

Mass transfer of cadmium ions in a hollow-fiber module by pertraction

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Received 23 June 2003; accepted 25 September 2003

Abstract

The facilitated transport of Cd(II) ions through a hollow-fiber-supported liquid membrane with bis-2-ethylhexyl phosphoric acid as carrier was studied. The mass transfer rate, expressed as permeability P , was measured as a function of mean aqueous solution velocity and carrier concentration. Characteristic ion permeabilities of $10\text{--}26 \times 10^{-7}$ m/s were measured at feed velocities between $1 \times 10^{-2}\text{--}19 \times 10^{-2}$ m/s at stripping velocities between $0.22 \times 10^{-2}\text{--}7 \times 10^{-2}$ m/s with constant feed flow. The measured permeabilities were compared to generally accepted mass transfer correlations. The predicted permeabilities adequately fit the experimental data, indicating that the rate limiting step in the transport of the ion was the diffusion through both aqueous films, feed and stripping, whereas the organic resistance of the membrane was negligible. Furthermore, the proposed model allowed the prediction of the permeability of cadmium for different experimental conditions, which is useful to perform experiments to reduce metal levels in water or other effluents.

Keywords: Cadmium; Coupled counter transport; Mass transfer; Mobile carrier; Bis-2-ethyl hexyl phosphoric acid; Hollow fiber; Liquid membrane

Introduction

Cadmium ranks fifth in order of its toxicity. It can cause a number of adverse health effects. Small quantities of cadmium occur naturally in air, water, soil and food. The application of phosphate fertilizers or sewage sludge may increase

cadmium levels in soil. The metal is not often encountered at levels of concern in water, although it can leach into water from pipes and solder or may enter water from chemical waste disposal sites. The largest source of cadmium release to the general environment is the burning of fossil fuels (such as coal or oil) or the incineration of municipal waste materials [1].

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The clean-up of polluted sites requires the development and use of cost-effective and efficient clean technologies for processing wastes. In this way supported liquid membranes present a growing interest for potential applications in membrane processes to water treatment, desalination, recovery of metal and metal separations, organic compounds removal, etc. [2–6]. When considering these advantages along with the small space requirements, moderate capital costs, and ease of operation, membrane technology provides a very competitive alternative to conventional technologies. Different configurations have been tested, but there are mainly three types of liquid membranes: bulk-, emulsion- and supported liquid membranes both in flat-sheet or hollow-fiber [7–10]. Taking into account that the hollow fiber provides a very large interfacial area per unit extractor volume without direct mixing of the aqueous and organic phases, with high stability, this work focused on the study of cadmium mass transfer in a hollow-fiber module.

Knowledge of the rate determining step is of importance for designing or modeling the transport process at large scale. The permeability of the ion was evaluated as a function of flow rate of both feed and stripping solution, as well as carrier concentration. Mass transfer models have been used to describe the cadmium permeability through the supported liquid membrane.

2. Modeling of cadmium mass transfer

The system consists of two aqueous phases, the feed solution (in the inner side of the fiber) and the stripping solution (on the outer side of the fiber). Both aqueous solutions are separated by the supported liquid membrane formed by the carrier denoted as (HX), and the organic diluent solution confined within the fiber pore via capillary action. This forms two aqueous–organic interfaces with well defined transfer areas. This system is represented in Fig. 1 and is referred to

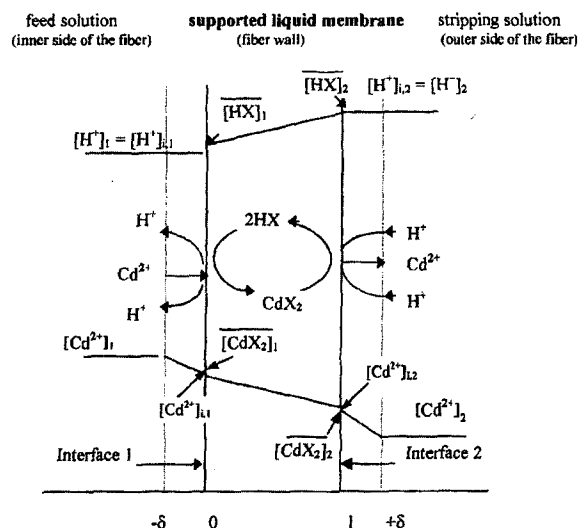
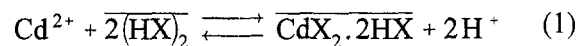


