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Removal of Glucocorticosteroids and Anesthetics from Water with RO/NF Membranes

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This work addresses the removal of glucocorticosteroids (hydrocortisone, HYDRO; and dexamethasone, DEXA) and anesthetics (procaine, PROCA; and lidocaine, LIDO), from water with commercially available reverse osmosis/nanofiltration (RO/NF) membranes. The RO/NF experiments were of long-run type (24 h) in order to accomplish steady-state and to obtain accurate rejection of the selected compounds. The removal of the examined compounds with the RO (XLE, SWC1, LFC–1) and the tight NF (NF90) membranes was higher than 98 %. Relating the solute rejections to membranes' properties has shown that the dominant rejection mechanism of the examined pharmaceuticals by all the membranes was the size exclusion effect.

Rejection factors for hydrophilic HYDRO and DEXA compounds confirm that they do not adsorb onto the active layer of the selected membranes. LIDO and PROCA, slightly hydrophobic compounds, had lower rejections after 24 h treatment compared to initial values, and probable they were adsorbed onto polymeric matrix of active layers.

Key words:
Reverse osmosis, nanofiltration, rejection, glucocorticosteroids, anesthetics

Introduction

Over the past decade, pharmaceuticals are considered as an emerging environmental problem due to their continuous release and persistence in the aquatic ecosystem even at low concentrations.[1,2] In recent years, the use of pharmaceuticals in veterinary and human medicine is widespread (annual consumption of 100,000 – 200,000 t globally) and consequently, the possibility of water contamination with such compounds has increased.[3] They have been detected worldwide in environmental matrices (surface, ground and even drinking water),[4,5] indicating their ineffective removal from water and wastewater using conventional treatment methods.[1,6,7]

Dexamethasone (DEXA) and hydrocortisone (HYDRO) belong to the glucocorticoid class of synthetic steroid hormones. Dexamethasone is used to treat many inflammatory and autoimmune conditions, such as rheumatoid arthritis, while hydrocortisone is released in response to stress and a low level of blood glucocorticoids. Hydrocortisone's primary functions are to increase blood sugar through gluconeogenesis, suppress the immune system and aid in fat, protein and carbohydrate metabolism.

Lidocaine (LIDO), an amide synthesized from cocaine, is one of the most extensively used local anesthetics and peripheral analgesics, effective in pain reduction. The second anesthetic investigated in this work was procaine (PROCA), a local anesthetic drug of the amino ester group. It is used primarily to reduce the pain of intramuscular injection of penicillin, and also used in dentistry.

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Membrane treatment technologies of reverse osmosis (RO) and nanofiltration (NF) are recognized as successful removal technologies for various pharmaceuticals from water.[8–11] The usage of these treatments is growing every year compared to other water treatment technologies and are becoming increasingly common in water treatment plants,[10,12–17] but according to the authors' knowledge, no articles on the removal of HYDRO, DEXA, LIDO and PROCA were published, except our previous paper for removal of DEXA.[18] In this paper the removal of DEXA from Milli-Q water with RO/NF membranes (XLE, LFC–1, NF90, NF270, NF and HL) was higher than 99 %. Therefore, the aim of this work was to investigate the removal of glucocorticosteroids (HYDRO and DEXA) and anesthetics (LIDO and PROCA) from water with RO/NF membranes in a long-term operation (24 h) to find accurate rejection.

Materials and methods

Chemicals

The purities of the drugs were ≥ 97 %, as determined by the supplier (Veterina, Croatia). The chemical structures of the pharmaceutical substances and their physico-chemical properties are presented in Table 1. These compounds represent a hydrophilic group (with little approach to hydrophobic for LIDO and PROCA) of micropollutants and are different in size and solubility, which could influence membrane rejection.

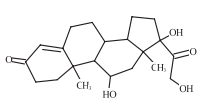
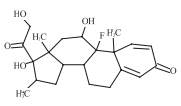
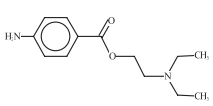
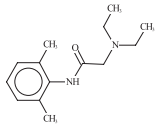
Solutions of the individual standards, and their mixture were prepared in Milli-Q water. The concentration of each drug in the solutions was around 15 mg L^{-1}.

