

## Effect of water matrices on removal of veterinary pharmaceuticals by nanofiltration and reverse osmosis membranes

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### Abstract

This study explored the removal of five veterinary pharmaceuticals (VPs) (sulfamethoxazole (SMETOX), trimethoprim (TMP), ciprofloxacin (CIPRO), dexamethasone (DEXA) and febantel (FEBA)) from different water matrices (Milli-Q water, model water, tap water and real pharmaceutical wastewater using four types of nanofiltration (NF) membranes (NF90, NF270, NF and HL) and two reverse osmosis (RO) membranes (LFC-1 and XLE). All VPs were added to different water matrices at a concentration of 10 mg/L. Rejections of VPs and water flux were measured. The rejection increased with increase of molecular weight. The highest rejections were obtained with RO membranes (LFC-1, XLE) and tight NF (NF90) membrane. In general, the rejection of VPs was higher in model water and tap water than in Milli-Q water, but the water flux was lower. This was mainly explained by ion adsorption inside the membranes pores. Narrower pore size counteracted the effect of presence of low concentration of natural organic matter (NOM) in tap water. The NOM was assumed to enhance the adsorption of VPs onto membrane surface, increased the size exclusion and electrostatic repulsion also appeared during the transport. Investigated water matrices had influence on water flux decline due to their complexity.

**Key words:** veterinary pharmaceuticals; water matrix; RO/NF treatment; rejection

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### Introduction

Until recently, pharmaceuticals have received comparatively little attention as pollutants in the aquatic environment which is surprising considering that unlike many other pollutants, pharmaceuticals have a direct biological action on microbes. Also, the presence of antibacterial agents in aquatic environments is of growing interest worldwide due to the emergence and development of antibiotic-resistant bacteria and disrupts key cycles/processes critical to aquatic ecology. In Europe, two-thirds of all pharmaceuticals are used in human medicine and one-third for veterinary application (Martínez-Carballo et al., 2007). Applied to farmlands (animal manure is used to agricultural fields as a fertilizer) the active ingredients reach the upper soil layer, where they may accumulate or may be rinsed off into surface waters or may leach to groundwater and thus can impact both human and environmental health. More than 30 pharmaceuticals substances have been found in sewage influent and effluent samples, in surface waters and even ground and drinking water (Kemper, 2008).

Water is a precious commodity in Croatia and its management is critical for preserving the future of this resource. Despite being the 5th in Europe and 42nd in the world (Hrvatske Vode, 2009) according to availability and abundance of water sources, wastewater effluents are not adequately treated and they are discharged into our natural aquifers. Initiatives such as FP6 project (EMCO, est. 2004) and Unity Through Knowledge Fund (UKF) grant agreement (REPHAD, est. 2007) have been established to improve removal of emerging contaminants and treatment of pharmaceutical wastewaters in our country. For example, Windhoek et al. (2007) (Namibia) has exhausted all available surface water supplies and is completely dependent on a direct potable reuse scheme.

The pharmaceutical industries are great polluters. Concentrations of pharmaceuticals may be different depending on production in the pharmaceutical industry. Babić et al. (2006) showed that concentrations of various pharmaceuticals can be higher than 500 µg/L, i.e., sulfamethazine (> 500 and 107.1 µg/L), sulfadiazine (111.4 µg/L), sulfaguanidine (211.1 µg/L) and enrofloxacin (23.7 µg/L) in two real wastewater samples from pharmaceutical industry.

Controlled experiments using bench-scale membrane

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testing can allow the quantification of rejection efficiency and the investigation of the influence of membrane, compound properties and composition of the solution on rejection. Wang et al. (2009) observed a higher rejection of cyclophosphamide by nanofiltration (NF) membranes from membrane bioreactor (MBR) effluent (around 60%) than in Milli-Q water (20%–40%). Teixeira and Rosa (2006) found that the background inorganic matrix greatly influenced the natural organic matter (NOM) removal by a negatively charged membrane. Nghiem et al. (2004) showed that the rejection of estrone and estradiol by NF and reverse osmosis (RO) was enhanced in the presence of organic matter in synthetic waters.

The aim of this study was to test the efficiency of four NF and two RO membranes to remove five selected veterinary pharmaceuticals (VPs) (sulfonamide antibiotic sulfamethoxazole (SMETOX) and their synergist trimethoprim (TMP), fluoroquinolone antibiotic ciprofloxacin (CIPRO), corticosteroid dexamethasone (DEXA) and anthelmintic febantel (FEBA)) and to investigate the effect of different water matrices on the rejection of these VPs and flux. This study examined and compared the rejection of VPs as a function of membrane type and compound properties.

## 1 Materials and methods

### 1.1 Compound selection and characterization

Five VPs were selected to be pharmaceutical classes of organic micropollutants found in wastewater and drinking water sources. These compounds also represent a range of properties (i.e., solubility, hydrophobicity/hydrophilicity, size) that are expected to influence membrane rejection. A summary of the VPs examined and their properties are presented in Table 1.

Chemical standards for TMP, DEXA and FEBA were purchased from Veterina (Kalinovica, Croatia), CIPRO from Pliva (Zagreb, Croatia) and SMETOX from Sigma

(Steinheim, Germany). All pharmaceutical standards used were of high purity grade (> 93.6%). Binary solutions of individual standards (10 mg/L) were prepared in Milli-Q water, model water and tap water with the exception of FEBA, which was dissolved in ethanol (0.4 mL) due to its poor solubility in water and then settled in water. Pharmaceuticals were also tested in mixtures. One mixture was SMETOX and FEBA in Milli-Q water. Mixture of all VPs was tested in waters stated above and in the pharmaceutical wastewater (PWW). Concentrations of substances (inorganic salts, organic acids and sugars) that were added in model waters similar to those from equalizing basins of the pharmaceuticals works are (mg/L): C<sub>2</sub>H<sub>5</sub>OH 100, MgCO<sub>3</sub> 15, CaCO<sub>3</sub> 15, Gelatin 5, C<sub>4</sub>H<sub>6</sub>O<sub>6</sub> 50, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> 100, C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> 50, and NaHCO<sub>3</sub> 100. The pH values of model waters were between 4.03–4.29. NaHCO<sub>3</sub> (100 mg/L) was added because of pH correction and after adding it was between 6.12–6.67.

