



Transport of uncharged organics in ion-exchange membranes: experimental validation of the solution-diffusion model

Lingshan Ma^{a,*}, Leonardo Gutierrez^{a,b}, Marjolein Vanoppen^a, De Neve Lorenz^a, Cyril Aubry^c, Arne Verliefde^a

^a Particle and Interfacial Technology Group, Ghent University, Belgium

^b Facultad del Mar y Medio Ambiente, Universidad del Pacífico, Ecuador

^c Masdar Institute, Khalifa University of Science and Technology, United Arab Emirates

ARTICLE INFO

Keywords:

Ion-exchange membrane
Organic solutes
Transport modelling
Industrial wastewater
Selective separation

ABSTRACT

The concentration-gradient transport of uncharged organics in ion-exchange membranes (IEMs) and the experimental validation of the solution-diffusion model were investigated. Free interaction energies between organics (paracetamol, theophylline, phenazone) and IEMs were above 0, indicating potential solute resistance against partitioning into the membrane phase. Experiments performed in diffusion cells showed a linear increase in the organics concentration in the receiving solution as a function of time, suggesting a purely diffusion-driven transport. A higher organics transport was observed in anion-EMs (AEMs) than in cation-EMs (CEMs), possibly due to the higher cross-linking and lower affinity to organics of CEMs. A correlation between transport and molecular weight was observed in all IEMs following the trend: paracetamol > theophylline > phenazone. The experimental validation of the solution-diffusion model showed that the model underestimated the solutes transport in IEMs. Monte Carlo analysis indicated that the discrepancy between modeled and measured fluxes could not be eliminated even after considering experimental errors. The method for determining contact angle would influence the modeled fluxes. Moreover, the definition of diffusive hindrance factor may lead to these discrepancies, requiring further investigation. This study contributes to the field of selective organics/inorganics separation in the treatment and resource recovery of organics-rich industrial wastewater.

1. Introduction

Wastewaters generated from industrial activities (e.g., food industry, pharmaceutical, textile wastewaters, and brines from Reverse Osmosis-RO operations) are often complex mixtures of high organic content and increased salinity [1–3]. This co-existence of salinity and organics significantly impacts wastewater treatment. While the former hinders the biological treatment of the organic content, the latter hinders the recovery of salts [4,5]. A selective separation of components is of great value to improve the treatability of these wastewaters and to further recover organics and inorganics. Ion-Exchange Membrane (IEM) technologies could be suitable to address this issue. In contrast to pressure-driven membrane processes (e.g., nanofiltration-NF and RO) which suffer from scaling and compact fouling layers, IEMs are less prone to fouling because of low water transport in the membranes, i.e. leading to lower deposition of foulants [6–10]. IEM technologies are currently implemented in a wide range of systems. Briefly, Electrodialysis (ED) and Membrane Capacitive Deionization (MCDI) are viable

IEM-based technologies to perform selective separation of organics and inorganics in complex streams [11–14]. Also, ED has been used in industrial applications (i.e. desalination, food, pharmaceutical, and fermentation industry), in complex broths (e.g., Microbial Electrolysis/Fuel Cells), and for salts, acids, and organics separation [15–17].

Despite the wide use of IEMs in complex streams, only a limited number of studies have focused on the intrinsic transport mechanisms of organics through IEMs [1,11,18–21], which is fundamentally important to achieve an efficient selective separation [22]. Briefly, Zhang et al. [11] observed that the selectivity of the separation of organics (e.g., formate, acetate, propionate, butyrate, tartrate, and aspartate) and inorganics (e.g., NaCl, MgSO₄, NaNO₃, NaHCO₃, and Na₂HPO₄) was influenced by current density, type and concentration of ions, and by the characteristics of the organics. Specifically, low current densities (43 A m⁻²) allowed a selective separation, while hydrophilic organic solutes of ionic size close to the free volume size of the IEM were prone to transport through the membrane. Vanoppen et al. [1] stated that the transport of trace organic contaminants in ED is mainly diffusion-

* Corresponding author.

E-mail address: Lingshan.Ma@UGent.be (L. Ma).

