Desalination and Water Treatment
www.deswater.com

51 (2013) 469–475
January

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doi: 10.1080/19443994.2012.694237

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NF/RO removal of enrofloxacin and its photodegradation products from water

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Received 27 February 2012; Accepted 10 May 2012

ABSTRACT

Once released into the environment pharmaceuticals undergo a series of processes leading to their degradation. Photolysis induced by sunlight is the most important way of pharmaceuticals degradation in water. In this work the removal of enrofloxacin (ENRO) and its photodegradation products with nanofiltration (NF) and reverse osmosis (RO) membranes was investigated. ENRO solution ($10\,\mathrm{mg\,L^{-1}}$, $\mathrm{pH}=8$) was irradiated under artificial light for 2 h. As a result the degradation of ENRO produced three photoproducts with molecular weights (MW) 389, 373 and $114\,\mathrm{g\,mol^{-1}}$. Reverse osmosis (LFC–1, SWC4+) and tight nanofiltration (NF90) membranes almost removed (>99.99%) all the compounds (parent and photodegradation products), but the other nanofiltration (DK, NF and HL) membranes removed more than 92%, with one exception (36.96% for the compound with MW $114\,\mathrm{g\,mol^{-1}}$) obtained using HL membrane.

Keywords: Enrofloxacin; Photolysis; Photodegradation products; Reverse osmosis; Nanofiltration

1. Introduction

Pharmaceuticals are released into surface water (very often drinking water resources) via a number of routes, the most important being through the excretion of pharmaceuticals partly metabolized by the body or their pharmacologically active metabolites [1] and their incomplete removal with conventional wastewater treatment plants (WWTPs) [2,3]. Numerous studies detected a large number of pharmaceuticals in the range of $\mathrm{ng\,L^{-1}}$ to $\mathrm{\mu g\,L^{-1}}$ [2,4–6]. Once in surface water, chemical processes like sunlight photolysis can lead to the degradation of pharmaceuticals.

Photolytic reactions are often complex, involving various competing or parallel pathways and leading to multiple reaction products. Therefore it should be remarked that photolysis could produce unpredictable compounds (e.g. undesirable chlorinated degradation products). In recent years, photodegradation of pharmaceuticals caused by sunlight (natural or artificial) has been investigated [7–11]. Problem in photolytic reactions is the formation of photodegradation prod-

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Presented at the International Conference on Desalination for the Environment, Clean Water and Energy, European Desalination Society, 23–26 April 2012, Barcelona, Spain

ucts (PPs). In most cases, the identity of these PPs is unknown and proper risk assessment with respect to the aquatic environment has not been conducted. Different transformation can take place, sometimes producing products that can differ in their environmental behavior and ecotoxicological profile. For example, photodegradation products of some organic pollutants are often more persistent than their corresponding parent compound [12] and exhibit greater toxicity [9,11,13]. Also certain authors [14,15] found that some metabolites are often more concentrated than their parent compounds.

Thus, the removal of PPs from water with reverse osmosis (RO) and nanofiltration (NF) membranes needs careful investigation. To the best of authors' knowledge there is lack of research works related to this issue. In our previous work [16], the removal of PPs of anthelmintic drugs (levamisole, albendazole, praziquantel, febantel) with RO (LFC–1 and XLE) and NF (NF90, NF270, NF and DK) membranes was investigated. The presence of eight photoproducts was observed and their removal was more than 95% with RO and NF90 membranes, whereas it ranged between 33 and 99.99% with other NF membranes.

With this context in mind, the aim of this study was to investigate the removal of enrofloxacin photodegradation products with characterized RO/NF membranes (LFC–1, SWC4+, NF90, NF, DK and HL). ENRO has been chosen as a compound with widespread use and detection in the environment.

2. Materials and methods

2.1. Chemicals

Enrofloxacin was supplied by Sigma-Aldrich. Solution of ENRO standard ($10\,\mathrm{mg\,L^{-1}}$) was prepared using Milli-Q water at pH = 8. All the solvents used were of HPLC grade supplied by Kemika (Zagreb, Croatia). Hydrochloric acid ($0.1\,\mathrm{mol\,L^{-1}}$) and sodium hydroxide solutions ($0.1\,\mathrm{mol\,L^{-1}}$) were used for the adjustment of water pH-value.