Fig. 1. Schematic representation of cadmium coupled transport with D2EHPA (HX) and concentration profiles in supported liquid membrane.

as counter coupled transport because the metal ion and the proton are transported simultaneously in opposite directions. The reaction between the metal and the organic carrier is an ion-exchange reaction which can be described by an equation like the following [11]:



The over bar indicates the concentration in the organic phase. The equilibrium constant, K_{eq} , can be represented by its logarithmic form:

$$\log \frac{[\overline{\text{CdX}_2} \cdot 2\overline{\text{HX}}]}{[\overline{(\text{HX})}_2]^2 [\text{Cd}^{2+}]} = \log K_{\text{eq}} + 2\text{pH} \quad (2)$$

The evaluation of K_{eq} was carried out by liquid–liquid extraction of cadmium as a function of equilibrium pH. The representation of the experimental data is shown in Fig. 2, from where the equilibrium constant is 9.33×10^{-4} and the value of the slope corroborates the proposed relationship [Eq. (1)].

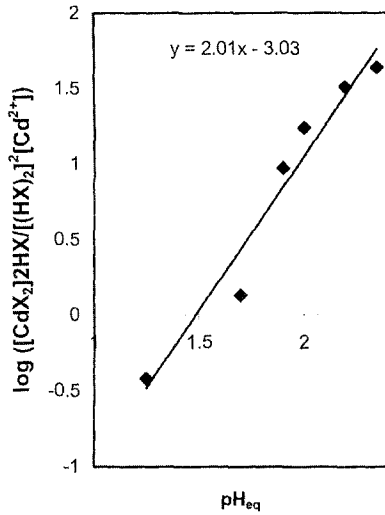


Fig. 2. Cadmium extraction with D2EHPA (HX) as a function of equilibrium pH ($T = 298 \pm 0.5$ K).

A flux density equation was derived by Marchese et al. [12] for a flat-sheet supported liquid membrane. It can be used for the description of the permeability through hollow-fiber liquid membranes because the elementary steps are the same, except for the correction of the cylindrical shape of the fibers. The model takes into consideration three resistances for transport:

- Step 1: the metal ion diffusion through the stagnant layer of the feed solution.
- Step 2: the metal complex diffusion through the fiber (membrane phase).
- Step 3: the metal ion diffusion through the stagnant layer of the stripping solution.

The resistance of other steps such as interfacial reactions of complexation and the diffusion of H^+ in both aqueous stagnant layers have been neglected. At low fractional saturation of the carrier species, the concentration of the free carrier (HX) is much higher than the concentration of the complexed carrier (CdX_2), valid that $[XH] = C_{HX}^0$ (initial carrier concentration). In the mathematical description the transport process through the stagnant layer and organic phase is governed by Fick's law.

Equating the different expression obtained for each step in steady state and adequate rearrangement, the overall permeability of cadmium P through the liquid membrane is given by:

$$P = \left[\frac{1}{[H^+]_1^2} - \frac{1}{[H^+]_2^2} \right] \frac{N_{Cd}}{\Delta [Cd^{2+}] / [H^+]^2} \tag{3}$$

$$= \left[\frac{R_0}{\left([H^+]_1^{-2} + [H^+]_2^{-2} \right) K_{eq} C_{HX}^2} + R_f + R_s \right]^{-1}$$

where N_{Cd} is the cadmium flux through the membrane and the fundamental resistances, R_0 , R_f and R_s are given by:

- organic phase resistance

$$R_0 = l_{ef} / D'_{CdX_2} \tag{4}$$

- aqueous feed phase resistance

$$R_f = 1 / k_f \tag{5}$$

- aqueous stripping phase resistance

$$R_s = 1 / k_s \tag{6}$$

where l_{ef} is the effective thickness of the membrane and D'_{CdX_2} the effective diffusion coefficient of the metal complex in the organic phase; k_f and k_s are mass transfer coefficients of the feed and stripping phases, respectively.

