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Transient Analysis of Mass-Transfer Rate in Recovering Metal Ions Using a Microporous Hollow Fiber Membrane and a Water-Soluble Chelating Polymer

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ABSTRACT

Microporous hollow fiber membranes were used with a water-soluble chelating polymer (polyacrylic acid) to recover and concentrate metal ions [copper(II)] from a solution. The polymer (chelator) solution was pumped through the bore of the fibers which was immersed in the metal ions solution. In this process the metal ions diffuse through the fiber porous space into the bore side and react with the chelator passing in the bore of the fiber. The transient change in concentration of metal ions at the outlet of the fiber were measured. The experimental data were well fitted by a one-dimensional convection equation which was derived with relatively simple assumptions and a steady-state theory, and reasonable values for the dispersion coefficient and an overall mass transfer coefficient were obtained.

Key Words. Microporous hollow fiber; Metal ions; Membrane extractor; Axial dispersion; Mass transfer coefficient

INTRODUCTION

A number of papers have recently been published concerning devices using microporous hollow fiber membranes such as gas–liquid contactors, membrane extractors, and others (1–4).

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We previously reported a new method using a water-soluble chelating polymer and a hollow fiber membrane for recovering and/or concentrating metal ions from aqueous solutions (5, 6). In the method, metal ions in an aqueous solution diffuse into a chelating polymer solution through a hollow fiber membrane owing to the concentration difference, and the reactions with the polymer to form metal-polymer complexes. Thus, it is possible to recover and/or to concentrate metal ions from aqueous solution even at low concentration. The method seems to be comparable to such conventional methods as extraction, adsorption, etc.

In this work, the mass-transfer rate of metal ions through a microporous membrane of hollow fibers was studied by a transient method. Experiments were made in the once-through mode. The transient change in outlet concentration was analyzed based on a one-dimensional axial dispersion model. The mass-transfer coefficient for metal ions and the axial dispersion coefficient were determined so as to fit the calculated time courses of the outlet concentration to the experimental ones. The effects of the membrane material and the pore size on the mass-transfer rate were examined. Two kinds of hollow fibers were used with four different pore sizes.

EXPERIMENTAL

Materials

The water-soluble chelating polymer used was commercially available polyacrylic acid (PAA) with a molecular weight of 90,000 (Aldrich Chemical Co.). The microporous hollow fibers used were polyacrylonitrile fibers and polysulfone fibers (Asahikasei Inc., Japan). The characteristics of the hollow fibers used are provided in Table 1. Aqueous solutions of metal ions [Cu(II)] were prepared by dilution of commercial standard solutions for atomic absorption spectroscopy.

TABLE I
Characteristics of the Hollow Fibers Used

	Inner diameter (mm)	Outer diameter (mm)	Length (m)	Molecular weight cut-off	Material
HF 1	0.8	1.4	1.2	6,000	Polyacrylonitrile
HF 2	0.8	1.4	1.2	13,000	Polyacrylonitrile
HF 3	1.4	2.25	1.2	13,000	Polyacrylonitrile
HF 4	1.4	2.0	1.2	10,000	Polysulfone

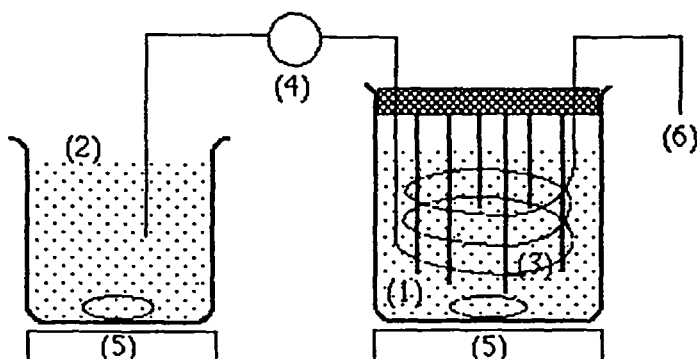


FIG. 1 Schematic diagram of the once-through mode for recovering metal ions: (1) sample solution of copper(II), (2) chelating polymer solution, (3) microporous hollow fiber, (4) peristaltic pump, (5) magnetic stirrer, (6) fraction collector or detector.

Procedure

A schematic diagram of the once-through mode is shown in Fig. 1. As shown in the figure, the hollow fiber was coiled in helical to six Teflon rods (6 mm diameter) which were fixed in a concentric configuration to the cap of the vessel (1 dm³). PAA solution flowed in the lumen (bore-side) of the hollow fiber of 1.2 m. For measurement of the transient changes in the concentration of metal ions recovered in the polymer solution, the hollow fiber was suddenly immersed into the solution of metal ions which was stirred with a magnetic stirrer at 500–600 rpm. The experiments were carried out at room temperature (about 25°C). The outlet polymer solution was sampled with a fraction collector, and the concentration of metal ions in the solution was measured with an inductively coupled plasma (ICP) spectrophotometer (ICP-5000, Simazu Seisakusho Co.).