Molecular size (length and width) of the compounds were determined with software package "HyperChem 8.0". The molecular mechanics was applied to optimize the conformation of each compound. The conformations with minimal energy were found using the Polak-Ribiere algorithm, with a convergence limit of 0.4184 kJ mol^{-1} or a maximum number of calculation cycles set at 390.

Membranes

The commercially available RO and NF membranes examined in this work included the XLE (Dow/FilmTec, Midland MI), LFC–1, CPA3 and SWC1 (Hydranautics, Oceanside, CA) polyamide RO membranes, and NF90 and NF270 (Dow/FilmTec) polyamide NF membranes. All membranes were stored in a dark, cold place (refrigerator) and their characteristics are presented in Table 2.

Table 1 – *Physico-chemical properties of the selected micropollutants*

Formula	HYDRO	DEXA	PROCA	LIDO
	$C_{21}H_{30}O_5$	$C_{22}H_{29}F_1O_5$	$C_{13}H_{20}N_2O_2$	$C_{14}H_{22}N_2O_1$
CAS number	000050-23-7	000050-02-2	000059-46-1	000137-58-6
MW (g mol^{-1})	362.47	392.47	236.32	234.34
log $K_{O/W}$ [a]	1.61	1.83	2.14	2.44
Water solubility [b] (mg L^{-1})	320	89	9450	4100
Dipole moment (μ) (D) [c]	4.14	6.30	4.00	3.54
pK_a [d]	13.86	13.48	8.05	8.01
d_c [e]	0.859	0.889	0.712	0.709
Molecular structure				
Width [f] (nm)	0.505	0.613	0.559	0.483
Length [f] (nm)	1.167	1.015	0.969	0.908

[a] Obtained from EPI SUITE™ v4.10

[b] HYDRO and DEXA at 25 °C and PROCA and LIDO at 30 °C

[c] dipole moment calculated by Gaussian[19]

[d] Obtained from Syracuse Corporation (SRC) PhysProp database (http://www.syrres.com/esc/physdemo.htm) and http://www.drugbank.ca

[e] d_c effective diameter of organic compound in water (d_c=0.065 · $(MW)^{0.438}$)

[f] calculated with HyperChem 8.0

Table 2 – *Membrane characteristics*

Membrane	LFC–1	XLE	NF90	NF270	SWC1	CPA-3
MWCO[18]	100	100	100–200	150–300	100	100
R_{NaCl} (%) [a]	91.06	92.44	83.40	20.53	98.64	76.02
R_{CaCl2} (%) [a]	96.07	98.74	96.38	43.33	83.21	96.29
J_w (L m^{-2} h^{-1}) [b]	24.30±0.64	83.79±4.22	84.76±8.15	145.11±10.42	7.13±0.92	27.79±1.26
Contact angle (°)[20–26]	16.4–23.8	46.4–66.3	44.7–63.2	29–55	41.7–55.9	73.0±10.0

[a] experimental from this study

[b] pure water flux (experimental data from this study (N=5))

The membranes were tested in a laboratory set-up shown and described previously in details in Dolar *et al.*[18] at the laboratory temperature of 25 °C, working pressure of 10 bar and cross-flow mode (flow rate 500 mL min^{-1}). The preserved membranes were first washed with demineralized water without pressure and then pressurized at 15 bar for 3 h. The nominal characteristics of the membranes were checked with solutions of sodium and calcium chloride (Kemika, Croatia). The concentration of the inorganic solutes in the feed was 300 mg L^{-1}.

The rejection factor R, defined as

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

with c_p and c_f as permeate and feed concentrations, respectively was determined in each experiment. NF/RO experiments with the pharmaceutical solutions were of the long-run type, each lasting for 24 hours. Samples of the individual compounds were taken at the beginning of the experiment (0 h), and after 2, 4, 6, 8, 12 and 24 h, and for the mixture at the beginning (0 h) and the end (24 h) of the experiment.

The membranes were cleaned after each experiment. Cleaning was performed at temperature around 35 °C with commercially available RoClean L211 (1.5 % alkaline agent) supplied by Avista Technologies Ltd (UK).