The PWW was taken from pharmaceutical industry Veterina, Kalinovica, Croatia. Physico-chemical properties of the PWW are presented in Table 2. Before membrane treatment it was pretreated with coagulation and filtration. In jar test the PWW was treated with FeCl<sub>3</sub> and AlCl<sub>3</sub>. Different concentration of Fe<sup>3+</sup> (1–5 mg/L) and Al<sup>3+</sup> (1–5 mg/L) were used. According to the obtained results (COD, NTU, conductivity) the best concentration for coagulation was 5 mg/L of Fe<sup>3+</sup> and after coagulation effluent was filtrated with 1 and 0.45 µm filter.

### 1.2 Membrane selection and characterization

High-pressure membranes examined in this experiment included the NF90, NF270 and NF (Dow/FilmTec) and HL (Desal, Osmonics, GE Infrastructure Water Process Tech., Vista, CA) polyamide NF membranes, and the XLE (Dow/FilmTec, Midland MI) and LFC-1 (Hydranautics, Oceanside, CA) polyamide RO membranes. The characteristics of these membranes are presented in Table 3. Pure water flux ( $J_w$ ) associated with each membrane were determined using bench-scale membrane filtration. The  $J_w$

**Table 1** Veterinary pharmaceuticals properties

Compound	Formula	MW (Da)	Water solubility <sup>a</sup> (mg/L)	log $K_{ow}$ <sup>a</sup>	$d_c$ <sup>b</sup> (nm)
SMETOX	C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> S	253.28	610	0.89	0.734
TMP	C <sub>14</sub> H <sub>18</sub> N <sub>4</sub> O <sub>3</sub>	290.32	400	0.91	0.779
CIPROxHClxH <sub>2</sub> O	C <sub>17</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub> F	331.35	30,000	0.28	0.826
DEXA	C <sub>22</sub> H <sub>29</sub> FO <sub>5</sub>	392.46	89	1.83	0.889
FEBA	C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> O <sub>6</sub> S	446.48	322	1.53	0.941

MW: molecular weight.

<sup>a</sup> Obtained from the Syracuse Research Corporation (SRC) PhysProp database (<http://www.syrres.com/esc/physdemo.htm>); <sup>b</sup>  $d_c$  effective diameter of organic component in water  $d_c = 0.065MW^{0.438}$ .

**Table 2** Physico-chemical properties of real pharmaceutical wastewater

Parameter	Concentration	Parameter	Concentration
TOC (mg/L)	162.12	Nitrate (mg/L)	0.5669
COD (mg O <sub>2</sub> /L)	596	Sulphate (mg/L)	26.2266
Conductivity (µS/cm)	428	Sodium (mg/L)	12.2413
Turbidity (NTU)	332	NH <sub>4</sub> <sup>+</sup> (mg/L)	7.7477
pH	6.96	Potassium (mg/L)	1.8008
Fluoride (mg/L)	0.0732	Magnesium (mg/L)	4.0764
Chloride (mg/L)	37.8575	Calcium (mg/L)	36.8147

**Table 3** Characteristics of investigated membranes

Type	Membrane	$J_w$ (L/(m <sup>2</sup> ·hr))	MWCO <sup>a</sup> (Da)	$R^b$ (%)
RO	XLE	101.57 ± 16.05	100	99.0 (NaCl)
	LFC-1	40.99 ± 0.84	100	99.0 (NaCl)
Tight NF	NF90	80.16 ± 5.15	100–200	> 97 (MgSO <sub>4</sub> )
	NF270	143.69 ± 5.73	150–300	> 97 (MgSO <sub>4</sub> )
Loose NF	NF	124.04 ± 4.44	150–300	98.0 (MgSO <sub>4</sub> )
	HL	93.16 ± 4.00	150–300	98.0 (MgSO <sub>4</sub> )

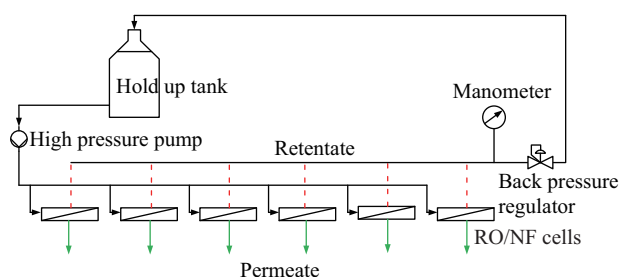
MWCO: molecular weight cut-off.

<sup>a</sup> Boussu et al., 2006; Radjenović et al., 2008; Xu et al., 2006; Zhang et al., 2004; López-Muñoz et al., 2009.

<sup>b</sup> Data given by manufacturers. Concentrations of MgSO<sub>4</sub> were 200 mg/L, and NaCl 500 mg/L (XLE) and 1500 mg/L (LFC-1).

was determined by taking the average flux of Milli-Q water through the membrane.

Removal of VPs in different matrices, with commercially available RO and NF membranes, was tested in the laboratory set-up illustrated schematically in Fig. 1 at a working pressure of  $15 \times 10^5$  Pa. The high pressure pump (H2-31 Bran+Luebbe, Norderstedt, Germany) delivered feed solutions to RO/NF cells at a flow rate of 350 mL/min. The six homemade RO/NF cells of the same type and dimensions, as described by Sourirajan and Matsuura (1985), were connected in parallel.

