Therefore the feed after coagulation–flocculation pretreatment was spiked with the selected antibiotics in addition to some antibiotic material already present in it. The operation conditions of the experiments were the same as in the water run. The permeate samples withdrawn from the unit were analyzed on the antibiotics content.

2.2. Target compounds

Target compounds in this study included three different classes of antibiotics: sulphonamides–sulfaguanidine, sulfadiazine, sulfamethazine; diaminopyrimidine–trimethoprim and fluoroquinolone–enrofloxacin. These target compounds were characterized as slightly hydrophilic or hydrophobic, with log $K_{O/W}$ (octanol–water distribution coefficient) between −1 and 1 and as the relatively large molecules with molecular mass between 200 and 350 g mol^{-1}. Effective size of the molecules was calculated by the energy optimization method using the Hyperchem procedure [17]. Physicochemical properties of the target compounds are summarized in Table 1.

Table 1
Physical–chemical properties of the examined antibiotics

Name (antibiotic class)	Formula	CAS number	Mol. mass/g mol^{-1}		pK_{a1}	log K_{OW}	Mol. length/nm	Mol. width/nm	D_{eff}*/nm = $\pi H/4 + D/2$
Sulfaguanidine SGUA (sulphonamides)	$C_7H_{10}N_4O_2S$	57-67-0	214.2		11.3	−1.07	1.0508	0.4268	1.0387
Sulfadiazine SDIAZ (sulphonamides)	$C_{10}H_{10}N_4O_2S$	68-35-9	250.3		6.5	−0.34	0.9568	0.4922	0.9976
Sulfamethazine SMETH (sulphonamides)	$C_{12}H_{14}N_4O_2S$	57-68-1	278.3		7.4	0.76	1.2402	0.6644	1.3064
Trimethoprim TMP (diaminopyrimidines)	$C_{14}H_{18}N_4O_3$	738-70-5	290.3		3.23	0.73	1.1972	0.7392	1.3099
Enrofloxacin ENRO (fluoroquinolones)	$C_{19}H_{22}FN_3O_3$	93106-60-6	359.4		6.27	0.70	1.2643	0.6213	1.3036

*Effective size of molecule calculated by energetic optimization method using the Hyperchem procedure [17].

2.3. Analytical methods

The analysis of the spiked wastewater samples was carried out by the extraction, concentration, separation and identification of components on the same principles as described previously [18]. Before analysis wastewater samples were filtered through the 0.45 μm nylon membrane filters and acidified with hydrochloric acid solution (0.1 mol l^{-1}) to pH 4.0. Solid-phase extraction (SPE) procedure was carried out at 60 mg Oasis HLB cartridges (Waters, Milford, Massachusetts) using 100 ml of filtered and acidified wastewater samples. The retained analytics were eluted with 2 × 5 ml of methanol and filtrates were evaporated to dryness at 40 °C. Residues were dissolved in 1 ml of methanol to obtain 100-fold preconcentration and analyzed by LC method. This was performed using a Varian ProStar 500 (Walnut Creek, California, USA) HPLC system consisting of a ProStar 230 tertiary pump system, ProStar autosampler, thermostated column compartment and ProStar 330 diode array detector (DAD). A LiChrosphere 100 CN, 125 mm × 4.0 mm, particle size 5 μm column (Merck, Darmstadt, Germany) was used to separate all compounds in the mixture. The mobile phase used in the chromatographic separation consisted of a binary mixture of solvents A (0.01 mol dm^{-3} oxalic acid) and B (acetonitrile). Simultaneous separations of studied pharmaceuticals were achieved at the following flow rate and mobile phase gradient program: the elution started with 100% of A which was maintained for 6 min, followed by a 19-min linear gradient to 50% of eluent B and 5-min linear gradient back to 100% of A. Flow rate started with 1.0 ml min^{-1} which was maintained for 6 min, followed by a 19-min linear gradient to 0.8 ml min^{-1} and 5-min linear gradient back to 1 ml min^{-1}. The separation was monitored at absorbance wavelength of 280 nm and the column temperature was set to 30 °C. The injection volume was 20 μl.

3. Results and discussion

The experimental results of the permeate flux measurement for three tested membrane elements in the pilot unit are displayed in Fig. 2. The membrane fluxes were measured at 8 × 10^5 Pa (8 bar). The permeate fluxes of the XLE and NF90 membrane elements were almost immediately stabilized, and there was an unexplained decrease of this parameter for the loose NF HL membrane element. The membrane permeate samples withdrawn from the unit were analyzed by the common analytical methods [19].