THEORETICAL ANALYSIS

Concentration Distribution in Cylindrical Membrane of Hollow Fiber

We will first discuss the concentration distribution of the metal ions in the cylindrical microporous membrane of the hollow fiber (see Fig. 2 for the coordinate system). In this study the concentration at the outer surface of the cylinder $r = r_o$ is assumed to be maintained at c_o , in the lumen $0 < r < r_i$ at $c = 0$, and the region $r_i < r < r_o$ is initially at $c = 0$. Provided there is a sufficient stoichiometric amount of PAA (chelating polymer), the concentra-

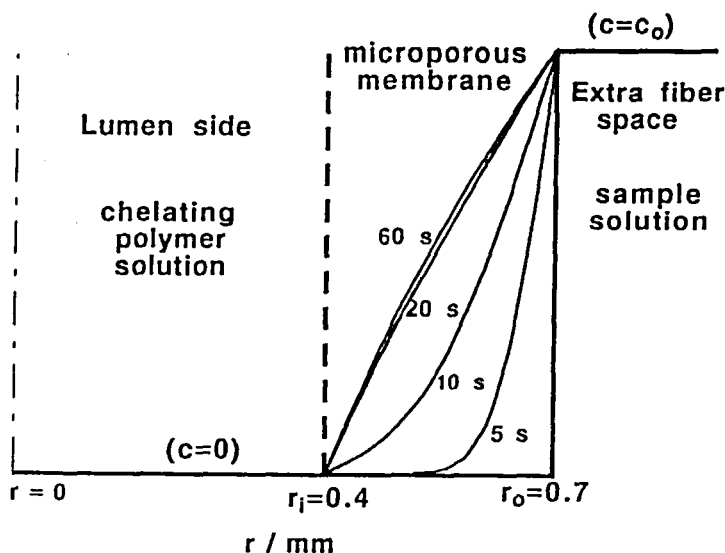


FIG. 2 Concentration distribution in a cylindrical hollow fiber wall at any axial position z .

tion of free metal ions in the polymer solution is negligible because the metal ions in the polymer solution should react with the chelating polymer to form PAA-metal complexes. Thus, assume the following:

1. The film resistances have been ignored so all we need to account for is diffusion through the actual hollow fiber.
2. Details of the pores are ignored and the fiber matrix is homogeneous and characterized by a characteristic diffusion coefficient D .
3. The problem is independent of the axial position of the fiber.

Therefore, the concentration distribution in the microporous hollow cylinder at time t is given as follows (7):

$$c/c_0 = [\ln(r/r_i)/\ln(r_o/r_i)] - \pi \sum H_n U_0(r\alpha_n) \exp(-D\alpha_n^2 t) \quad (1)$$

where $U_0(r\alpha_n)$ and H_n are defined by Eqs. (2) and (3), respectively:

$$U_0(r\alpha_n) = J_0(r\alpha_n)Y_0(r_o\alpha_n) - J_0(r_o\alpha_n)Y_0(r\alpha_n) \quad (2)$$

$$H_n = J_0^2(r_i\alpha_n)/[J_0^2(r_i\alpha_n) - J_0^2(r_o\alpha_n)] \quad (3)$$

The α_n 's are the positive roots of Eq. (4):

$$U_0(r_i \alpha_n) = 0 \quad (4)$$

In Eqs. (1)–(3), J_0 and Y_0 are Bessel functions of the first and second kind, respectively.

Time Course of Outlet Concentration of Metal Ions Recovered

On the basis of a one-dimensional axial dispersion model, the change in metal ion concentration of the polymer solution flowing in the lumen of the hollow fiber is expressed as

$$\frac{\partial c}{\partial t} = E \frac{\partial^2 c}{\partial z^2} - u \frac{\partial c}{\partial z} + \frac{4K_f}{d_i} (c_0 - c_f) \quad (5)$$

where c_0 is the metal ion concentration of the sample solution in the extra-fiber space. The free metal ion concentration in the polymer solution, c_f , is assumed to be negligible as mentioned above. The conditions in this case are

$$\text{Initial Condition: } c(t = 0, z) = 0 \quad (6)$$

$$\text{Boundary Condition: } c(z = 0, t) = 0, c(z \rightarrow \infty, t) = \text{finite} \quad (7)$$

As discussed below, the concentration distribution in the cylindrical membrane of the hollow fiber should approach steady-state within about 1 minute. Therefore, it is reasonable to assume that the third term on the rhs in Eq. (5) is steady. Thus, the solution of Eq. (5) by use of Laplace transforms gives the outlet concentration of metal ions recovered in the polymer solution as follows (see Appendix):

$$c_{\text{out}}/c_0 = (4/d_i)K_f\tau \int_0^\theta \left[1 - \frac{1}{2} \left[\exp(\text{PeB}) \operatorname{erfc} \left\{ \frac{\sqrt{\text{PeB}}}{2} \left(\frac{1}{\sqrt{\theta}} + \sqrt{\theta} \right) \right\} + \operatorname{erfc} \left\{ \frac{\sqrt{\text{PeB}}}{2} \left(\frac{1}{\sqrt{\theta}} - \sqrt{\theta} \right) \right\} \right] \right] d\theta \quad (8)$$