The chemical structure and physico-chemical characteristics of ENRO are shown in Fig. 1.

2.2. Photolysis experiments

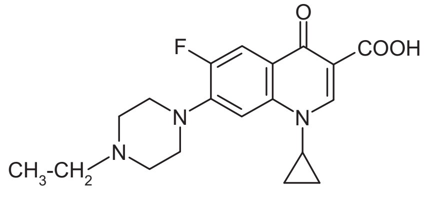
The photolysis experiments were conducted using a Suntest CPS + simulator (Atlas, Germany) equipped with a Xenon lamp and temperature sensor. The device emitted radiation in the wavelength range of 300–800 nm to simulate sunlight. During the experiments the radiation intensity was maintained at $500\,\mathrm{W\,m^{-2}}$ and the reaction temperature was varied between 25 and 27 °C.

ENRO solution was irradiated for 2 h. The distance between the liquid surface and the lamp was 14 cm. Water as a solvent can only absorb the light less than 220 nm while ENRO can absorb light in the wavelength range of 230–350 nm. Thus the solvent cannot influence the light absorption behavior of ENRO. Control samples had the same composition as ENRO solutions, and they were handled under the same conditions and protected from the effects of light. The control samples helped to establish that ENRO degradation was affected only by light and not by temperature.

2.3. Membranes

The commercially available RO and NF membranes used in this experiment include the LFC–1 and SWC4+ (Hydranautics, Oceanside, CA, USA) RO membranes, NF90 and NF (Dow/FilmTec, USA), and HL and DK (Desal, Osmonics, GE Infrastructure Water Process Techn., Vista, CA, USA) nanofiltration membranes. All membranes were stored in dark and cold place (refrigerator).

Membrane characterization and the removal of ENRO and its photodegradation products were carried out in laboratory set-up (described in details in [17]) at working pressure of 10 bar and a flow rate of $750\,\mathrm{mL\,min^{-1}}$. First, the preserved membranes were washed with demineralized water without pressure and then pressurized at 15 bar for approximately 3 h in order to stabilize permeate flux. Nominal characteristics of the membranes were checked by testing sodium chloride (NaCl) and calcium chloride ($CaCl_2$)



CAS number: 93106-60-6

Molecular formula: $C_{19}H_{22}F_1N_3O_3$

Molecular weight (MW): 359.40 g mol^{-1}

Log K_{OW}=0.70

Water solubility: 3397 mg L^{-1}

All data obtained by EPI SUITE$^{\mathrm{TM}}$ 4.10 (03.01.2012).

Fig. 1. Chemical structure and physico-chemical characteristics of enrofloxacin.

solutions, while the membrane-selective layers were characterized by determining the pore size and pore size distributions (PSDs) as described previously by Košutić et al. [18].

2.4. Analytical determination

The concentration of inorganic salts (feed concentration 300 mg L^{-1}) was determined using a conductometer (Instruments Lab 960 SCHOTT, Germany).

To determine the rate of ENRO degradation and its degradation products, samples were analyzed using HPLC-MS-MS, which was performed with an Agilent 6410 triple-quadrupole mass spectrometer equipped with an ESI interface coupled with an Agilent (Santa Clara, CA, USA) Series 1,200 HPLC. Synergy Fusion C18 embedded column (150 × 2.0 mm, particle size 4 μm) supplied by Phenomenex was used for separation. The analysis was performed using 0.1% formic acid in Milli-Q water as eluent A and 0.1% formic acid in acetonitrile as eluent B in gradient elution mode at a flow rate of 0.2 mL min^{-1}. The elution gradient started with 100% of eluent A and linearly decreasing to 92% A over the first 2.30 min, then decreasing to 90% A over the next 3.70 min. For another 5 min elution gradient was decreased to 70% A, continuing decreasing to 40% A within the following 4 min. In 18 min the percentage of eluent A was decreased to 5% and these conditions were held for 10 min before the initial mobile phase composition was restored at 28.10 min. After gradient elution, the column was equilibrated for 12 min before another injection. An injection volume of 5 μL was used in all analyses [19].

