



Rejection modeling of ceramic membranes in organic solvent nanofiltration



Stefanie Blumenschein^{a,b,*}, Axel Böcking^c, Uwe Kätzel^a, Stefanie Postel^c,
Matthias Wessling^{c,d}

^a Merck KGaA, Frankfurter Str. 250, 64293 Darmstadt, Germany

^b TU Dortmund University, Department of Biochemical and Chemical Engineering, Laboratory of Fluid Separation, Emil-Figge-Strasse 70, 44227 Dortmund, Germany

^c Chemical Process Engineering, AVT.CVT, RWTH Aachen University, Turmstr. 46, 52056 Aachen, Germany

^d DWI – Leibniz-Institute for Interactive Materials, Forckenbeckstr. 50, 52074 Aachen, Germany

ARTICLE INFO

Article history:

Received 30 October 2015

Received in revised form

2 February 2016

Accepted 20 February 2016

Available online 3 March 2016

Keywords:

Ceramic membranes

Inorganic membranes

Organic solvent nanofiltration

Solvent resistant nanofiltration

Transport models

ABSTRACT

In this work, a transport model based on equations for aqueous nanofiltration has been adapted to describe the rejection of ceramic membranes for nanofiltration in organic solvents. Required membrane parameter were taken from permoporometry measurements of the respective membrane. The calculated results were validated by rejection measurements with different membranes of MWCOs between 350 and 1200 g/mol. By selecting an appropriate standard deviation of the pore size, rejection curves measured with polystyrenes in THF were successfully described using the model without any fitting parameters. Differences between the calculated and the experimental rejections were smaller than 0.7% for the membrane with the smallest pore size. The use of the model for a real life solute system has been checked with different specialty chemicals and indicates a good transferability. Variations of process parameters as temperature, pressure and feed velocity were in excellent accordance with the experimental observations. However, to reflect the incomplete rejection of membranes with a high amount of defect pores (detectable by the permoporometry measurement), the model has to be extended as well as for the applicability to different solvents.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Organic solvent nanofiltration is a new emerging technology. As it allows to use the advantages of membrane technology as low energy consumption and processing at mild temperature conditions in organic solvents it is a very promising tool for process intensification in chemical and pharmaceutical industries. Studies concerning real life applications are published more and more in literature [1–6]. Meanwhile first OSN processes have been established in industry [7,8].

However, the lack of transport models for a priori process simulations hinders OSN to become a widespread standard downstream tool. For polymeric membranes a lot of effort has been put into the clarification of underlying transport phenomena during the last years. Some authors found good correlations with experimental results for pore-flow models [9], others could reflect

their experimental data better by solution-diffusion [10–13] or Maxwell–Stefan [14–16] approaches. Up to now, there is still no universal transport model applicable for all the different membrane types and materials.

Ceramic membranes are superior to polymeric membranes in some important properties as chemical, mechanical and thermal stabilities. Furthermore, they can be stored dry and do not show any swelling behavior in organic solvents that might affect membrane performance over lifetime. Despite those advantages, hitherto only one ceramic membrane with a hydrophobized surface for OSN is commercially available. Therefore, transport characteristics are much less investigated compared to polymeric membranes. Additionally, due to the multifaceted interactions between membrane, solvent and solute, the prediction of transport mechanism in OSN is much more complicated compared to aqueous applications. Marchetti et al. [17] investigated the separation behavior of different ceramic membranes in solvent/water mixtures. They studied the effect of the competition between solvent-membrane and solute-membrane affinities and found that preferential solvation affects the rejection. Hosseinabadi et al.

* Corresponding author at: Merck KGaA, Frankfurter Str. 250, 64293 Darmstadt, Germany.

E-mail address: stefanie.blumenschein@merckgroup.com (S. Blumenschein).

[18,19] developed Grignard functionalized ceramic nanofiltration membranes and found a correlation between the rejection and the solubility parameter of the solvent and the solute reflecting the interactions of the three components. Based on the single commercial OSN membrane and further membranes for aqueous applications, some authors found correlations for the prediction of solvent fluxes through ceramic membranes [20–22]. However, no models predicting solute transport and rejection have been published so far.

Here, performance data of ceramic OSN membranes are presented, which are calculated by the transport model of Bowen and Welfoot [23], originally developed for transport modeling of ceramic nanofiltration membranes in aqueous applications. To consider effects of the organic solvents and interactions of the solutes (polystyrenes) computation of unknown solute parameters in dependence of the solvent was included in the model. The results were validated with low molecular weight cut-off ceramic membranes for organic solvent nanofiltration [24] of different mean pore sizes.

2. Theoretical background

In general three different types of transport models can be distinguished:

- (1) Irreversible thermodynamic models,
- (2) pore-flow models and
- (3) solution-diffusion models.