In accordance with our experimental conditions, the proton concentration in both feed and stripping sides have been kept constant and $[H^+]_1 \ll [H^+]_2$, so the overall permeability of the metal can be written as:

$$P = \left[B + \frac{1}{k_f} + \frac{1}{k_s} \right]^{-1} \tag{7}$$

where

$$B = \left[\frac{\ell_{\text{ef}}}{D'_{\text{CdX}_2} K_{\text{eq}} C_{\text{HX}}^{\circ 2} [\text{H}^+]_1^{-2}} \right] \quad (8)$$

2.1. Evaluation of effective membrane thickness, ℓ_{ef}

The fiber geometry is known, but the membrane thickness has to be corrected for the spherical shape of the fiber by means of the inner and outer fiber diameter [13], as follows:

$$\ell_{\text{ef}} = r_f \ln \frac{d_o}{d_i} \quad (9)$$

where r_f is the radius of the fiber on the feed side and d_o and d_i refer to the outer and inner diameter of the fiber, respectively. The aqueous films are also spherically shaped, but this effect is already included in the mass transfer coefficient.

2.2. Evaluation of effective diffusion coefficient, D'_{CdX_2}

The effective diffusion coefficient through the supported membrane depends upon the diffusion coefficient of cadmium complex in the organic phase, D_{CdX_2} , calculated by the Stokes–Einstein equation, as well as the tortuosity ($\tau \approx \sqrt{2}$) and the porosity (ϵ) of the support [9].

$$D'_{\text{CdX}_2} = \frac{D_{\text{CdX}_2} \epsilon}{\tau} \quad (10)$$

2.3. Evaluation of the mass transfer parameters

For the calculation of the permeability from Eq. (7), mass transfer rate parameters have to be known. These include the mass transfer through the aqueous film layer of the feed phase and the mass transfer through the aqueous film layer of the stripping phase. In this work the feed solution flowed inside the fibers and the stripping solution on the outer side of the fibers.

The flow through the hollow fibers, which is in the tube side, can be calculated to be always laminar. The following correlation is commonly used to describe the mass transfer coefficient, k_s , in the stripping solution [14,15]:

$$Sh = a Gz^b \quad (11)$$

$$\frac{k_s d_h}{D_{\text{aq}}} = a \left[\frac{d_h^2 \langle v_2 \rangle}{LD_{\text{aq}}} \right]^b \quad (12)$$

where Sh is the Sherwood number, Gz the Graetz number, d_h is the hydraulic diameter, defined as four times the cross-sectional flow area divided by the wetted perimeter, $\langle v_2 \rangle$ the mean liquid velocity in the outer side of the fibers and L their length, and D_{aq} is the aqueous diffusion coefficient of the metal salt.

For the feed solution, the mass transfer coefficient (k_f) is given by the equation

$$\frac{k_f d_i}{D_{\text{aq}}} = m \left(\frac{d_i^2 \langle v_1 \rangle}{LD_{\text{aq}}} \right)^n$$

where $\langle v_1 \rangle$ is the mean liquid velocity inside the fibers.

3. Experimental

3.1. Reagents and membrane

Di(2-ethyl hexyl) phosphoric acid (D2EHPA) from Fluka was used as the carrier. It is freely miscible with non-polar organic solvents in which it exists mainly as a dimer [16]. Kerosene was used as the organic solvent for its low solubility in water, high surface tension and low volatility, which makes the liquid membrane highly stable. The kerosene was JP1 grade (relative density: 825 kg m⁻³, viscosity: 0.15 kg m⁻¹s⁻¹, boiling point: 525–573 K) used without further purification.

The aqueous feed solution was an aqueous solution of Cd(II) as CdCl₂ (Merck) at an ionic concentration of 0.1 g L⁻¹ in distilled water buffered with acetic-acetate to keep the pH value near 5 where the extraction of cadmium ions is maximum. The stripping solution was distilled water buffered to an appropriate value (pH ≈ 1.8). Analytical grade reagents were used throughout.

The hollow fiber membrane was microporous polytetrafluoroethylene fibers (Goretex, Japan). The support has excellent properties such as flexibility and high chemical and mechanical resistance. Some characteristics of the fibers are shown in Table 1.

3.2. Apparatus for transport measurements

The experimental transport measurements for cadmium were carried out with a hollow-fiber module (HFM) whose characteristics are described in Table 2. Fig. 3 shows a schematic of the experimental equipment. It has a bundle of four fibers disposed vertically inside a glass tube

Table 1
Characteristics of the hollow fiber

Porosity (ϵ), %	45–55
Maximum pore size, μm	1.5–2.0
Inner diameter (d_1), m	8×10^{-4}
Outer diameter (d_2), m	1.80×10^{-3}
Hydraulic diameter (d_h), m	9.55×10^{-3}
Membrane thickness (ℓ_{ef}), m	6.49×10^{-4}

Table 2
Characteristics of the hollow fiber module

Length of fibers (L), m	0.18
Number of fibers	4
Inner surface (A_1), m ²	1.809×10^{-3}
Outer surface (A_2), m ²	4.071×10^{-3}
Housing diameter (d_c), m	0.015
Fraction of the cross-sectional area occupied by the tubes	0.058

with double wall for thermostated water circulation.