The analyses performed in positive-ion mode. The conditions for the analyses were: drying gas temperature 350 ℃; capillary voltage 4.0 kV; drying gas flow 11 L min^{-1} and nebulizer pressure 35 psi (2.41 bar).

Instrument control, data acquisition and evaluation were performed with Agilent MassHunter 2003–2007 Data Acquisition for Triple Quad B.01.04 (B84) software.

3. Results and discussion

3.1. Membrane characterization

In the beginning of the experiment membranes were tested with inorganic salts (NaCl and $CaCl_2$) in order to compare the basic characteristics and the rejection mechanism of the investigated membranes. The rejection factors, R, of tested NaCl and $CaCl_2$ with average water flux, J_w, are displayed in Table 1.

In the case of nanofiltration membranes, the rejection factors of sodium and calcium chloride showed relatively wide differences indicating the strong repelling action of NF membranes on divalent ions, confirming the presence of a noticeable electrical charge on these membranes. The rejection of NaCl and $CaCl_2$ for NF membrane was not in agreement with the Donnan exclusion theory, which stated that for negatively charged membranes, as it is the case, an increase in the co-ion charge and a decrease in the counter-ion charge will give an increased retention of the salt: $R(\mathrm{NaCl}) > R(\mathrm{CaCl_2})$ [20]. The lowest NaCl rejection of 12.11% was for loose HL membrane. This value is lower than the previous data of 27.1% [17] and 34.5% [21] and there is no explanation for this. HL nanofiltration membrane is water softening element and manufacturers are testing them with magnesium sulfate [22]. Thus, it cannot be compared with manufacturers' data.

Rejections of inorganic salts for RO membranes were higher than 95% and there is no difference indicating that the basic mechanism in RO is the size exclusion. For the LFC–1 size exclusion as a basic mechanism can be confirmed with neutral charge of this membrane [23].

Water flux for the investigated membranes was between 14.31 and 87.53 L m^{-2} h^{-1} whereas the highest flux was for loose HL nanofiltration membrane and the lowest for seawater reverse osmosis SWC4+ membrane.

The results were supported by the experimental determination of thin layer porosity of the membranes. Therefore the pore size and PSDs were determined for all the membranes by the modified examination method based on the specific solutes

Table 1
Rejection factors of inorganic salts with average water flux and SD ($N = 5$)

	DK	SWC4+	LFC–1	NF	HL	NF90
R_{NaCl} (%)	61.65	98.60	95.10	64.81	12.11	84.70
$R_{\mathrm{CaCl_2}}$ (%)	83.28	98.32	97.07	46.12	65.19	96.94
J_w (L m^{-2} h^{-1})	30.58	14.31	21.17	70.59	87.53	59.50
SD	0.87	0.31	3.37	2.96	2.58	1.36

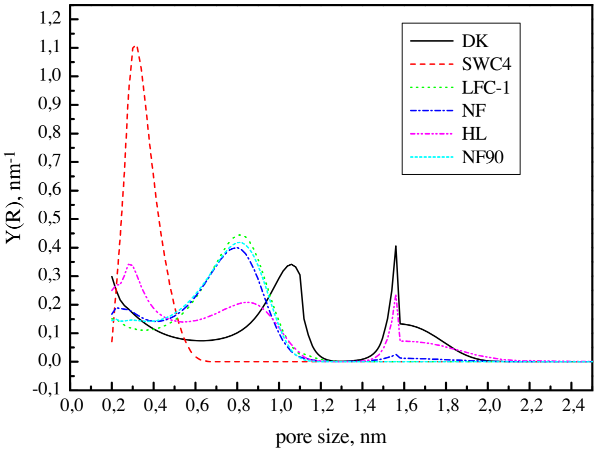


Fig. 2. Pore size distributions of investigated membranes at 10 bar.