For the first type the membrane is represented as a black-box. The other models are based on an assumption about the membrane structure and thus take membrane properties such as pore sizes into account [25].

Irreversible thermodynamic models assume that the permeate flux of each species is proportional to its respective driving force at steady state. Kedem and Katchalsky [26] developed a model for water desalination which was improved by Spiegler and Kedem [27]. These models are most effective in the description of nanofiltration and reverse osmosis applications in aqueous systems. However, their applicability is limited in organic solvent nanofiltration (OSN). The derivations of the previous models are based on several simplifications which are unsuitable for an adaption to OSN, for instance the absence of pressure dependence on solute transport. In addition, many of the model parameters (permeability of the solvents or local permeability, e.g.) are often unknown and difficult to measure. Hence, usually the model is reduced to a membrane dependent pore-flow model. Van der Bruggen et al. [28] and Geens et al. [29] described some of these reduced models for aqueous NF and OSN.

In such pore-flow models the transport of solvent and solutes occurs as a consequence of a pressure gradient in the membrane. The solvent transport is calculated with a Hagen–Poiseuille or Carman–Kozeny-correlation [30].

$$J_V = \frac{r_p^2 \epsilon \Delta p_{eff}}{8\tau\eta \Delta x} \quad (2.1)$$

$$J_V = \frac{\epsilon^3}{K\eta S_A^2 (1 - \epsilon)^2} \frac{\Delta p_{eff}}{\Delta x} \quad (2.2)$$

with the effective pressure Δp_{eff}

$$\Delta p_{eff} = (\Delta p - \Delta \pi). \quad (2.3)$$

As a consequence of the concentration difference of solutes

between feed and permeate an osmotic pressure arises. Thereby, the transport comprises convection and diffusion. To consider these phenomena the flux-equations are usually derived from the Maxwell–Stefan-Equation. They incorporate relations between hindrance factors for convection K_c and diffusion K_d and the ratio of solute radius to pore radius λ [25]. Charged solutes can be taken into account as well.

Combe et al. [31] presented a model that includes concentration polarization. They determine the hindrance factors by the equations of Bungay and Brenner [32]. These factors are valid for $0 \leq \lambda \leq 1$ [33]. Solutes with $\lambda > 1$ are completely retained.

Bowen and Welfoot [23] developed another model from the Donnan–Steric Pore Model (DSPM) which starts with the extended Nernst–Planck-Equation. They assume a constant pressure gradient at the membrane and completely retained solutes with $\lambda > 1$. The flexibility of this model is a big advantage. Thus, this model can be extended by pore size distribution as well as by concentration polarization [34].

3. Model development

Due to its flexibility and extensibility the model of Bowen and Welfoot [23] assuming a pore membrane was identified as the most suitable to predict the rejection of uncharged solutes by ceramic OSN membranes. The membrane model was implemented in the commercial model development program Aspen Custom Modeler™ (ACM) from Aspen Technology, Inc., Cambridge, Massachusetts, USA.

3.1. Initial model

The initial model is based on the Nernst–Planck-Equation. Assuming a constant activity of the solute in the membrane, the extended Nernst–Planck-Equation can be written as:

$$J_m = K_c c_s v - K_d D \frac{dc_s}{dx} - \frac{c_s K_d D}{RT} \bar{V}_s \frac{dp}{dx}. \quad (3.1)$$

The permeate flux of the solvent is described by the Hagen–Poiseuille relationship. Considering laminar flow in the pores, the pressure gradient can be obtained by the solvent velocity:

$$\frac{dp}{dx} = \frac{\Delta p_{eff}}{\Delta x} = \frac{8\eta v}{r_p^2} \quad (3.1.a)$$

In addition, the equation for solute flux is given by:

$$J_m = c_{sp} v. \quad (3.2)$$

After substitution of J_m and $\frac{dp}{dx}$ and rearrangement of Eq. (3.1) the concentration gradient can be calculated as follows:

$$\frac{dc_s}{dx} = \frac{v}{K_d D} \left[\left(K_c - \frac{K_d D}{RT} \bar{V}_s \frac{8\eta}{r_p^2} \right) c - c_{sp} \right]. \quad (3.3)$$

The concentrations at the membrane walls are calculated with the partition coefficient $\Phi = (1 - \lambda)^2$ [31,35]. Thus, concentration polarization is not taken into account. Furthermore, it is assumed that diffusivity and molar volumes of the solutes are not dependent on their concentrations [23]. This leads to the following boundary conditions:

$$c_{s, x=0} = \phi \ c_{sF} \quad (3.4)$$

$$c_{s, x=\Delta x} = \varphi \ c_{sP} \quad (3.5)$$

Via integration of Eq. (3.3) with this boundary conditions the

Download English Version:

<https://daneshyari.com/en/article/7020676>

Download Persian Version:

<https://daneshyari.com/article/7020676>

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