Analytical determination

The concentrations of inorganic salts NaCl and $CaCl_2$ were determined by the conductometer (Instruments Lab 960 SCHOTT, Germany).

The glucocorticosteroids and anesthetics were analyzed using a Varian ProStar 500 (Walnut Creek, CA, USA) HPLC system consisting of a ProStar 410 autosampler, ProStar 230 tertiary pump system, ProStar 330 diode array detector, and thermostatted column compartment. The column temperature was set to 20 °C and injection volume was 30 µL. C18 Synergy Fusion 150 mm × 4.6 mm, particle size 4 µm column (Phenomenex) was used to separate DEXA and HYDRO, and Luna CN 100 mm × 4.6 mm, particle size 3 μm column (Phenomenex) was used to separate PROCA and LIDO. The same 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). Same mobile phase gradient program was used for both columns: elution started with 2.5 min linear gradient from 0 % A to 8 % B, followed by 3.5 min linear gradient to 10 % B, 5 min linear gradient to 30 % B, 4 min linear gradient to 60 % B and finally 3 min linear gradient to 95 % B which was maintained for 10 min and then 0.1 min linear gradient back to 100 % of A. The flow rate was 0.5 mL min^{-1}. The separation was monitored at absorbance wavelength of 245 nm for DEXA and HYDRO, for PROCA at 300 nm and for LIDO at 210 nm. The limits of detections (LODs) were 0.012 mg L^{-1} for DEXA and HYDRO and 0.050 mg L^{-1} for PROCA and LIDO.

Results and discussion

The nominal characteristics of membranes were checked with two typical inorganic salts, sodium and calcium chloride, while their initial rejection factors are shown in Table 3. The rejection of ionic inorganic solutes by a membrane is regularly measured in order to compare basic properties and the rejection mechanism of the examined membranes. The proximity of the R_{NaCl} and R_{CaCl2} values in case of the RO membranes (XLE, SWC1 and LFC–1) indicates the governing size exclusion mechanism of the solute rejection.[18,27,28] Initial value of R_{NaCl} obtained on CPA3 RO membrane was only 76.0 %, and this was assumed an experimental error since the manufacturer guarantees 99.7 %. Comparing the flux values measured in this work (2.8 L m^{-2} h^{-1} bar^{-1}) and guaranteed by the manufacturer (3.0 L m^{-2} h^{-1} bar^{-1}), aforementioned

experimental error was confirmed. Relatively larger differences between rejection factor of monovalent and divalent salts in case of nanofiltration NF270 membrane, indicate strong repelling action of NF membranes on divalent ions, confirming the presence of a noticeable electrical charge on these membranes. This result shows that the charge exclusion effect prevails for ionic solutes rejection by NF membranes.[18,27,28]

Except at the beginning, the rejection factors of inorganic salts were also measured two times, after processing of the individual DEXA solution and after passing the mixture solution, followed by cleaning, in order to examine the changes on membrane characteristics due to adsorption of organic compounds. The negligibly increase in rejection of inorganic salts for almost all the membranes (Table 3) confirms that the membranes had not been permanently fouled, and that their structure had not been changed. The rejection factors of $CaCl_2$ were the same at the beginning and end.

Table 3 – *Rejection factors, R of inorganic salts NaCl and $CaCl_2$ during membrane treatment*

		R / %					
		XLE	SWC1	LFC–1	NF270	CPA3	NF90
NaCl	1	92.4	98.6	91.1	20.5	76.0	83.4
	2	97.6	98.8	96.1	22.5	94.4	94.5
	3	97.4	98.3	97.5	28.6	94.0	94.8
$CaCl_2$	1	96.1	98.7	96.4	43.3	83.2	96.3
	3	96.8	98.1	96.3	–	88.3	96.4

1 – start (initial)

2 – after processing the DEXA followed by cleaning

3 – after processing the mixture followed by cleaning

RO/NF experiments with pharmaceutically active compounds were performed in a long-term operation (24 h) in order to examine the physicochemical interactions in membrane system between the solute and the membrane and to obtain accurate rejection of the selected compound. It should be also pointed that the objective of this work was to examine the removal of emerging contaminants, so holdup tank and flasks for collecting permeate were covered with aluminum foil to prevent photodegradation.[29]

Due to accomplishing steady-state, samples of permeate were taken at 0, 2, 4, 6, 8, 12 and 24 h of the treatment, and Kimura *et al.*[30] showed that steady-state was accomplished after 6 hours.