<https://doi.org/10.1016/j.memsci.2018.07.029>

Received 1 May 2018; Received in revised form 18 June 2018; Accepted 12 July 2018

0376-7388/ © 2018 Elsevier B.V. All rights reserved.

driven, irrespective of current densities within a 100–200 A m⁻² range, while the transport of trace organic contaminants was suppressed in the presence of salts. Conversely, Han et al. [18,19] observed that convective drag of organics by transported salts was not negligible compared to diffusive transport at high desalination degrees (i.e. depending on the current, the diffusive and convective flux densities could be in the same order of magnitude for a specific solute), and proposed a phenomenological model to predict the transport of salts and organics in ED.

In contrast, there is a vast amount of studies on the transport mechanisms of organics in NF/RO (dense) membranes [23,24]. Briefly, according to the solution-diffusion model (i.e. successfully used for predicting the transport of uncharged solutes in dense membranes), solutes are suggested to first partition into NF/RO membrane top layers, followed by diffusion through the membrane pores [25]. Sata [26] has proposed that this model would be also applicable to IEMs, also considered as dense membranes. No attempt to model uncharged organic transport in IEMs using the solution-diffusion model has been conducted. Although the partitioning of a solute in a membrane is mainly dependent on the solute-membrane interface (i.e. partition coefficient), previous studies on dense membranes have only focussed on steric exclusion [27,28]. Recent references have shown that other mechanisms (i.e. electrostatics, Lewis acid/base, and Van der Waals interactions) play a major role. To the best of our knowledge, the influence of the physicochemical characteristics of uncharged organic solutes and membranes, as well as their interactions, on the transport of organics in IEMs has not been mechanistically investigated or physically described (i.e. modeled), representing a key gap in knowledge.

In the current study, the concentration gradient-based transport (i.e. diffusive transport) of uncharged organics in IEMs was investigated and subjected to the assumptions of the solution-diffusion model. The influence of the physicochemical characteristics of uncharged organics and membranes on the diffusive transport were studied through a rigorous characterization using sensitive experimental methods (i.e. ¹H NMR, SEM, ESEM, FIB, and contact angle measurements). Commercial anion and cation exchange membranes (AEM and CEM Fujifilm type I and II) were selected and compared. Paracetamol, theophylline, and phenazone (uncharged pharmaceuticals) were selected as model organics due to their well-known characteristics and environmental relevance. Specifically, these uncharged compounds have been widely detected in natural aquatic environments and water-treatment systems [1,23,29,30]; thus, potentially affecting (Reverse) ED-based processes (i.e., where organic micropollutant-contaminated fresh water is used as the low salinity stream) and selective separation processes in organics/inorganics-rich industrial wastewater streams. The transport of these uncharged organics in IEMs was described using the solution-diffusion model and a rigorous statistical analysis of the uncertainty of experimentally determined parameters was conducted. Results from this study could highly assist in the development of a predictive tool for organics transport in IEMs.

2. Materials and methods

2.1. Theory

According to the solution-diffusion model (Eq. (1)) [31], uncharged organic solutes transport through dense membranes by dissolution (i.e. partitioning), followed by diffusion toward the receiving side,

$$J_s = B \cdot \Delta C = \frac{D_{s,m} \cdot \phi \cdot \varepsilon}{\Delta x} \cdot \Delta C \quad (1)$$

where J_s is the solute flux (g m⁻² s⁻¹), B is the solute permeability constant (m s⁻¹), $\Delta C = C_f - C_p$ is the concentration gradient across the membrane (i.e. C_f is the concentration of organic solutes at the feed side, and C_p is the concentration of organic solutes at the receiving side) (g m⁻³), $D_{s,m}$ is the solute diffusion coefficient in the membrane (m²