The organic phase was introduced by capillary action by filling the fiber lumen and maintaining it for 1 h; then the organic phase was removed from the module by gravity. A stream of water removes the excess.

Feed and stripping solutions are fed concurrently upwards by two peristaltic pumps (Masterflex) at various flow rates. The feed solution was circulated through the inner side of the fiber and the stripping one on the outer side.

Acidity was measured with a Metrohm-Herisau pH-meter and a combined glass Ag/AgCl electrode. The permeation of cadmium was monitored by periodically sampling both effluent solutions at steady state and was analyzed after appropriate dilution by a Varian AA 50 atomic absorption spectrophotometer. The measurements were made in duplicate, and the difference between the two values was less than 5%.

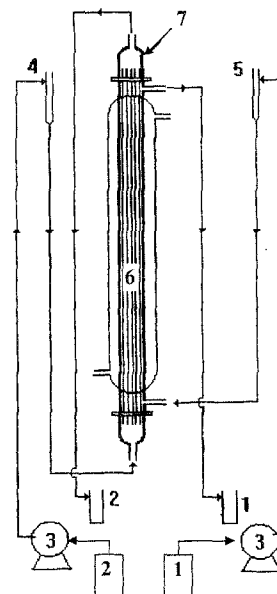


Fig. 3. Schematic representation of the equipment with the hollow-fiber module used in permeation experiment of cadmium ions (1 stripping solution, 2 feed solution, 3 peristaltic pumps, 4 and 5 level vessels, 6 hollow fibers, 7 hollow fiber module).

The experimental tests were carried out over periods of time of 2 to 4 h. During the runs no substantial change in the SLM behavior because of breakdown, fouling or liquid depletion was noticed. The experimental mass balance was calculated by: $Fv_1([Cd]_0 - [Cd]_{e,1}) = Fv_2 [Cd]_{e,2}$; where Fv is the volumetric flux; $[Cd]$ is cadmium ion concentration at steady state; and the subscripts o, e, 1, 2 refer to initial, exit, feed and stripping, respectively. In all the cases it closed within an error of $\pm 10\%$.

The experimental variables investigated were the extraction of cadmium ions with the reagent D2EHPA and the effects upon cadmium permeability of the carrier concentration in the organic phase and the feed and stripping solution velocity.

4. Results and discussion

Permeation experiments were performed to investigate both the influence of carrier concentration in the HFM and the flow rate of solutions upon cadmium permeability. In all the experiences the feed solution was an aqueous solution of Cd at pH = 5 and the stripping solution was distilled water buffered to pH 1.8. These conditions were established from liquid–liquid extraction determination. The carrier concentration in the fiber was varied between 0.2 and 2 M. The feed velocity was varied between 1×10^{-2} and 19×10^{-2} m/s (Reynolds number, Re , between 9.5 and 152.5) with constant stripping velocity, and then the latter was varied in the range 0.22×10^{-2} to 7.2×10^{-2} m/s (Re between 21 and 687.6) with constant feed velocity ($\langle v_1 \rangle = (14.6 \pm 0.5) \times 10^{-2}$ m/s).

The experimental value of permeability, P_{ex} , was calculated from Eq. (3), with $[H^+]_2 \gg [H^+]_1$.

$$P_{ex} = \frac{N_{Cd}}{[Cd]_{m,1}} = \frac{Fv_2 [Cd]_{e,2}}{A_m [Cd]_{m,1}} \quad (14)$$

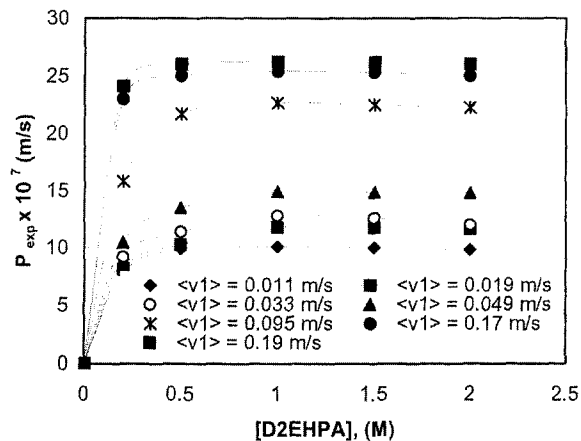


Fig. 4. Experimental permeability of cadmium ions as a function of carrier concentration and feed velocity ($\langle v_2 \rangle = (0.23 \pm 0.005) \times 10^{-2}$ m/s).