Rejection factors of the selected compounds at the sampling times are presented in Table 4.

Table 4 – *Rejection factors, R of the selected compounds during 24 h treatment*

		R / %			
		LIDO	PROCA	HYDRO	DEXA
XLE	0 h	98.4	99.6	99.3	99.3
	2 h	97.3	96.0	99.3	99.5
	4 h	97.7	96.4	99.3	99.5
	6 h	97.5	95.5	99.3	99.4
	8 h	97.2	95.0	99.3	99.4
	12 h	98.1	95.7	99.3	99.5
	24 h	98.3	96.0	98.8	99.6
SWC1	0 h	>99.9	>99.9	99.9	99.9
	2 h	99.3	99.3	99.6	99.6
	4 h	98.6	98.4	99.6	99.6
	6 h	98.8	98.0	99.6	99.6
	8 h	98.5	97.5	99.5	99.6
	12 h	98.3	97.7	99.5	99.6
	24 h	98.6	97.6	99.6	99.6
LFC–1	0 h	>99.9	>99.9	99.6	99.8
	2 h	>99.9	99.4	99.5	99.7
	4 h	>99.9	99.4	99.6	99.8
	6 h	>99.9	99.3	99.5	99.7
	8 h	>99.9	99.4	99.5	99.8
	12 h	>99.9	99.4	99.4	99.7
	24 h	>99.9	99.4	99.7	99.8
NF270	0 h	60.8	69.1	94.8	99.1
	2 h	56.8	50.7	94.9	99.0
	4 h	55.3	50.0	95.2	99.0
	6 h	56.6	48.7	95.1	99.1
	8 h	59.0	44.9	95.2	99.0
	12 h	63.0	47.3	95.6	99.2
	24 h	61.6	43.2	95.7	99.1
CPA3	0 h	98.8	99.6	95.8	98.2
	2 h	86.8	93.2	92.2	96.3
	4 h	81.8	90.4	93.9	96.6
	6 h	82.9	89.0	93.6	96.8
	8 h	84.0	86.0	94.0	96.8
	12 h	82.5	88.3	94.6	96.7
	24 h	77.2	91.6	94.5	97.1
NF90	0 h	99.3	99.6	99.4	99.6
	2 h	99.4	98.5	99.3	99.6
	4 h	99.1	98.5	99.3	99.6
	6 h	99.1	98.6	99.4	99.6
	8 h	99.1	98.4	99.3	99.6
	12 h	99.2	98.7	99.4	99.6
	24 h	99.2	98.8	99.4	99.7

At the beginning of the experiment (0 h), the highest rejections were for RO membranes, i.e. all investigated compounds were removed more than 98 %. This can be explained with size exclusion mechanism, because molecular weight (MW) of the compounds (Table 1) are larger than molecular weight cut off (MWCO) of the RO membranes[20] (Table 2). In addition, molecular lengths of the compounds are between 0.908 nm and 1.167 nm, compared to pore sizes of reverse osmosis membranes, less than 1 nm.[18,28] The same behavior was displayed by the tight NF90 nanofiltration membrane, which has similar porous structure to RO membrane. The second tight NF270 membrane had rejection 60.8 % and 69.1 % for smaller compounds (LIDO and PROCA) and due to the size exclusion mechanism, rejection increased with MW, i.e. molecular length. Košutić *et al*.[28] classified NF90 and NF270 into tight NF membranes and showed that the pore size distribution of NF270 membrane is bimodal with the main peak at 0.90 nm and an additional peak at 1.56 nm, making the distribution similar to those of the loose NF membranes. The presence of larger pores in active layer of NF270 membranes makes it permeable for smaller compounds of LIDO and PROCA.

Rejection factors obtained for HYDRO, presented in Table 4, were constant for all used membranes, except for NF270 and CPA3, which had negligibly increase. The same results can be observed for DEXA (Table 4). All rejection factors were relatively constant. HYDRO and DEXA are hydrophilic compounds due to log $K_{O/W}$ 1.61 and 1.83, respectively. The rejection factors confirm that these hydrophilic compounds do not adsorb on the membrane polymeric matrix (membrane active layer or "skin")[31] but were effectively rejected by RO/NF membranes via steric hindrance or the size exclusion mechanism[30,31] due to larger length of the compounds than pores of the selected membranes.