Fig. 3 and Table 2 show the results of the antibiotics separation. HPLC-DAD chromatograms of feed wastewater and XLE, NF90 and HL membrane permeates are displayed in Fig. 3, showing the contents of sulfamethazine (SMETH), sulfaguanidine (SGUA), sulfadiazine (SDIAZ), trimethoprim (TMP) and enrofloxacin (ENRO).

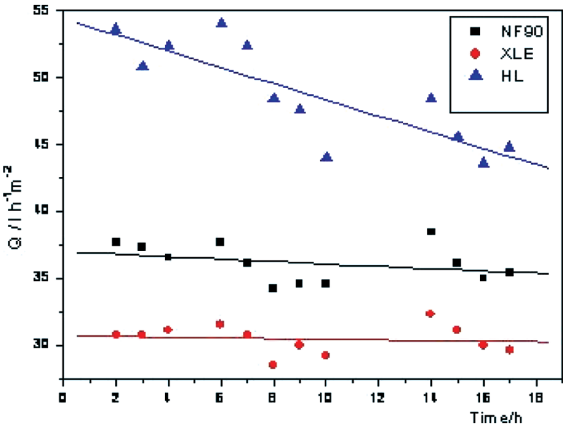


Fig. 2. Permeate flux changes of the examined membrane elements.

The calculated results on the antibiotics removal are shown in Table 2. The almost complete rejection of all antibiotics was achieved by tight NF90 and RO XLE membrane elements. The loose NF HL membrane element rejected TMP and ENRO completely, SDAIZ and SMETH satisfactorily. Rejection of sulfaguanidine, the smallest molecule by the HL element was only 65%. These results confirm the previous laboratory findings [4], and the conclusion that among the three acting rejection mechanisms, size exclusion, charge exclusion physicochemical interactions between solute, solvent and a membrane [20], the first mechanism was the dominant one for the examined unionazable antibiotics by all the used membranes. Such a conclusion follows from a relation between the solute rejections and the membranes' porosity. The porosities of the used membrane elements were characterized on model waters [21]. The pore size distribution (PSD) curves (Fig. 4) of the examined membranes obtained at 8 bar display the obvious differences among the membrane types. The loose nanofiltration membrane HL is characterized by the wide PSD and the bimodal distribution with maxima at 1.02 nm and 1.56 nm. The largest pores (those of 1.56 nm) of this membrane are responsible for the lowest rejection of the organic molecules below 200 Da. The PSD of tight NF90 membrane is practically unimodal with most pores located at 0.840 nm and RO XLE membrane have unimodal distribution with the maximum at 0.548 nm, i.e. it is the densest one.

The analytical results showed also the presence of other substances than antibiotics in wastewater. The UV spectra of feed displayed more peaks and their disappearance in the permeate streams (Fig. 3) points to