**Fig. 1** Schematic representation of RO/NF laboratory set-up.

The pressure was measured with a high-accuracy pressure gauge (Wika, Klingenberg, Germany) and the pressure was maintained by a back pressure regulator (Tescom 26-1700, Selmsdorf, Germany). The RO/NF cell consists of two detachable parts. The upper part is a high pressure chamber provided with inlet and outlet openings for the flow of the feed solution under pressure. The lower part contains outlet opening for the membrane permeate. The membrane is mounted on a stainless steel porous plate embedded in the lower part of the cell and the surface layer of the porous membrane faces the feed solution on the high pressure side of the membrane. The RO/NF cells were connected parallel due to decrease of concentration polarization. The surface area of the membranes was 10.75 cm<sup>2</sup>. First, the preserved membranes were washed with demineralized water without pressure and then pressurized at  $20 \times 10^5$  Pa for 5 hr. After pressure pretreatment, the pure water flux was measured.

Conditions for determining pore size and pore size distributions (PSDs) in the selective membranes' layer, have been described previously (Košutić et al., 2006). The fine-pore model was used in this work. According to Matsuura (1993) this is the most realistic model. The pore size and PSDs were obtained for all membranes by the modified examination method based on the specific solutes

(markers) transport.

### 1.3 Chemical analysis

The concentrations of inorganic salts (feed concentrations: 300 mg/L) were determined by the conductometer (Instruments Lab 960 SCHOTT, Germany). Measurement range of the used conductometer was 0.0–500.0 mS/cm and measurement accuracy  $0.5\% \pm 1\%$  digit. Conductivity was measured once until the stabilization of the value. Total carbon (TC), inorganic carbon (IC) and total organic carbon (TOC) were analyzed using a carbon analyzer (TOC-V<sub>WS</sub>, Shimadzu, Japan) in a measurement range of 0–3500 mg/L, detection limit 0.5 µg/L and accuracy (reproducibility) of maximum 1.5%. These parameters were measured three times and the standard deviation (SD) was always below 1.5%. Concentrations of sulphates and concentration of cations and anions from PWW samples were determined with ion chromatograph (Dionex ICS-3000, USA). The COD was measured according to Standards Methods (APHA et al., 1995). The turbidity and pH were analyzed with turbidimeter (WTW TURB 430 IR, Germany) and pH meter (Schott pH meter CG842, Germany), respectively. Rejection ( $R$ ) of each investigated compound and parameter was calculated as:

$$R = \frac{c_f - c_p}{c_f} \times 100\% \quad (1)$$

where,  $c_f$  (mg/L) and  $c_p$  (mg/L) are concentrations of a compound in feed and permeate stream, respectively.

The analyses of VPs were performed using a Varian ProStar 500 (Walnut Creek, California, USA) HPLC system consisting of a ProStar autosampler, ProStar 230 tertiary pump system, ProStar 330 diode array detector, and thermostatted column compartment. The column temperature was set to 30°C, and the injection volume was 30 µL. C18 Synergy Fusion 150 mm×4.6 mm, particle size 4 µm column (Phenomenex) was used to separate all investigated compounds in the mixture. The mobile phase used in the chromatographic separation consisted of a binary mixture of solvents A (0.01% formic acid in water) and B (0.01% formic acid in acetonitrile). A simultaneous mobile phase gradient program was used: the elution started with a 2.5 min linear gradient from 100% A to 8% B, followed by a 3.5 min linear gradient to 10% B, a 5 min linear gradient to 30% B, a 4 min linear gradient to 60% B and finally a 3 min linear gradient to 95% B which was maintained for 10 min and then a 0.1 min linear gradient back to 100% of A. The flow rate was 0.5

mL/min. The separation was monitored at an absorbance wavelength of 254 nm.

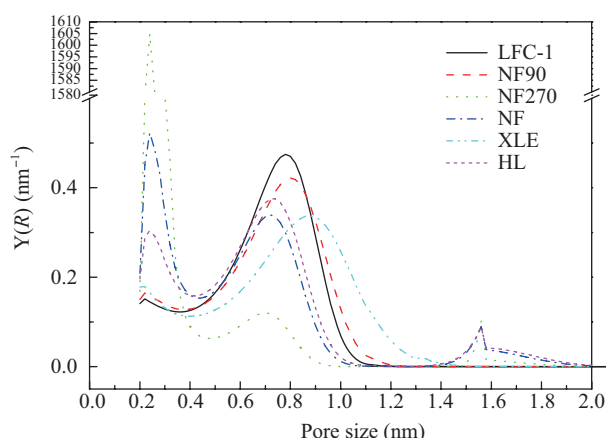
## 2 Results and discussion

### 2.1 Membrane characterization

Rejection factors,  $R$  of inorganic salts, sodium and calcium chloride, and magnesium sulfate are displayed in Table 4. Nanofiltration membranes showed low rejection factors for sodium and calcium chloride. Rejections of magnesium sulfate shown in Table 4 are in an agreement with manufacturers' data (Table 3). Little deviations can be attributed to lower concentration of  $\text{MgSO}_4$ .

According to presented results the appreciably higher rejection factor for sodium and calcium chloride by the RO rather than the NF membranes are evident. In the case of RO membranes there are little differences of  $R(\text{NaCl})$  and  $R(\text{CaCl}_2)$  in contrast to wide differences of their values for NF membranes. Both facts point to differences in the active layer porosities of the examined membranes, which have been shown in PSD curves (Fig. 2). The PSDs of all the NF membranes are located at evidently wider pores, which are responsible for the lower sodium chloride retention. Thus, the size exclusion mechanism is prevailing. The higher rejection of calcium chloride observed with NF membranes are the consequence of the additional charge exclusion which resulted from the repelling action of the NF membranes' electric charge on the divalent ions. Membrane XLE had less rejection of sodium chloride than expected which can be explained with the higher pore size as shown by the PSD curve.