where Fv_2 is the volumetric flow of the stripping solution and A_m is the mean surface of transfer, $[Cd]_{e,2}$ is the average cadmium ions concentration in the exit of the stripping solution and $[Cd]_{m,1}$ the mean concentration of the cadmium ions in the feed.

Cadmium permeation experiments at different lineal velocity, $\langle v_1 \rangle$, ($\langle v_1 \rangle = Fv_1 / r^2 \pi$) are given in Fig. 4 as a function of carrier concentration with a stripping velocity of $(0.23 \pm 0.005) \times 10^{-2}$ m/s. The results show that the permeability is dependent on the feed flow rate but not on the carrier concentration above a concentration of 0.2–0.5 M. The transport rate is therefore limited through the aqueous film on the feed side of the membrane in this region.

To calculate the permeability P from the model with Eq. (7), constant parameters are needed: $[H^+]_1 = 6.31 \times 10^{-6}$ M, $D_{aq} = 4.99 \times 10^{-10}$ m²/s; $D'_{CdX_2} = 2.67 \times 10^{-11}$ m²/s. The value of k_f can be obtained by calculation from Eq. (13), where m and n are the values of Seider and Tate correlations: 1.86 and 0.33, respectively. This correlation was derived in analogy with the heat transfer correlation, and it is used to describe laminar flow through a tube [17].

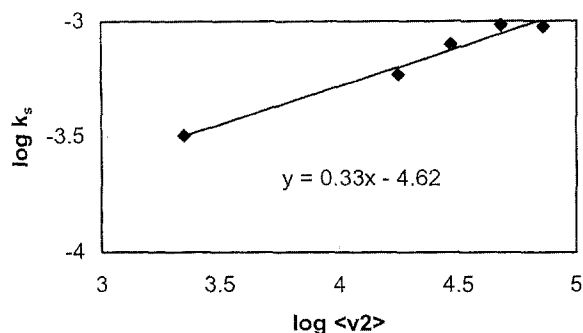


Fig. 5. Logarithmic representation of Eq. (11) for different stripping velocity ($\langle v_1 \rangle = (14.6 \pm 0.5) \times 10^{-2}$ m/s, [D2EHPA] = 1 M).

To evaluate the k_s , experiments of Cd(II) permeability as a function of stripping linear velocity, $\langle v_2 \rangle$, with constant feed solution velocity of 14.57×10^{-2} m/s were carried out. The carrier concentration was 1 M. The fitting parameters $a = 4.57$ and $b = 0.33$ for the mass transfer coefficient of stripping were evaluated from the logarithmic representation of Eq. (12), which is shown in Fig. 5. The fitting of the experimental data is very good as is shown in Fig. 6. This result confirms the proposed model for cadmium coupled transport and the correlations used in the calculations of the mass transfer coefficients. The term B , which contains the organic resistance, is much lower than the other contributions, so it can be neglected.

With the mass transfer rate parameters determined, Eq. (7) was also used to fit the experimental value of permeability of cadmium through the aqueous feed. The results are shown in Fig. 6 for a carrier concentration of 1 M. The predicted mass transfer rate parameters adequately interpreted the experimental permeability values calculated from Eq. (14), validating the model. The results confirm that in these operating conditions the aqueous layer resistances are the dominant step in cadmium transfer through the liquid membrane.

To obtain a higher mass transfer rate, the flow rate of the feed can be increased, but the higher

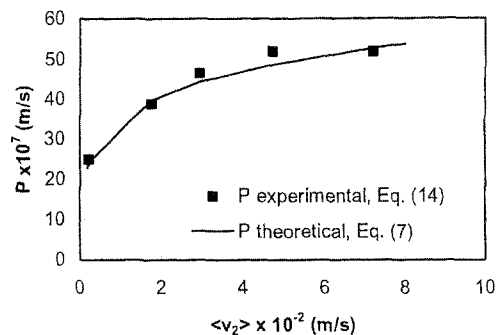


Fig. 6. Model fitting of cadmium ions permeability as a function of stripping velocity ($\langle v_1 \rangle = (14.6 \pm 0.5) \times 10^{-2}$ m/s, [D2EHPA] = 1 M).

the flow rate, the higher the pressure drop over the module and the larger the possibility of the leaching of the carrier. The optimal flow rate will be a balance between pressure drop and mass transfer rate. The carrier concentration can be kept low (0.5–1 M) because the reaction rate and the diffusion through the membrane are not rate limiting.

