Journal of Membrane Science 498 (2016) 57–66

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Assessment of the hindered transport model in predicting the rejection of trace organic compounds by nanofiltration

Fan-xin Kong [a], Hong-wei Yang [a], Xiao-mao Wang [a,*], Yuefeng F. Xie [a,b]

[a] State Key Joint Laboratory of Environmental 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

Article history:
Received 30 July 2015
Received in revised form
25 September 2015
Accepted 27 September 2015
Available online 30 September 2015

Keywords:
Nanofiltraton (NF)
Model prediction
Mass transport
Diffusion cell test
Trace organic compounds (TOrCs)

ABSTRACT

The DSPM&DE (Donnan steric pore model and dielectric exclusion) model was employed to predict the rejection of six haloacetic acids (HAAs) and six pharmaceuticals (PhACs), selected to have different molecular weight, hydrophobicity and charge, by two commercial nanofiltration (NF) membranes (HL and NF270). Increasing filtration pressures were applied to vary the rejection ratios. Glucose and NaCl were used as the probe solutes for the determination of the three adjustable parameters involved in the model. Results showed that the model could accurately predict the rejection of the HAAs by both NF membranes with general deviations less than 5%, but it generally over-predicted the rejection of the PhACs. According to the DSPM&DE model, diffusion was the predominant mass transport mechanism in the membrane for both the HAAs and the probe solutes. Experimental determination by conducting diffusion cell test however showed that diffusion only played a minor role in the overall mass transport normally with a contribution less than 10%. The disagreement of model calculation from experimental determination might be due to the improper quantification of the coefficients for solute partitioning between the water phase and the solid (membrane) phase and the hindrance factors for convection and diffusion by the DSPM&DE model. The high accuracy of the model in predicting the rejection of HAAs was owing to the high similarity in physicochemical properties of HAAs with the used probe solutes. If nizatidine were used as the probe solute, the rejection of ciprofloxacin and chloramphenicol by both HL and NF270 would be well predicted.

1. Introduction

Since the development of nanofiltration (NF) membranes in the late 1980's, continual efforts were devoted to understand the mass transport of both water and the contained solutes during NF. It is now generally accepted that NF differs from reverse osmosis in that NF membranes are more porous and as such convection with water, in addition to molecular diffusion, can substantially contribute to the overall mass transport of solutes across the membrane [1,2]. Based on the above understanding, a number of NF models were developed which aim at predicting and interpreting the abilities of NF membranes in rejecting the various solutes under different operational conditions. Successful models can also be utilized for the selection of suitable membranes and optimization of operational conditions. The DSPM&DE (Donnan and Steric Pore Model and Dielectric Effect) is an NF model which is found to be able to predict the rejection ratios for a variety of inorganic solutes with fairly high accuracy [1,3]. The DSPM&DE model is relatively simple to use and involves only three adjustable parameters including average pore size, effective thickness and surface charge density of the membrane [1,4,5]. The three parameters are pre-determined by model-fitting of the rejection data for some simple probe solutes (e.g. glucose and NaCl) by the membrane of interest [1]. Nevertheless, more parameters are in actuality implicitly involved in the DSPM&DE model, which may include the partitioning coefficients for the solutes between the water phase and the solid (membrane) phase, and the hindrance factors for the solute transport in the membrane. It was assumed in the model that the partitioning is determined by both the steric and the electrostatic effects and both the solute convection and diffusion are hindered by the steric effect [6–8].

Nowadays, NF is increasingly used to remove trace organic compounds (TOrCs) from either source water or finished drinking water which is contaminated by these compounds [9–11]. However, both laboratory and onsite studies showed that the rejection ratios for TOrCs were greatly dependent on the membrane characteristics and the physicochemical properties of their own

---

[*] Corresponding author. Fax: +86 10 6277 1472.
E-mail address: wangxiaomao@tsinghua.edu.cn (X.-m. Wang).

http://dx.doi.org/10.1016/j.memsci.2015.09.062
0376-7388/

[12,13]. The DSPM&DE model was used to predict the rejection ratios. Results showed that the model generally over-predicted the rejection of most tested TOrCs apart from a few exceptions [14–17]. The lower-than-predicted rejection was attributed to the high hydrophobicity that is common for organic compounds [18]. A more hydrophobic substance tended to partition more in the membrane material and transported across the membrane with a higher rate, which in turn results in a lower rejection ratio [11,19–21]. A later refinement of the DSPM&DE model by taking into consideration the solute–membrane affinity improved the prediction accuracy for some TOrCs, but not for others [22,23]. A re-assessment of the DSPM&DE model is therefore necessary to further improve its applicability in predicting the rejection of TOrCs.

One way to assess the model is to compare the respective mass transport flux (contributed by diffusion, convection and electromigration) obtained from model calculation with that from experimental determination. Model calculation in previous studies showed that diffusion was often the predominant mass transport mechanism for a number of inorganic solutes (including mineral ions, arsenic and nitrogen compounds) [3,5,24–26]. In contrast, experimental determination of the diffusion flux by conducting diffusion cell test indicated that diffusion played a minor role in mass transport of a number of organic solutes (including some disinfection by-products and pharmaceuticals (PhACs)) [27,28]. Though different solutes and NF membranes were used in the previous studies and as such a direct comparison may not be appropriate, contradiction between model calculation and experimental determination regarding the predominant mass transport mechanism during NF may indicate the improper quantification of the partitioning coefficients and the hindrance factors in the DSPM&DE model.