There are noticeable differences in PSD curves between



**Fig. 2** Pore size distributions (PSD) of selected RO and NF membranes at  $15 \times 10^5$  Pa.

RO and NF membranes. The PSDs for LFC-1 and XLE membranes confirm that these membranes are RO because the pores are smaller than 1 nm, i.e., the pores for LFC-1 and XLE membranes are 0.78 and 0.88 nm, respectively. The PSDs of two tight NF membranes have the main peak at a similar pore size, 0.79 nm and 0.70 nm for NF90 and NF270 membrane, respectively. In the case of the tight NF270 membrane there was also an additional peak at 1.56 nm, making the distribution similar to those of the loose NF membranes. Hence, loose NF membranes show bimodal PSD curves with two clearly separated peaks. The pores with highest incidence in this case are those of 0.72 nm (NF) and 0.73 nm (HL) followed by large pores, sized between 1.32 and 2.03 nm.

Figure 3 presents PSD curves after the treatment of model waters and cleaning (Fig. 3a) and after the treatment of the PWW and cleaning (Fig. 3b). Table 5 presents differences in pore sizes on the beginning of work and after treatment of model waters and the PWW. Results presented in Fig. 3 and Table 5 indicate changes in the skin of investigated membranes. For XLE, LFC-1 and NF90 membranes there weren't significant changes in pore sizes during the experiment. The NF and HL membranes had little changes in pore sizes but it is important to note that the maximum of the second picks were higher. This means a greater number of these pores which can have big influence on rejection. The biggest changes were for loose NF270 membrane. First pick increased from 0.70 to 0.89 nm and in the last PSD this pick was almost gone. The second maximum for this membrane was at the same pore size but it was much higher and wider, and the pores are in the range from 1.43–2.80 nm after the treatment of real PWW.

### 2.2 Rejection of VPs from Milli-Q water

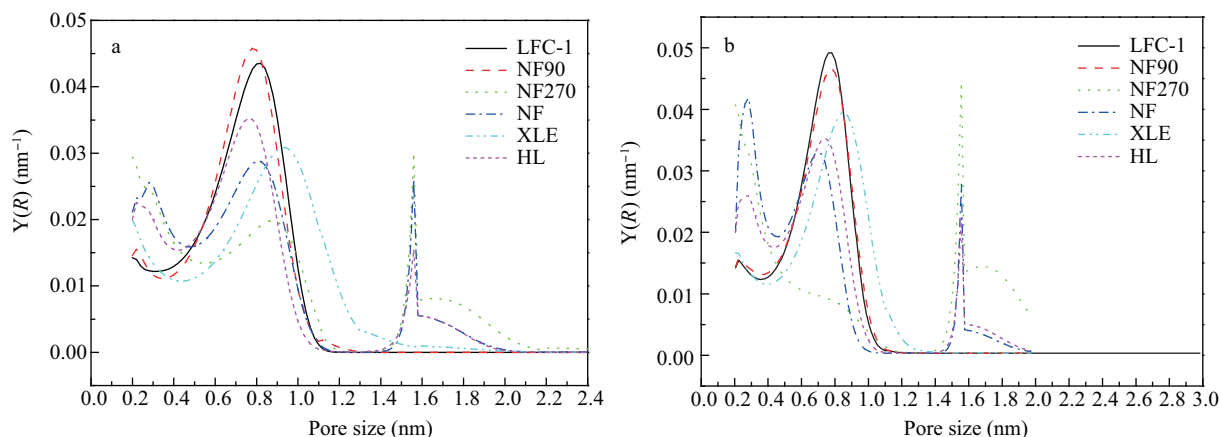
Rejection of solutes on RO/NF membranes will be affected by solute properties (MW, molecular size,  $\text{pK}_a$  and  $\log K_{ow}$ ), membrane properties (molecular weight cut-off (MWCO), pore size, surface charge, hydrophobic-

**Table 5** Differences in pore sizes for investigated membranes

	Pore size (nm)		
	At beginning	After model waters	After real PWW
XLE	0.88	0.93	0.85
LFC-1	0.78	0.81	0.76
NF90	0.79	0.78	0.77
NF270	0.70 and 1.56	0.89 and 1.56	1.35–2.04
NF	0.72 and 1.56	0.80 and 1.56	0.70 and 1.56
HL	0.73 and 1.56	0.76 and 1.56	0.73 and 1.56

**Table 4** Rejection factors of inorganic salts with permeate flux and effective number of pores

	Rejection (%)			$J_p$ (L/(m <sup>2</sup> ·hr))	$N_{eff}$ ( $\times 10^{16}$ m <sup>-2</sup> )
	NaCl	CaCl <sub>2</sub>	MgSO <sub>4</sub> ·7H <sub>2</sub> O		
XLE	89.5	96.4	99.2	69.38 $\pm$ 11.00	1.199
LFC-1	96.5	98.1	99.7	38.38 $\pm$ 2.18	0.874
NF90	89.9	98.0	99.4	77.92 $\pm$ 6.05	1.413
NF270	13.6	28.1	90.7	109.16 $\pm$ 18.82	1.188
NF	24.6	37.3	98.2	98.53 $\pm$ 14.57	1.004
HL	27.1	82.9	94.1	88.48 $\pm$ 7.05	0.758



**Fig. 3** Pore size distributions of membranes. (a) after the treatment of model waters and cleaning with alkali agent; (b) after the treatment of the PWW and cleaning with alkali agent.

ity/hydrophilicity and surface morphology), feed composition (pH, ionic strength, hardness and the presence of organic matter) and operating conditions. Solutes can be rejected by one or a combination of three basic mechanisms: size exclusion (sieve steric effect), charge exclusion (electrical, Donnan) and physico-chemical interactions between solute, solvent and membrane (Bellona et al., 2004).

