Journal of Membrane Science 551 (2018) 37–46

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Quantifying the influence of solute-membrane interactions on adsorption and rejection of pharmaceuticals by NF/RO membranes

Yan-ling Liu[a], Xiao-mao Wang[a,*], Hong-wei Yang[a], Yuefeng F. Xie[a,b]

[a] State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China
[b] Environmental Engineering Programs, The Pennsylvania State University, Middletown, PA 17057, USA

ARTICLE INFO

Keywords:
Pharmaceuticals
Nanofiltration
Adsorption
Rejection
Isoelectric point (IEP)

ABSTRACT

The solute-membrane interactions between trace organic compounds (TrOCs) and nanofiltration (NF) or reverse osmosis (RO) membranes result in the adsorption of TrOCs onto membranes and in turn affect the rejection of TrOCs. This study investigated the adsorption and rejection of four positively charged, two neutral and one negatively charged pharmaceuticals (PhACs) by four commercial NF/RO membranes to correlate the adsorbed amount and the steady-state rejection, and to quantitatively evaluate the role of various solute-membrane interactions in adsorption and rejection. The adsorbed amounts of PhACs were determined in static adsorption tests using the isolated polyamide (PA) layers when the RO and tight NF membranes were used, and were calculated from the decline of rejection during filtration when the two loose NF membranes were used. The impacts of electrostatic and non-electrostatic interactions (including hydrophobic interaction and hydrogen bonding) were quantified for positively charged PhACs by comparing the respective adsorption and rejection at neutral pH with that at the isoelectric point (IEP) of each membrane. Results showed that at neutral pH, the adverse effect of adsorption on the steady-state rejection was < 6% for the tight ESPA1 and NF90 membranes and 7–36% for the loose NF270 and HL. A higher adsorbed amount generally corresponded to a larger relative decrease of rejection for all the four membranes. The adsorbed amounts of the positively charged PhACs onto the isolated PA layers of ESPA1 and NF90 at neutral pH were primarily attributed to electrostatic attraction (generally > 65%). Electrostatic attraction was also found to cause the rejection of the tight membranes for the positively charged PhACs to decrease by 0.8–4.3%, that of the loose membranes to decrease by 13.4–28.3%, while the impact of non-electrostatic interactions on the rejection was 1.1–2.3% for the tight membranes and 4.0–9.8% for the loose membranes.

1. Introduction

In recent years, a wide range of organic micro-pollutants were detected in the aquatic environment all over the world, at concentration levels in the ng/L–μg/L range [1,2]. These trace organic compounds (TrOCs), comprising of steroid hormones, pharmaceuticals and personal care products (PPCPs), pesticides, and other extensively used chemicals, can pose potential hazards to both the environment and human health [3,4]. The TrOCs in source water, escaped from wastewater treatment trains, could not be sufficiently removed by the conventional drinking water treatment processes either [5]. High-pressure membrane technologies, including nanofiltration (NF) and reverse osmosis (RO), are considered as promising technologies in the removal of TrOCs with a high reliability and stability [6,7].

It is widely accepted that rejection of TrOCs by NF and RO is primarily determined by the size exclusion mechanism [8]. However, the steady-state rejection of some TrOCs by NF/RO was found to be lower to various extents than the predicted value based solely on size exclusion [9–11]. This was attributed to adsorption of TrOCs onto membranes. The effect of adsorption on TrOC rejection was qualitatively investigated in a number of studies. Steinle-Darling et al. [12] reported that adsorbing TrOCs were generally rejected less than the non-adsorbing ones of similar sizes. A greater adsorption tendency of TrOCs generally resulted in a lower steady-state rejection [13]. However, a direct evidence was by far absent. Determination of the amounts adsorbed or the adsorption capacity would be important for a better understanding of the influence of adsorption on rejection of TrOCs by NF/RO membranes.

A number of methods were available for the determination of amounts adsorbed of TrOCs on membranes. The TrOCs adsorbed in membrane during filtration could be extracted from the membrane by using organic solvent, which however was found to be incomplete [9].

---

[*] Corresponding author.
E-mail address: wangxiaomao@tsinghua.edu.cn (X.-m. Wang).

https://doi.org/10.1016/j.memsci.2018.01.035
Received 9 October 2017; Received in revised form 3 January 2018; Accepted 16 January 2018

Nomenclature

b	rate constant for the exponential decline of rejection (s^{-1})
c_f	solute concentration in the feed water ($kg\ m^{-3}$)
c_p	solute concentration in the permeate water ($kg\ m^{-3}$)
d_h	hydraulic diameter (m)
D_∞	solute diffusion coefficient in water ($m^2\ s^{-1}$)
J_v	permeate flux ($m\ s^{-1}$)
k_f	mass transfer coefficient ($m\ s^{-1}$)
K_c	convection hindrance coefficient
K_d	diffusion hindrance coefficient
Pe	Peclet number
r_p	average pore radius (m)
r_s	Stokes radius of solute (m)
Re	Reynold number
R_0	initial rejection
R_o	observed rejection
R_r	real rejection
R_s	rejection predicted solely by size exclusion
R_{ss}	steady-state rejection
$R(t)$	real rejection over time
ΔR	relative decrease of rejection
S	adsorbed amount of solute ($kg\ m^{-2}$)
Sc	Schmidt number
Sh	Sherwood number
t	time (s)
t_0	initial time for the decline of rejection (s)

