Available online at www.sciencedirect.com
ScienceDirect
Separation and Purification Technology 53 (2007) 244–249
Separation and Purification Technology
www.elsevier.com/locate/seppur

Removal of antibiotics from a model wastewater by RO/NF membranes

K. Košutić *, D. Dolar, D. Ašperger, B. Kunst

University of Zagreb, Faculty of Chemical Engineering and Technology, Department of Physical Chemistry, Marulicev trg 20, 10000 Zagreb, Croatia

Received 2 June 2006; received in revised form 17 July 2006; accepted 22 July 2006

Abstract

Removal of antibiotics by reverse osmosis/nanofiltration (RO/NF) from a model wastewater of a manufacturing plant producing pharmaceuticals for veterinary use was investigated. The rejection of the examined antibiotics by the selected RO and the tight NF membranes is acceptably high, exceeding in most cases 98.5%. The loose NF membrane retains the smaller antibiotics molecules less effective. Relating the solute rejections to the membranes' porosity has shown that the prevailing rejection mechanism of the examined antibiotics by all the membranes was the size exclusion effect. The rejection of the low molecular organic compounds by all the examined membranes is lower, ranging from 0.517 to 0.976 for the RO and tight NF membranes, and from 0.247 to 0.506 for the loose NF membrane. The rejections also follow the order of the solutes' molecular size. However, the specific physicochemical effects can influence the rejection of some low molecular organics by the examined membranes.

Keywords: Nanofiltration; Reverse osmosis; Membranes; Antibiotics removal; Wastewater; Pore size distribution

1. Introduction

Increased quantities of organics such as pesticides, pharmaceuticals and other organic micropollutants can be found today in the aquatic environment and are of great concern in drinking water, wastewater, and water reuse applications. A large source of such pollutants are industrial waste streams that should be cleaned from such substances before discharge into water bodies. An interesting waste stream is the wastewater of a manufacturing plant producing pharmaceuticals for veterinary use, containing residuals of antibiotics and other organics.

The optimal water and wastewater treatment is sought for each specific case, and membrane processes, particularly reverse osmosis (RO) and nanofiltration (NF) are broadly used for these purposes [1–4]. Although the interest in the RO/NF removal of pharmaceutically active compounds has increased lately [5–9], the results on the removal of antibiotics are still scarce [6,10]. Therefore the novel additional data on the removal efficiency and rejection mechanisms of various membranes would contribute to an improved understanding of antibiotics rejection.

The mechanisms of the organic compounds rejection are usually investigated by the pesticides removal from waters and wastewaters [11–17]. Most of the relevant papers reviewed recently by Bellona et al. [18] show that transport of uncharged organic compounds through RO and NF membranes is controlled primarily by the sieving mechanism. There is a general notion that nonionazable organic solutes of molecular mass ranged between 200 and 300 $\mathrm{g\,mol^{-1}}$ are efficiently rejected by the NF/RO membranes [6]. The rejection of the uncharged organics by RO/NF membranes is, however, often affected by physico-chemical properties of the system, and in case of ionizable organics, the charge exclusion plays significant role in the rejection process.

The sieving mechanism of solute rejection is based on the relation between the size of solute molecules and the size of the membrane pores. The later quantity is often estimated from the manufacturers molecular weight cut-off (MWCO) data. It can also be calculated [17] as the effective pore radius from the rejection data of uncharged molecules, and it can be measured [19] as the membrane's porosity, i.e. a pore size distribution of a membrane's selective layer. In any case, characterizing a RO/NF membrane's porosity and relating it to specific solutes retentions is valuable for understanding a membrane's rejection of various organics.

The objective of this study was to investigate the removal of antibiotics from model wastewaters of a manufacturing plant producing pharmaceuticals for veterinary use, and to find the optimal membrane type and the operating conditions for the

* Corresponding author. Tel.: +385 1 45 97 231; fax: +385 1 45 97 250.
E-mail address: kkosutic@fkit.hr (K. Košutić).

1383-5866/$ – see front matter
doi:10.1016/j.seppur.2006.07.015

pilot experiments with the real wastewater. The efficiency of several RO/NF membranes to remove some frequently used antibiotics and other organics from wastewaters was determined. By relating the solute rejections to membranes' porosity the rejection mechanism of specific solutes can be better understood and the optimal conditions for the antibiotics removal can be found.

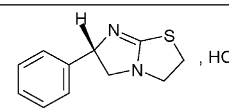
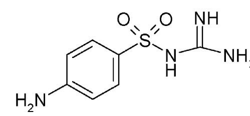
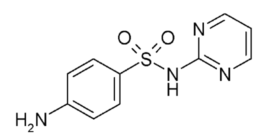
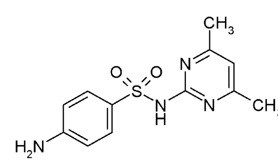
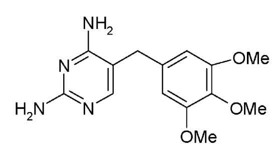
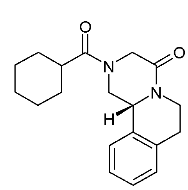
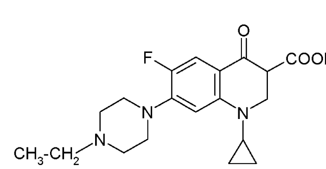
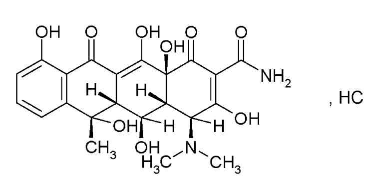
2. Experimental

2.1. Materials and methods

Table 1 lists the antibiotics examined in this work.

Different membranes were chosen for the examinations: the reverse osmosis membranes: XLE and HR95PP from

Table 1
List of the examined antibiotics

Name	Formula	CAS number	Molecular mass (g mol^{-1})	Molecular structure	pK_{a1}	log K_{OW}
Levamisole	$C_{11}H_{12}N_2S{\cdot}HCl$	16595-80-5	240.8			2.87
Sulfaguanidine	$C_7H_{10}N_4O_2S$	57-67-0	214.2		11.3	−1.07
Sulfadiazine	$C_{10}H_{10}N_4O_2S$	68-35-9	250.3		6.5	−0.34
Sulfamethazine	$C_{12}H_{14}N_4O_2S$	57-68-1	278.3		7.4	0.76
Trimethoprim	$C_{14}H_{18}N_4O_3$	738-70-5	290.3		3.23	0.73
Praziquantel	$C_{19}H_{24}N_2O_2$	55268-74-1	312.4			2.42
Enrofloxacin	$C_{19}H_{22}FN_3O_3$	93106-60-6	359.4		6.27	0.70
Oxytetracycline	$C_{22}H_{24}N_2O_9{\cdot}HCl$	2058-46-0	496.9		3.27	−2.87