The rejections of the selected VPs (Milli-Q water) in laboratory scale RO and NF treatment are depicted in Table 6. Rejections of investigated VPs from Milli-Q water for RO membranes were higher than 95%. Such results were expected for XLE and LFC-1 membranes because MW of the VPs are bigger than MWCO values. Molecular weights of investigated VPs were between 290–450 g/mol and MWCO were 100 Da. Rejection higher than 97% showed tight NF90 membrane because its MWCO was 100–200 Da. According to these results it could be concluded that the main rejection mechanism was size exclusion. Better confirmation for this conclusion can be explained on other investigated membranes (NF270, NF and HL) due to greater MWCO (150–300 Da). Rejection of VPs increases with MW. Molecular weights for SMETOX and TMP are lower than MWCO of examined membranes and rejections are between 15.4%–81.8% and increases with MW. CIPRO, DEXA and FEBA show rejection higher than 97% because MWs are higher than 330 g/mol.

These results can be also explained with comparing the pore sizes of the membranes and effective diameter

of organic component in water ( $d_c$ ) presented in Table 1. This formula represents relationship between MW of an organic component and its  $d_c$ . The MW is not a direct measure of the dimensions of a molecule but it still reflects the molecular size. According to Van der Bruggen and Vandecasteele (2002) this correlation is valid for the molecular weight up to  $\pm 600$  g/mol. Effective diameter of investigated VPs is in the range of 0.734–0.941 nm and increases with MW. CIPRO, DEXA and FEBA are completely removed with XLE, LFC-1 and NF90 membranes because  $d_c$  is bigger than 0.826 nm and pore sizes of these membranes are 0.88, 0.78 and 0.79, respectively. SMETOX and TMP show rejection between 94.8%–98.9% due to similar values of  $d_c$  of these VPs and pore sizes of RO and tight NF90 membranes. For other NF membranes (NF270, NF and HL) rejection increased with  $d_c$ . Rejection of SMETOX and TMP was lower due to larger pores in skin ( $>1.32$  nm) which are presented in Fig. 2. The RO and NF membranes provide effective barriers rejection of contaminants because all VPs with MW higher than 300 g/mol are rejected almost completely ( $> 97\%$ ).

Table 6 also presents results obtained for mixture of all VPs in Milli-Q water and shows that the rejections were higher than in binary solutions because of a combination of basic mechanisms. The main mechanisms that influenced the rejection of VPs were size exclusion and physico-chemical interactions between solutes and membrane.

**Table 6** Rejection of VPs by RO/NF membranes from Milli-Q water with average permeate flux

	Rejection (%)					
	XLE	LFC-1	NF90	NF270	NF	HL
SMETOX	98.9	97.2	97.2	15.4	29.4	24.7
TMP	94.8	98.3	97.9	68.3	81.8	65.6
CIPRO	$> 99.9$	$> 99.9$	$> 99.9$	$> 99.9$	97.2	98.2
DEXA	$> 99.9$	99.2	99.4	$> 99.9$	$> 99.9$	$> 99.9$
FEBA	$> 99.9$	$> 99.9$	$> 99.9$	$> 99.9$	$> 99.9$	$> 99.9$
Mixture of:						
SMETOX	97.2	98.6	98.52	77.6	89.2	50.9
TMP	99.2	99.3	$> 99.9$	86.9	92.9	78.0
CIPRO	$> 99.9$	$> 99.9$	$> 99.9$	$> 99.9$	97.2	98.2
DEXA	$> 99.9$	99.2	99.42	$> 99.9$	$> 99.9$	$> 99.9$
FEBA	$> 99.9$	$> 99.9$	$> 99.9$	$> 99.9$	$> 99.9$	$> 99.9$
$J_p$ (L/(m <sup>2</sup> ·hr))	$71.19 \pm 5.23$	$37.33 \pm 2.87$	$66.07 \pm 2.25$	$97.19 \pm 14.57$	$88.51 \pm 9.41$	$80.41 \pm 2.72$



### 2.3 Removal of VPs from different water matrices

The rejection of investigated VPs from different water matrices is shown in Fig. 4 (VPs dissolved individually) and Fig. 5 (mixture of all VPs). In the case of the RO and tight NF90 membranes, no significant difference between rejection from the various waters is observed because these membranes provides excellent rejection (> 90%) under all conditions. When comparing the different matrices used (other NF membranes: NF270, NF and HL), it can be seen that the rejections of VPs are generally higher than those from Milli-Q water. The rejections were highest in tap water and this phenomenon is usually explained by the influence of NOM (Van der Bruggen et al., 2001). Lower rejections of some VPs in model waters for XLE,

NF270 and NF can be explained with Fig. 2, Fig. 3a and Table 5. XLE membrane showed bigger pore sizes during the treatment of model waters. Biggest changes were for NF270 membrane due to the increase in pore sizes from 0.70 to 0.88 nm (main pick) and the high second pick (increase of the number of these pores).