(markers) transport [24]. The results are presented in Fig. 2.

PSDs for the investigated RO membranes showed unimodal distribution. As SWC4+ is a seawater RO membrane and pore sizes are with the highest incidence at the size of 0.32 nm, it had highest rejection for inorganic salts and lowest flux (Table 1). Pore sizes for the second reverse osmosis membrane, LFC–1, shifted toward wider pores, 0.81 nm, but is still below 1 nm what is characteristic for reverse osmosis membranes.

Among the nanofiltration membranes (DK, NF and HL) used in this study, DK showed typical bimodal distribution with two separated picks [18]. First pick, or pores with the highest incidence, is located at 1.06 nm followed by a significant number of pores located between 1.36 and 2.0 nm. NF membrane also showed bimodal distribution but with few differences compared with DK membrane. Pores with the highest incidence are located at narrower pores (0.76 nm) and the wider pores with very small incidence located between 1.48 and 1.84 nm. Pore size distribution is not specifically distributed for loose nanofiltration HL membrane. Košutić et al. [18] showed bimodal distribution at 8 bar while Dolar et al. [17,21] showed distribution between bimodal and trimodal and was similar to the distribution observed in this study. Possible explanation could be molecular weight cut-off (MWCO) of the membrane and higher working pressure. According to the manufacturer, HL is a water-softening nanofiltration membrane and characterized by an approximate MWCO of 150-300 Da [22]. It can be assumed that higher pressure opened narrower pores located between 0.29 and 0.85 nm but it cannot be said that pores are located at certain pore radius.

3.2. *Photodegradation of ENRO and the removal of photodegradation products*

Photolysis induced by sunlight is one of the most important causes of pharmaceuticals degradation in natural aquatic environment. The PPs as a result of photolysis are also undesirable components but they are less toxic than the parent compounds. Therefore it is important to find an appropriate removal treatment.

In this study, the ENRO solution was prepared using Milli-Q water without adding any solutes because previous studies showed that nitrate [25], humic acid (HA) [25] and water hardness [26] had influence on photolysis rate. Li et al. [25] demonstrated that nitrate suppressed the photolysis of ENRO. But the results were contradictory for the effect of HA on photolysis rate. According to Li et al. [25], the presence of HA dramatically inhibited the photolysis of ENRO while Fisher et al. [27] and Werner et al. [28] reported that HA was a significant promoter of organic compound photolysis. Werner et al. [26] indicated that water hardness was an important photochemical parameter for the photodegradation of tetracycline.

Irradiation under artificial light for two hours was not long enough for complete ENRO degradation. However, photodegradation resulted in three PPs as shown in Table 2. It is important to emphasize that none of these products were detectable in either the control samples or an enrofloxacin standard solution indicating that ENRO degradation was affected only by light.

ENRO as a parent compound was completely removed with all the investigated membranes except the loose HL nanofiltration membrane. Košutić et al. [29] showed removal rates ranging from 97 to 99.4% with RO/NF membranes (XLE, NF90 and HL), but in this study it was little bit higher, except for HL nanofiltration membrane.

The effective diameter of ENRO and its photodegradation products in water ($d_c = 0.065\mathrm{MW}^{0.438}$ [30]) together with the rejection of photodegradation products are also shown in Table 2. For ENRO d_c is 0.855 nm and is higher than almost all the pores determined for the investigated membranes and it can be assumed that the main removal mechanism was size exclusion but with addition of physico-chemical interactions between PPs. For DK membrane the modified examination method, based on the specific solutes (markers) transport, showed pores higher than 1 nm but still the removal was almost complete (>99.99%) or concentrations were below the limit of detection ($\mathrm{LOD}_{\mathrm{ENRO}} = 0.5\,\mathrm{ng\,L}^{-1}$ [19]). Therefore it can be con-