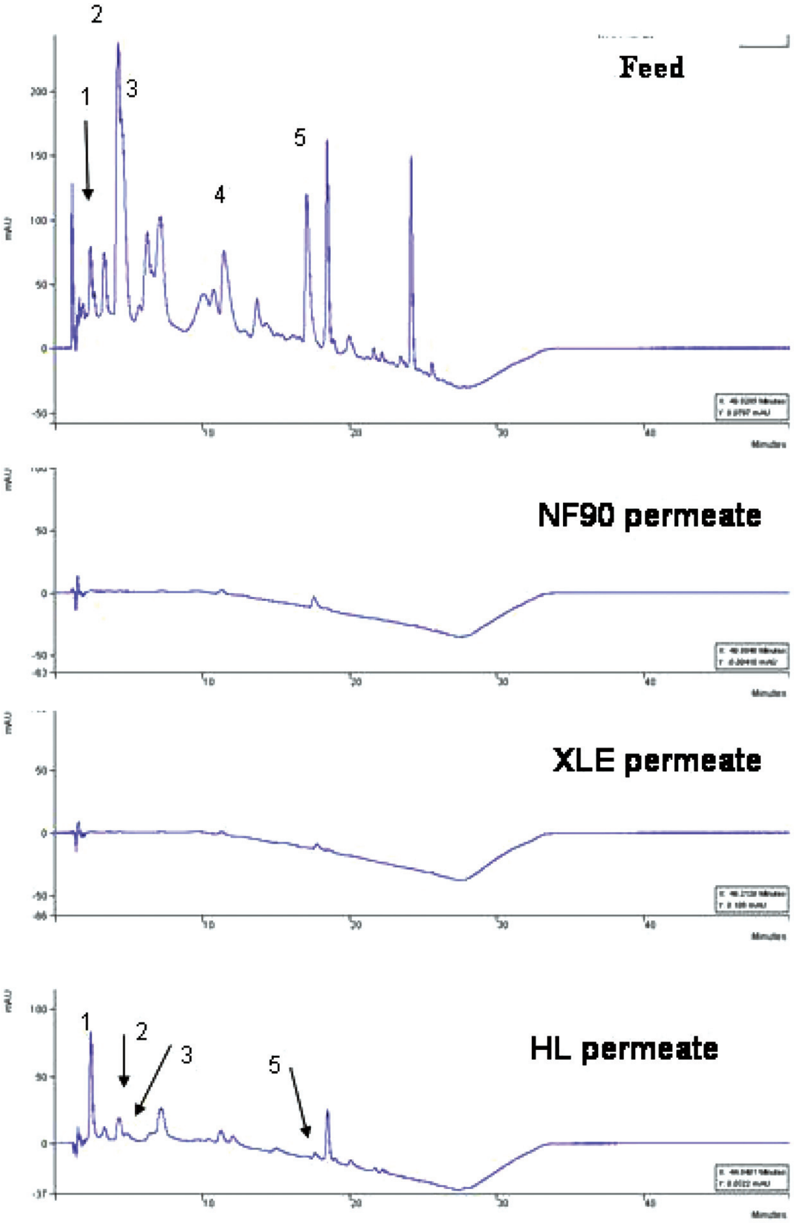


Fig. 3. HPLC-DAD chromatograms of feed and XLE, NF90 and HL membrane permeates (1, SGUA; 2, SDIAZ; 3, SMETH; 4, TMP; 5, ENRO).

high rejections of such so far unknown compounds by tight NF90 and RO XLE membranes while rejection of these substances by the looser HL membrane is somewhat lower.

Additionally, it should be emphasized that the results of reduction of the TC and conductivity contents (Table 3) meet the regulation values for industrial wastewater discharge in Croatia (NN 40/1999 and NN 6/2001).

The next step of investigation will be focused on identification of the presently unknown substances, including antibiotic degradation products, and on finding of an optimal pretreatment method to reduce the fouling phenomena.

4. Conclusion

The performance results obtained on the pilot unit showed the complete removal of all the antibiotics by the RO and by the tight nanofiltration membrane NF90 elements. Only the loose nanofiltration HL

Table 2. Separation of antibiotics

Membrane type	Feed/µg L^{-1}	R_{permeate} (%) NF90	XLE	HL
Antibiotic				
SGUA	495	>99.99	>99.99	65.45
SDIAZ	810	>99.99	>99.99	88.27
SMETH	560	>99.99	>99.99	94.54
TMP	406	>99.99	>99.99	>99.99
ENRO	89.5	>99.99	>99.99	98.93

Table 3. Reduction of total carbon and conductivity

	Feed	Permeate NF90	XLE	HL
pH	6.82	6.29	5.98	6.39
TC/ppm C	233.6	10.66	8.527	55.63
R		0.954	0.964	0.762
NTU	6.9	0.3	0.4	0.3
χ/µS cm^{-1}	504	12.6	6.95	135.1
R		0.975	0.999	0.732

membrane element removed the smallest sulphonamide antibiotic incompletely (65%).

The comparison of these results to the PSD curves of the examined membrane elements confirms the size exclusion as the decisive antibiotics removal mechanism.

Qualitative and quantitative analysis of the veterinary plant wastewater showed the presence of many others organics in wastewater stream and a satisfactory membranes' ability to remove them.

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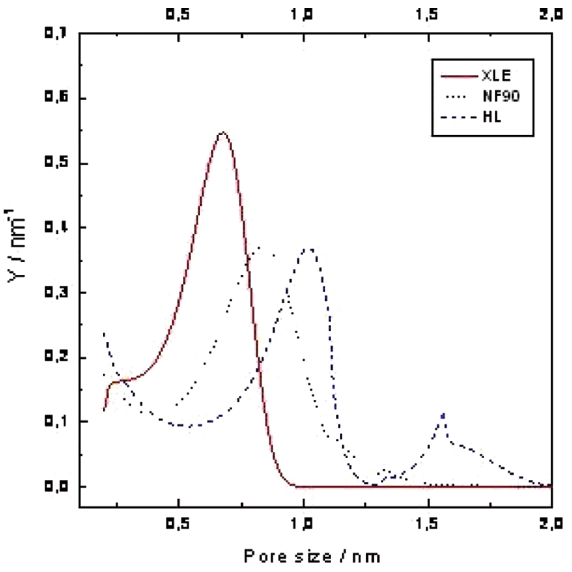

Fig. 4. PSD of membranes tested in laboratory NF/RO set-up and applied in pilot plant.