With the exception of some VPs in model water, bigger molecules (MW > 300 g/mol) are completely removed by NF membranes in all water matrices. The reasons are the same as in previous section with an emphasis on high physico-chemical interactions between solutes and membranes. In general the highest rejections were observed in tap water. These can be explained with the presence of relatively high ion concentration and low NOM concentration (Zhang et al., 2004). The presence

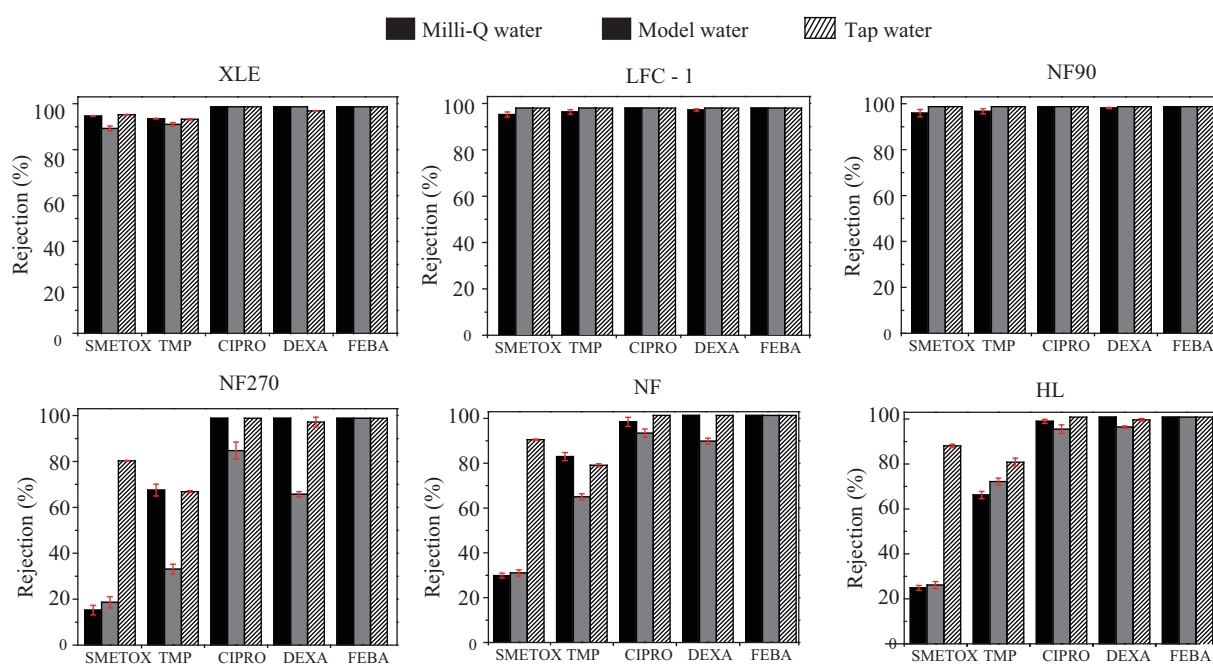


Fig. 4 Rejection of VPs dissolved individually in different water matrices. Rejections are presented as mean values  $\pm$ SD ( $n = 3$ ).

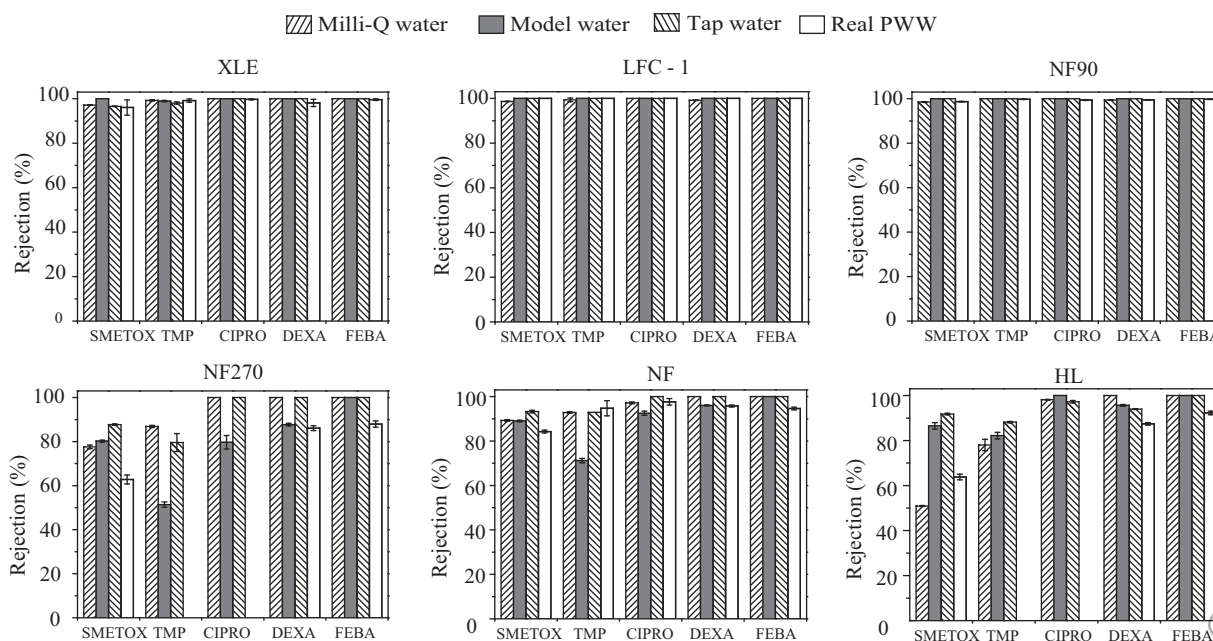


Fig. 5 Rejection of VPs dissolved as mixture in different water matrices. Rejections are presented as mean values  $\pm$ SD ( $n = 3$ ).

of divalent ions, calcium in particular, has been found to increase compound adsorption to a membrane surface (Plakas et al., 2006). However, low concentration of calcium ions in model waters (6 mg/L) could not have a major impact on rejection of VPs. Pharmaceuticals can associate with the functional groups present on NOM and form macromolecular complex, which increases the effect of size exclusion and the adsorption of pharmaceuticals onto outer surface or inside pores of membrane caused by hydrophobicity of NOM. The key difference between the model water and the tap water is the presence of relatively high ion concentration except the presence of NOM. Organic compounds are even higher in model water matrix. Thus, the difference in rejection should be caused by interactions between ions and the membrane. Indeed it has been evidenced that ion adsorption might play a significant role in nanofiltration (Thanuttamavong et al., 2002), which may narrow the membrane pores and lead to higher rejections. The rejection for SMETOX and TMP indicate that ions adsorb on the membrane surface or inside pores, narrowing the pores and decreasing the transport of pharmaceuticals. The pore structure of membranes is so tight that together with VPs molecules, the major part of ions are removed, which caused high conductivity rejection for model and tap water matrix (Tables 7 and 8).