5. Reduction of cadmium content in water

The cadmium ion is one of the heavy metals that affects the feeding chain, causing a biocumulative effect between the organisms. This is due to high persistence of the ion in the environment. The quantity of cadmium that can be discharged into water or disposed of as solid wastes from factories that manufacture or employ cadmium has been regulated [18]. A maximum contaminant level of 0.01 mg/L for cadmium in drinking water has been established.

From the experimental study in the HFM, conditions for cadmium content reduction in water can be identified. With an initial ion concentration of 0.012 ± 0.03 mg/L in water, a reduction of 40% of cadmium is obtained with D2EHPA concentration of 1 M, feed and stripping velocity of 1.1×10^{-2} and 0.22×10^{-2} m/s, respectively. Even though the initial ion concentration was duplicate, the final concentration in

the feed solution was below the maximum contaminant level.

6. Conclusions

The permeation of cadmium ions was investigated with D2EHPA as the carrier in a hollow-fiber module. It was found that the rate limiting step in the transport of the ion was the diffusion through both aqueous films: the feed and the stripping sides of the membrane. The permeation of Cd(II) is increased with the increase in the flow rate which makes evident the existence of boundary layers in the aqueous phase. The organic resistance of the membrane was negligible since the permeability of cadmium is practically constant with the variation of carrier concentration in the fiber above 0.2 M.

A mass transfer model to predict extent of Cd(II) permeation was proposed, taking into account resistances typically present in a coupled transport process: aqueous stagnant layer and organic resistances. Accepted mass transfer correlations were used and the fitting parameters were evaluated to compare measured permeability. The results were in reasonable agreement for the experimental conditions examined and confirm that the permeation rate was limited by diffusion through aqueous film, irrespective of the carrier concentration. The proposed model permits the calculation of cadmium permeability for different feed and stripping rate velocities in a hollow-fiber system like that used in this work.

The studied system was effective for performing a reduction of cadmium content in water to permit levels without any contamination of the environment and was fast and economical; however, it is necessary to perform a complete analysis of the experimental conditions such as carriers, organic solvent, pH of aqueous phases, membrane stability, and transfer area in order to obtain a process more suitable for industrial operations.

7. Symbols

A_m	— Mean surface of mass transfer, m^2
B	— Term defined in Eq. (8)
C_{HX}^0	— Initial concentration of the carrier, M
d	— Diameter, m
D	— Diffusion coefficient, $m^2 s^{-1}$
F_v	— Volumetric flow, $m^3 s^{-1}$
K_{eq}	— Equilibrium constant, Eq. (2)
k_f	— Mass transfer coefficient of the feed phase, $m s^{-1}$
k_s	— Mass transfer coefficient of the stripping phase, $m s^{-1}$
L	— Length of fiber, m
N_{Cd}	— Cadmium flux, $mol m^{-2} s^{-1}$
P	— Permeability, $m s^{-1}$
r_f	— Internal radius of the fiber, m
R_f	— Aqueous feed phase resistance, $s m^{-1}$
R_o	— Organic phase resistance, $s m^{-1}$
R_s	— Aqueous stripping phase resistance, $s m^{-1}$
$\langle v \rangle$	— Mean liquid velocity through fibers, $m s^{-1}$

Greek

δ	— Stagnant layer thickness, m
ε	— Support porosity
ν	— Kinematic viscosity, Pa s
τ	— Support tortuosity

Subscripts, superscripts

a, b	— Exponential and pre-exponential factors in Eq. (12)
ℓ_{ef}	— Membrane effective thickness, m
m, n	— Exponential and pre-exponential factors in Eq. (13)

Dimensionless numbers

Gz	— Graetz number ($d^2 \langle v \rangle / L D_{aq}$)
Re	— Reynolds number ($d \langle v \rangle / \nu$)
Sh	— Sherwood number ($k_s d / D_{aq}$)

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