Greek letters

δ	membrane thickness (m)
ε	membrane porosity
λ	ratio of solute radius to pore radius
μ	solution dynamic viscosity ($N\ s\ m^{-2}$)
ν	cross-flow velocity ($m\ s^{-1}$)
ρ	water density ($kg\ m^{-3}$)
φ	steric partition coefficient

The amounts adsorbed could also be calculated based on mass balance from the decline of TrOC concentration in the feed [14]. Steinle-Darling et al. [12] proposed a different calculation method based on the decline of time-dependent rejection which could be correlated by exponential equations. The merits of the last method were that it is more direct and can be more accurate in that the decline of rejection is independent of the concentration decrease in the feed by volatilization, hydrolysis, and adsorption onto the filtration system in addition to adsorption on the membrane.

The amounts adsorbed could also be measured by conducting static adsorption experiment as long as the thin polyamide (PA) active layer can be separated from the membrane. It was the active layer, rather than the polysulfone (PS) support layer or the polyester backing layer, which determines the rejection performance of the membrane [8]. The adsorption in the active layer is therefore expected to directly affect the rejection. Conducting static adsorption experiment by using the active layer together with the PS layer could be problematic in that the PS layer could not only slow down the adsorption rate but also increase the amounts adsorbed [9,15,16]. The method is especially suitable when either the TrOC concentration in the feed or the TrOC rejection does not decline with filtration, which is usually the case when RO membranes are used.

Adsorption results from a variety of solute–membrane interactions. These include electrostatic, hydrophobic and some specific interactions (e.g. hydrogen bonding) [17,18]. All these interactions were proved to play an important role in rejection of TrOCs in addition to size exclusion [19–21]. These interactions were incorporated into mathematical models for a better prediction of the rejection of TrOCs by NF/RO membranes. Yang et al. [22] improved the prediction accuracy substantially for the rejection of negatively charged hydrophilic haloacetic acids by combining the Debye length accounting for electrostatic repulsion to the Stokes radius accounting for size exclusion. Lin et al. [16] obtained a good prediction of rejection for most negatively charged pharmaceuticals and personal care products (PPCPs) using the simplified charge concentration polarization model. Wang et al. [23] reported that the rejections of many TrOCs were still over-predicted by the model taking account of both size exclusion and electrostatic interactions. This was attributed to lacking consideration of hydrophobic interactions and hydrogen bonding. Notwithstanding the above understanding, the relative importance of the various solute–membrane interactions on adsorption and in turn the respective effect on TrOC rejection were scarcely experimentally determined. This was especially true for positively charged TrOCs, for which the adverse effect of electrostatic attraction on rejection was pointed out [8,24], yet the significance was rarely quantified.

In this study, the adverse impact of adsorption on rejections of several pharmaceutically active compounds (PhACs) by one RO membrane, one tight NF membrane and two loose NF membranes was investigated. The amounts adsorbed of PhACs were determined by conducting static adsorption test when the RO and tight NF membranes were used, and were calculated from the decline of rejection during filtration when the two loose NF membranes were used. Special attentions were also paid to the adsorption and rejection at the isoelectric point (IEP) of each membrane. The rationale was that, at the IEP, because the membrane surface became non-charged, there were no electrostatic interactions between the PhACs and the membrane regardless of the pK_a values of the PhACs. As such, the impact of electrostatic interactions on adsorption and rejection at neutral pH could be quantified by comparing the respective values at the IEP. This study was dedicated to a better understanding of the TrOCs–membrane interactions and their impact on adsorption and rejection.

Table 1
Membrane properties.

Membrane	Type	Active layer material	Manufacturer	Water permeability (m/s/bar)	Pore radius (nm)	Zeta potential (mV, pH 7.4)	Isoelectric point	Water contact angle (°)	Active layer thickness (nm)
ESPA1	LPRO	Fully aromatic PA	Hydranautics	1.60×10^{-6}	0.35	− 15	3.0	62.3	220
NF90	Tight NF	Fully aromatic PA	Dow Filmtec	2.51×10^{-6}	0.36	− 32	3.8	61.6	250
NF270	Loose NF	Semi-aromatic PA	Dow Filmtec	4.19×10^{-6}	0.44	− 33	3.0	54.3	35
HL	Loose NF	Semi-aromatic PA	GE	3.11×10^{-6}	0.44	− 18	3.7	57.8	55