Rejections of VPs dissolved as a mixture in all investigated water matrices is shown in Fig. 5. The RO and tight NF90 membranes show almost complete removal of all VPs in all investigated water matrices. This was to expect because these membranes have pores smaller than 0.88 nm and were present significant interactions between solutes and membranes. In general, rejection of investigated VPs increases with complexity of water matrix (Milli-Q, model, tap waters and PWW). As mentioned above, for some membranes rejection of VPs was lower in model waters than in Milli-Q water, due to increase of pore size and number of larger pores. The same reason was responsible for lower rejection of VPs in real wastewater. For NF270

membrane there was a very small amount of pores at size of around 0.80 nm and big amount of pores at pores higher than 1.35 nm (Fig. 3b and Table 5). For NF and HL membranes larger amount of bigger pores (>1.42 nm) was responsible for lower rejection of VPs in real wastewater than in tap water. The membrane surface consists of two distinct distributions of pore sizes: tight “polymer network” pores and wider “polymer aggregate” pores. As indicated by Košutić and Kunst (2002) the reason for lower rejection was plugging of the tight network pores in the membranes surface and even their disappearance during fouling, and the enlargement of the wider aggregate pores. The rejections of TMP and CIPRO for NF270 and HL membranes in the PWW are not presented because it was impossible to recognize them. Their absorption curves were not similar to absorption curves of standards.

In the treatment of the real PWW, other parameters were determined, due to its complexity. The results of removal efficiency of different parameters and substances obtained by selected RO/NF membranes are given in Table 9. Concentrations of SMETOX, TMP, CIPRO, DEXA and FEBBA in PWW were 8.22, 27.68, 17.48, 13.56 and 1.02 mg/mol, respectively. It can be seen that apart from removal of VPs, there was also a significant removal of other components. The COD and TOC rejections were between 22.6%–62.0%, which confirms the fact that this water contained small organic components (MW < 100 g/mol). In addition, investigated membranes had a relatively high rejection on monovalent ions. For NF membranes this was not expected, because it is generally assumed that the rejection of monovalent ions is low. Size exclusion, electrical charge and physico-chemical interactions may cause this effect. The large rejection of ions was also evidenced by the reduction of the conductivity, which amounts to around 97% (XLE, LFC-1, NF90) and around 50% for other nanofiltration membranes (NF270, NF and HL).

**Table 7** Membranes performances (conductivity and TOC) in model water matrix

Parameter	Conductivity (μS/cm) (Feed: 167.44 ± 8.53)		TOC (mg/L) (Feed: 144.60 ± 12.55)	
	Permeate	R (%)	Permeate	R (%)
XLE	7.58 ± 2.81	95.5	35.74 ± 5.79	75.3
LFC-1	3.15 ± 0.38	98.1	30.27 ± 3.46	79.1
NF90	2.72 ± 0.29	98.4	35.60 ± 5.35	75.4
NF270	54.45 ± 12.07	67.5	53.51 ± 6.58	63.0
NF	40.01 ± 7.42	76.1	47.43 ± 4.74	67.2
HL	27.40 ± 4.02	83.6	44.24 ± 5.61	69.4

**Table 8** Membranes performances (conductivity and TOC) in tap water matrix

Parameters	Conductivity (μS/cm) (Feed: 689.67 ± 17.86)		TOC (mg/L) (Feed: 20.94 ± 3.12)	
	Permeate	R (%)	Permeate	R (%)
XLE	18.38 ± 3.15	97.3	0.69 ± 0.22	96.7
LFC-1	8.62 ± 1.04	98.7	0.43 ± 0.22	97.9
NF90	9.13 ± 1.67	98.7	0.38 ± 0.11	98.2
NF270	411.50 ± 44.28	40.3	9.04 ± 2.42	56.8
NF	330.83 ± 49.38	52.0	5.81 ± 1.12	72.2
HL	192.90 ± 6.69	72.0	3.78 ± 0.64	81.9

**Table 9** Removal efficiency of membranes in treatment of real pharmaceutical wastewater

Parameter	Feed	Removal efficiency (%)					
		XLE	LFC-1	NF90	NF270	NF	HL
Conductivity ( $\mu\text{S}/\text{cm}$ )	592	96.5	98.1	97.9	45.1	57.9	62.3
TOC ( $\text{mg}/\text{L}$ )	730.34	60.9	62.0	60.2	28.6	31.2	29.2
COD ( $\text{mg O}_2/\text{L}$ )	1826	56.9	57.3	55.0	22.6	25.3	24.0
Fluoride ( $\text{mg}/\text{L}$ )	0.1151	100	100	100	54.7	65.9	83.3
Chloride ( $\text{mg}/\text{L}$ )	59.4974	98.4	98.6	99.1	22.6	32.4	36.8
Nitrate ( $\text{mg}/\text{L}$ )	0.1380	26.4	–	60.9	17.2	21.0	33.5
Phosphate ( $\text{mg}/\text{L}$ )	0.4533	100	100	100	100	100	100
Sulphate ( $\text{mg}/\text{L}$ )	26.2266	98.6	98.7	98.9	96.2	98.6	98.3
Sodium ( $\text{mg}/\text{L}$ )	14.7979	98.4	92.7	96.7	46.6	26.8	35.6
$\text{NH}_4^+$ ( $\text{mg}/\text{L}$ )	7.5458	92.3	96.5	88.5	48.9	41.1	30.4
Potassium ( $\text{mg}/\text{L}$ )	1.7498	90.7	85.0	87.2	28.3	16.7	55.5
Magnesium ( $\text{mg}/\text{L}$ )	4.5697	98.1	98.7	97.6	82.5	65.6	93.6
Calcium ( $\text{mg}/\text{L}$ )	36.8147	99.4	98.1	98.6	67.1	57.2	85.5
pH	7.50	6.71	6.59	6.05	8.01	7.91	7.74