For PROCA and LIDO, the rejection factors decreased for some membranes (SWC1, NF270 and CPA3). These compounds are smaller (MW around 230 g mol^{-1}) with log $K_{OW} > 2$, representing slightly more hydrophobic compounds. This is important for removal because Nghiem *et al.*[32] stated that hydrophobic trace organics can adsorb onto the membrane surface and subsequently may diffuse through RO and, in particular, NF membranes. For both compounds, the rejections were constant during long-term operation for XLE, LFC-1 and NF90 membranes. Therefore, it could be concluded that they did not adsorb or diffuse through membrane polymeric matrix. For other membranes (SWC1, NF270 and CPA3) rejections were not constant, therefore, adsorption has to be taken into account together with size exclusion, showing that removal of some hydrophobic compounds can actually be lower than that predicted based solely on a steric hindrance transport model. Decrease in rejection confirmed that smaller and slightly hydrophobic compounds can adsorb onto active membrane layer and consequently can diffuse through it.

In the mixture solution, (Table 5), RO/NF membranes almost completely removed all investigated compounds, and, in general, it can be concluded that the rejection is even better than from individual solutions. In the case of RO and tight NF90 membranes, no significant difference between rejection in individual and mixture solutions is observed because these membranes provided high removal (≥ 97 %) which is consistent with Dolar *et al*.[18,27] In addition, rejection of LIDO in the mixture solution with CPA3 membrane was higher than in an individual solution. This proves the positive synergy (an effect arising between two or more compounds that produces an effect greater than that of their individual effects) concerning the rejection effectiveness.[9,18,27]

Table 5 – *Rejection factors, R of the selected compounds in mixture solution at the beginning (0 h) and the end of treatment (24 h)*

		R / %			
		LIDO	PROCA	HYDRO	DEXA
XLE	0 h	98.9	99.4	99.0	99.5
	24 h	99.0	97.8	99.1	99.6
SWC1	0 h	99.9	99.9	99.9	99.9
	24 h	98.5	97.4	99.6	99.8
LFC–1	0 h	99.9	99.9	99.7	99.9
	24 h	99.8	99.4	99.7	99.9
NF270	0 h	87.8	57.8	93.8	96.7
	24 h	91.8	70.1	96.7	97.6
CPA3	0 h	99.2	99.7	98.0	98.7
	24 h	93.2	90.8	95.2	97.2
NF90	0 h	99.4	99.6	99.4	99.8
	24 h	99.5	99.2	99.7	99.7

Rejection of LIDO and PROCA obtained on nanofiltration NF270 membrane were higher in mixture which could be also attributed to the synergy effect, i.e. larger molecules (HYDRO and DEXA) increased separation of smaller molecules (LIDO and PROCA).

Conclusions

The efficiency of several RO/NF membranes in removing some frequently used glucocorticostero-

ids and anesthetics drugs from Milli-Q water was determined. The removal of the examined pharmaceuticals by the RO (XLE, SWC1, LFC–1) and the tight NF (NF90) membranes is higher than 98 %. The second tight nanofiltration NF270 membrane however did not retain the smaller LIDO and PROCA molecules satisfactorily (60.8 % and 69.1 %, respectively). Relating the solute rejections to membranes' properties has shown that the dominant rejection mechanism of the examined unionizable drugs by all the membranes was the size exclusion effect.

In the mixture solution additional synergistic effect was observed and had influence on rejection, i.e. higher rejection of smaller LIDO and PROCA molecules were obtained.

Rejection factors for hydrophilic HYDRO and DEXA compounds were very similar and confirm that they do not adsorb onto the active layer ("skin") of polymeric polyamide membranes. Compounds with slightly higher log $K_{O/W}$ values (LIDO and PROCA), i.e. with weak hydrophobic characteristics, had lower rejections after 24 h treatment compared to initial values and were probably adsorbed onto the polymeric matrix and even diffused through it.

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