Table 2
Mass-to-charge ratio (m/z), retention time (t_R), molecular weight (MW), effective diameter of ENRO and its photodegradation products in water (d_c) together with rejection

m/z	360	390	374	115
t_R (min)	16.570	8.819	16.231	1.972
MW (g mol^{-1})	359	389	373	114
d_c[a] (nm)	0.855	0.886	0.870	0.517
		R (%)		
DK	>99.99	>99.99	>99.99	95.35
SWC4+	>99.99	>99.99	>99.99	>99.99
LFC–1	>99.99	>99.99	>99.99	>99.99
NF	>99.99	>99.99	>99.99	94.59
HL	92.08	>99.99	94.86	36.96
NF90	>99.99	>99.99	>99.99	>99.99

[a] Effective diameter of organic compound in water [30].

cluded that compounds in the solution were interacting between each others and these physico-chemical interactions were the reasons for the increase of rejection. Only for HL membrane the rejection was 92%. The lower rejection with HL membrane can be explained with trimodal PSD which is not typical pore size distribution and wide MWCO range (150–300 Da) determined by the manufacturer.

Two photodegradation products had higher MW than the parent compound, first with MW 389 g mol^{-1} and second with 373 g mol^{-1}. Higher MW reflected both higher effective diameter of organic compound and removal rates. All compounds were removed almost completely. Photodegradation products with MW 389 and 373 g mol^{-1} were removed with HL membrane >99.99 and 94.86%, respectively. Removal with HL membranes showed that the size of the molecule is an important factor in determining removal mechanism and it is in agreement with the previous works [31,32]. Therefore, the removal of these two PPs was higher than removal of the parent compound and the reason is explained in the previous paragraph but with higher impact on size exclusion mechanism.

Photodegradation product with MW 114 g mol^{-1} was the smallest one ($d_c = 0.517$) and this finding can have influence on its removal. As can be seen in Table 2 this PP was completely removed with RO membranes (SWC4+ and LFC–1) and with tight NF90 nanofiltration membrane. MWCO of RO and tight NF90 membranes is 100 Da and PSD curves of these membranes showed pores smaller than 0.9 nm had influence on very high removal.

Other nanofiltration (DK, NF and HL) membranes showed rejection between 36 and 95% where the smallest one (36.96%) was for HL membrane. When considering pore size distributions and MWCO [17,22,33] of the examined membranes, size exclusion in combination with physico-chemical interaction between photodegradation products is the main removal mechanism.

Putting together these results with those published on this compound in wastewater effluents (guaranteeing their continuous input into receiving waters), it is essential to point out that ENRO and its degradation products are compounds of environmental concern. Since photolysis is one of the most important causes of pharmaceuticals degradation in surface water, the next very important goal of this study will be the identification of photodegradation products, elucidation of photolysis-reaction and toxicity of photodegradation products.

4. Conclusions

Due to the widespread use of ENRO relatively large quantities are released into the environment. Once released into the environment ENRO undergoes a series of processes leading to its degradation. Photodegradation is actually a major removal pathway in water.

Photolysis for two hours was not long enough for complete degradation of enrofloxacin, still three photodegradation products and parent compound were present in the solution. Two PPs were with higher molecular weight (389 and 373 g mol^{-1}) and one with lower (114 g mol^{-1}) compared with the parent compound (359 g mol^{-1}).

According to this study, nanofiltration and especially reverse osmosis showed to be effective barrier for removal of enrofloxacin and its photodegradation products. Both reverse osmosis and tight NF90 nanofiltration membrane removed almost all photodegradation products and their parent compounds. Other nanofiltration membranes (DK, NF and HL) had rejection more than 92%, except for HL membrane with removal rate of 36.96% for PP with lowest MW. The main removal mechanism for both reverse osmosis and tight NF90 membrane was size exclusion, whereas in the case of other investigated nanofiltration membranes it was a combination of size exclusion and physico-chemical interaction.

Acknowledgements

This work was supported by the Croatian Ministry of Science, Education and Sports Projects: 125-1253008-3009 "Membrane and adsorption processes for removal of organic compounds in water treatment," and 125-1253008-1350 "Advanced analytical methods for pharmaceuticals determination in the environment."

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