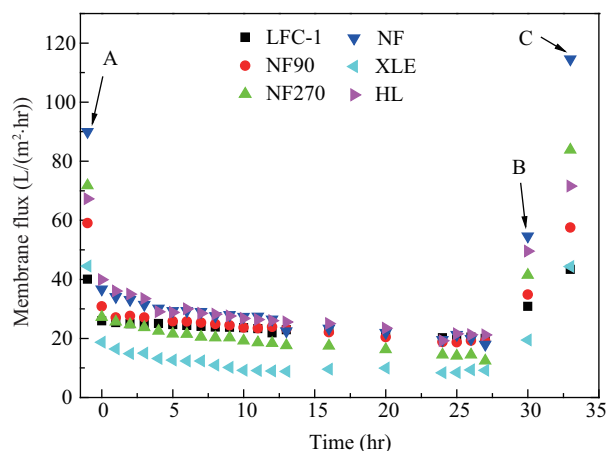
**Table 10** Average permeate flux ( $J_p$ ) with standard deviation for all investigated water matrices

		XLE	LFC-1	NF90	NF270	NF	HL
Milli-Q water	$J_0$ ( $\text{L}/(\text{m}^2\cdot\text{hr})$ )	84.86	39.95	74.71	134.40	115.60	88.65
	$J_p$ ( $\text{L}/(\text{m}^2\cdot\text{hr})$ )	69.16	36.86	64.66	92.71	85.55	78.79
	S.D.	6.82	2.82	4.31	17.03	11.10	4.66
Model water	$J_p$ ( $\text{L}/(\text{m}^2\cdot\text{hr})$ )	38.04	35.45	47.77	46.84	61.51	52.62
	S.D.	5.94	3.01	4.06	9.05	12.17	5.58
Tap water	$J_p$ ( $\text{L}/(\text{m}^2\cdot\text{hr})$ )	25.87	32.76	38.91	37.28	44.78	42.89
	S.D.	7.08	1.53	5.89	7.26	7.54	4.81
Real PWW	$J_p$ ( $\text{L}/(\text{m}^2\cdot\text{hr})$ )	18.71	25.91	30.86	27.20	36.66	39.88

## 2.4 Influence of water matrices on membrane flux

To obtain the flux decline, the permeate flux of the membrane before testing with VPs ( $J_0$ ), was measured with demineralized water at 25°C. The  $J_0$  values of each membrane are presented in Table 10. Also the values of flux for VPs in different water matrices (measured for few days) and standard deviations are shown in Table 10. The smallest flux decline was observed for Milli-Q waters due to low organic compounds concentrations and the highest for real PWW. The flux decline was obtained for all membranes but the highest had NF270 and NF membranes. Flux decline is attributed to adsorption of ions inside the membrane pores. This is in agreement with the increased rejection of VPs described above.

The NF270 and NF membranes showed unstable flux due to high values of standard deviations. The LFC-1 membrane showed the most stable flux because S.D. was in the range 1.5–3.0. According to manufacturer (Hydranautics, 2010) LFC (low fouling composite) membrane has the advantages of composite membrane (low pressure, high flow and high rejection) in addition to membrane chemistry advances that enhance resistance to fouling. This neutrally charged RO membrane is designed to minimize the adsorption of organic foulants onto the membrane surface (flux degradation due to build up of organic foulants is minimized). This was confirmed because LFC-1 showed lowest flux decline (Fig. 6) compared to other examined membranes. Flux of real PWW for examined membranes is shown on Fig. 6. All membranes showed flux decline (30%–59%) when treatment of real wastewater started probable because of pore blocking and adsorption onto membrane surface. The highest decline (59%) showed



**Fig. 6** Membrane flux ( $J$ ) in treatment of the real PWW. A: initial membrane flux of demineralized water before treatment of real PWW; B: flux after cleaning only with demineralized water; C: flux after cleaning with alkali agent.

NF and NF270 membranes and the lowest LFC-1 (30%). There wasn't permanent pore blocking during the treatment of real wastewater because after cleaning with alkali agents pure water flux returned to initial water flux.

## 3 Conclusions

1. The pore size and PSDs of selected RO/NF membranes were determined using the fine-pore model. The pore sizes of RO and tight NF90 membranes are less than 1 nm and their PSDs are unimodal, while loose NF membranes (HL and NF) have bigger pores, between 1.32 and 2.03 nm, with bimodal PSDs.

2. The obtained pore sizes and PSDs for LFC-1, XLE



and NF90 membranes presented stability during the treatment with various complex water matrices. The NF270 had big changes in skin structure because PSDs showed continuous increase in pore sizes during the experiment.

3. An excellent removal of all VPs, in all investigated water matrices, was achieved with RO (LFC-1, XLE) and tight nanofiltration (NF90) membranes. These membranes showed that the main separation mechanism was size exclusion. Other NF membranes showed good removal of bigger VPs molecules and there was an impact of two other mechanisms (charge exclusion and physico-chemical interactions).

4. The rejection of VPs was higher in model and tap water than in Milli-Q water due to ion adsorption inside the membranes pores.

5. The best membranes for removal of VPs and treatment of real PWW were LFC-1 and NF90 due to almost complete removal of all VPs and stable flux.

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