In this study, the DSPM&DE model was applied to predict the rejection ratios for six haloacetic acids (HAAs) and six neutral PhACs by two NF membranes. Given the fact that a number of previous studies [14–17] have been devoted to test the applicability of the model in predicting the rejection of TOrCs, this study was conducted primarily to assess the model by comparing the model-calculated and experimentally-obtained diffusion fluxes of both TOrCs (HAAs in particular) and probe solutes (glucose and NaCl). HAAs are usually formed from chemical disinfection of secondary effluent, source water and drinking water. HAAs are small, hydrophilic and negatively charged compounds in circumneutral water. HAAs would behave similarly with the probe solutes and as such a comparison of HAAs with the probe solutes would therefore be reasonable. The prediction of rejection of HAAs by NF membranes was not practiced yet. In comparison, PhACs are much more diverse, which may include antibiotics, antidepressants, anti-inflammatory, lipid regulators, X-ray contrast media and psychiatric control medicines. PhACs were frequently detected in natural surface water and drinking water. Different PhACs may have very different physicochemical properties (e.g. molecular size, hydrophobicity and charge). Most PhACs would behave differently from the probe solutes. Previous studies [16,17] showed that the DSPM&DE model generally over-predicted the rejection of PhACs by NF membranes. The ultimate goal of this study was to further increase the applicability of the DSPM&DE model to predict the rejection of organic compounds.

2. Theories

When the solute concentrations in the feed water (C_f) and the permeate (C_p) are known, the apparent rejection ratio for the solute can be calculated by

$$R = 1 - \frac{C_p}{C_f} \tag{1}$$

Due to the effect of concentration polarization, the solute concentration in the closest vicinity to the membrane (C_m) is higher than the bulk concentration in the feed water. As such, the true rejection ratio for the solute is

$$R_{tr} = 1 - \frac{C_p}{C_m} \tag{2}$$

The DSPM&DE was developed to model the mass transport during NF. More details could be found in the original Refs. [1,29]. In brief, the selective layer of an NF membrane was assumed to have a number of parallel tubular nanopores of identical size through which water and the solutes could transport. The water transport flux (J_w) is described by the Hagen–Poiseuille equation,

$$J_w = \frac{r_p^2(\Delta P - \Delta\pi)}{8\mu\delta} = A(\Delta P - \Delta\pi) \tag{3}$$

where r_p and δ are the average pore size and effective thickness of the membrane, respectively, ΔP and $\Delta\pi$ are the hydraulic pressure and osmotic pressure differences across the membrane, respectively, μ is the water viscosity, and A is the water permeability coefficient. The solute transport flux (J_i) is described by the extended Nernst–Planck equation,

$$J_i = K_{i,c} c_i J_w - K_{i,d} D_{i,\infty} \frac{dc_i}{dx} - \frac{z_i c_i K_{i,d} D_{i,\infty}}{R_g T} F \frac{d\psi}{dx} \tag{4}$$

where c_i and Ψ are the solute concentration and electrical potential in the membrane pores at a distance of x from the membrane outer surface, respectively, $D_{i,\infty}$ is the diffusion coefficient of the solute in a dilute solution, $K_{i,c}$ and $K_{i,d}$ are the hindrance factors for convection and diffusion, respectively (refer to Section S1 in Supplementary materials for the mathematical expressions), z_i is the valence of the solute (if any), R_g is the gas constant, T is the water temperature, and F is the Faraday constant. The solute concentration in the permeate is related with the solute and the water fluxes by

$$C_p = J_i / J_w \tag{5}$$

The first, second and third terms on the right-hand side of Eq. (4) are the contributions by convection, diffusion and electro-migration, respectively. By integrating each term one obtains the respective flux [24,26],

$$J_{i,C} = K_{i,c} J_w \frac{c_{i,x=0} + c_{i,x=\delta}}{2} \tag{6}$$

$$J_{i,D} = K_{i,d} D_{i,\infty} \frac{c_{i,x=0} - c_{i,x=\delta}}{\delta} \tag{7}$$

$$J_{i,E} = \frac{z_i K_{i,d} D_{i,\infty} F}{R_g T} \frac{c_{i,x=0} + c_{i,x=\delta}}{2} \frac{\psi_{x=0} - \psi_{x=\delta}}{\delta} \tag{8}$$

where the subscripts C, D and E denote convection, diffusion and electro-migration, respectively.

At the feed water–membrane interface, partitioning of the solute between the liquid phase (i.e. the feed water) and the solid phase (i.e. the membrane) is described by

$$c_{i,x=0} = \Phi_{i,f} C_m \tag{9}$$

where $\Phi_{i,f}$ is the partitioning coefficient in the feed water side which is determined by both the solute and membrane properties through the steric, Donnan and dielectric effects. Similarly, the