s⁻¹), ϕ is the partition coefficient (-), ε is the membrane porosity (%), and Δx is the thickness of the membrane (m). Eq. (1) describes the flux of a solute as a function of the concentration difference between feed and receiving solutions across the membrane. The solute flux J_s can be obtained from diffusion experiments as a function of concentration difference ΔC . $D_{s,m}$ (m² s⁻¹) = $K_d \cdot D_{s,w}$ is described as the product between K_d (hindrance factor against diffusion) and $D_{s,w}$ (diffusion coefficient of the solute in water). The hindrance factor (Eq. (2)) describes the resistance of the solute to transport in the membrane matrix for which several correlations have been proposed in literature [32]. The correlation modified by Bowen was selected due to its wide λ range (i.e. $0 < \lambda \leq 0.8$), where $\lambda = r_s / r_p$ is the ratio of solute radius (r_s) to the hypothetical membrane pore radius (r_p):

$$K_d = 1 - 2.3\lambda + 1.154\lambda^2 + 0.224\lambda^3 \quad (2)$$

r_p represents the average radius for membrane voids or space between polymer chains, assuming a size distribution (m). The partition coefficient (Eq. (3)) is determined by both steric effects and solute-membrane affinity (ΔG_i),

$$\phi_s = (1-\lambda)^2 \cdot \exp\left(-\frac{\Delta G_i}{k \cdot T}\right) \quad (3)$$

ΔG_i is defined as the free energy of interaction between solute and membrane in the water phase (J), k is the Boltzmann constant (m² kg s⁻² K⁻¹), and T is the absolute temperature (K). This free energy is described as a quantification of attractive or repulsive solute-membrane affinity interactions (Eq. (4)), which can be determined from solute (S), membrane (M), and water (W) surface tension components, as previously described [33]:

$$\begin{aligned} \Delta G_i = A \cdot \Delta G_{SMW} = 2 \cdot A \cdot [& \sqrt{\gamma_S^{LW} \cdot \gamma_W^{LW}} + \sqrt{\gamma_M^{LW} \cdot \gamma_W^{LW}} - \sqrt{\gamma_S^{LW} \cdot \gamma_M^{LW}} - \gamma_W^{LW} \\ & + \sqrt{\gamma_S^+ \cdot \gamma_S^-} + \sqrt{\gamma_M^-} - \sqrt{\gamma_W^-} + \sqrt{\gamma_W^-} (\sqrt{\gamma_S^+} + \sqrt{\gamma_M^+} - \sqrt{\gamma_W^+}) \\ & - \sqrt{\gamma_S^+ \cdot \gamma_M^-} - \sqrt{\gamma_S^- \cdot \gamma_M^+}] \end{aligned} \quad (4)$$

where A is the contactable surface area between the solutes and the membrane (m²), ΔG_{SMW} is the free energy of interaction per unit area, γ_i^{LW} is the apolar component of the surface tension of component i (J m⁻²), and γ_i^+ and γ_i^- describe the polar/acid-base (electron-acceptor and electron-donor) components of the surface tension of component i (J m⁻²).

All these parameters can be experimentally measured or analytically calculated for different solutes, except for two unknown parameters: membrane pore radius (r_p) and membrane porosity (ε). These two unknown parameters were obtained by solving the equations with data from two solutes, and were further used to predict the transport of a third solute in IEMs. The model was validated by comparing a predicted flux with a measured flux of the third solute. In addition, a sensitivity analysis was performed to explore the error propagation of experimentally-measured parameters and to explain potential discrepancies between model-predicted and measured flux, as well as to investigate the most influential parameters impacting organic solute transport in IEMs.

2.2. Selection of organic solutes for diffusion experiments

Pharmaceutical compounds were selected as model organics due to their relatively small size (no expected fouling/poisoning in IEMs), well-characterized structure and properties, environmental relevance, and their ease to analyze and quantitatively measure. Three pharmaceutical compounds of analytical grade and different characteristics (e.g., molecular weight, functional group, pKa, etc.) were selected: paracetamol, theophylline, and phenazone. Under environmental conditions (i.e. no pH-adjustment) > 99% of the species of the three solutes were non-charged (Fig. S1, Table 1). Their radii were calculated by the Stokes-Einstein equation (Eq. (5)):

Download English Version:

<https://daneshyari.com/en/article/7019645>

Download Persian Version:

<https://daneshyari.com/article/7019645>

[Daneshyari.com](https://daneshyari.com)