References

[1] A.I. Schäfer, A.G. Fane and T.D.Waite, Nanofiltration – Principles and Applications, Elsevier Oxford, UK, 2005.
[2] N. Bolong, A review of the effects of emerging contaminants in waste water and options for their removal, Desalination, 239 (2009) 229-246.
[3] S-Z. Li, X-Y. Li and D-Z. Wang, Membrane (RO-UF) filtration for antibiotic wastewater treatment and recovery of antibiotics, Sep. Purif. Technol., 34 (2004) 109-114.
[4] K. Kosutic, D. Dolar, D. Asperger and B. Kunst, Removal of antibiotics from a model wastewater by RO/NF membranes, Sep. Purif. Technol., 53 (3) (2007) 244-249.
[5] R.M. Sharpe and D.S. Irvine, How strong is the evidence of a link between environmental chemicals and adverse effects on human health? Br. Med. J., 323 (2001) 447-451.
[6] T. Heberer, Occurrence, fate, and removal of pharmaceuticals residues in the aquatic environment: a recent research data, Toxicol. Lett., 131 (2002) 5-17.
[7] P. Xu, J.E. Drewes, C. Bellona, G. Amy, T.U. Kim, M. Adam and T. Heberer, Rejection of emerging organic micropollutants in nanofiltration-reverse osmosis membrane applications, Water Environ. Res., 77 (2005) 40-48.
[8] K. Kimura, S. Toshima, G.A. Amy and Y. Watanabe, Rejection of neural endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes, J. Membr. Sci., 245 (2004) 71-78.
[9] T.U. Kim, G. Amy and J.E. Drewes, Rejection of trace organic compounds by high pressure membranes, Water Sci. Technol., 51 (2005) 335-344.
[10] Y. Yoon, P. Westerhoff, S.A. Snyder and E.C. Wert, Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products, J. Membr. Sci., 270 (2006) 88-100.
[11] Y. Yoon, P. Westerhoff, S.A. Snyder, E.C. Wert and J. Yoon, Removal of endocrine disrupting compounds and pharmaceuticals by nanofiltration and ultrafiltration membranes, Desalination, 202 (2007) 16-23.
[12] S.A. Snyder, S. Adham, A.M. Redding, F.S. Cannon, J. DeCarolis, J. Oppenheimer, E.C. Wert and Y. Yoon, Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals, Desalination, 202 (2007) 156-181.
[13] A.G. Fane, Sustainability and membrane processing of wastewater for reuse, Desalination, 2002 (2007) 53-58.
[14] A.M. Comerton, R.C. Andrews, D.M. Bagley and C. Hao, The rejection of endocrine disrupting and pharmaceutically active compounds by NF and RO membranes as a function of compound and water matrix properties, J. Membr. Sci., 313 (2008) 323-335.

[15] S.D. Kim, J. Cho, I.S. Kim, B.J. Vanderford and S.A. Snyder, Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking and waste waters, Water Res., 41 (5) (2007) 1013-1021.

[16] L. Braeken, R. Ramaekers, Y. Zhang, G. Maes, B. Van der Bruggen and C. Vandecasteele, Influence of hydrophobicity on retention in nanofiltration of aqueous solutions containing organic compounds, J. Membr. Sci., 252 (2005) 195-203.

[17] HyperChem, Standard Release 5.11 for Windows, Molecular Modelling System, Hypercube Inc., Waterloo, Ontario, 1999.

[18] S. Babic, D. Asperger, D. Mutavdzic, A.J.M. Horvat and M. Kastelan-Macan, Solid phase extraction and HPLC determination of veterinary pharmaceuticals in wastewater, Talanta, 70 (2006) 732-738.

[19] Standard Methods for the Examination of Water and Waste Water, 19th ed., APHA, AWWA, American Public Health Association, Washington, 1995.

[20] B. Kunst, K. Košutić, Removal of emerging contaminants in water treatment by nanofiltration and reverse osmosis, D. Barcelo and M. Petrovic, eds., Hdb, Env, Chem., Springer-Verlag, Berlin, Heidelberg, vol. 5, Part 5S/2, 2008, pp. 103-125.

[21] K. Košutić, D. Dolar and B. Kunst, On experimental parameters characterizing the reverse osmosis and nanofiltration membranes' active layer, J. Membr. Sci., 282 (2006) 109-114.