RESULTS AND DISCUSSION

Concentration Distribution and Outlet Concentration

Figure 2 shows the calculated concentration distributions in the cylindrical microporous membrane of the hollow fiber at different times. The value of the copper(II) diffusion coefficient, $D = 1.5 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$, was used for calculation. The concentration distribution approaches steady-state within about 1 minute.

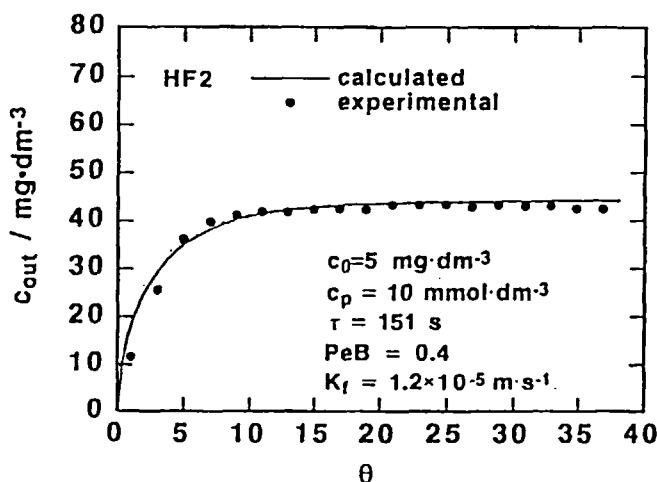


FIG. 3 Time courses of outlet concentration of metal ions recovered.

Typical examples of the time courses of metal ion concentration at the outlet are shown in Figs. 3 and 4. In every case the concentration increased sharply, approaching a steady-state value. Theoretical curves were calculated using the values of K_f and PeB shown in the figures. Two parameters, K_f and

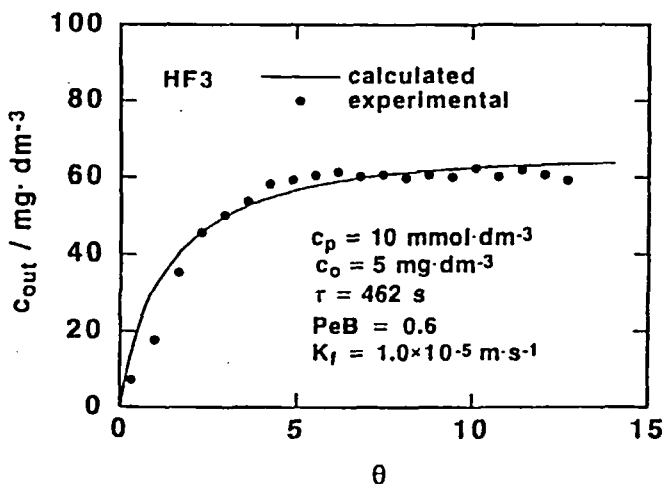


FIG. 4 Time courses of outlet concentration of metal ions recovered.

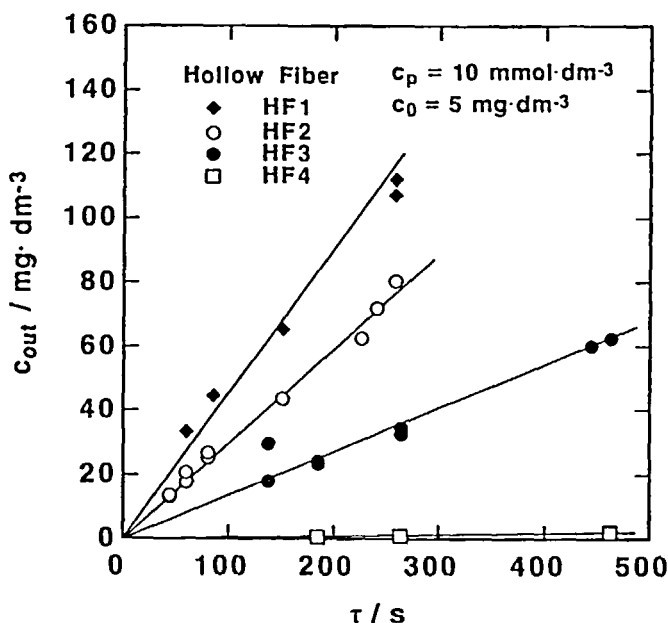


FIG. 5 Relationship between outlet concentration of metal ions and space time.

PeB, were obtained through a fitting of the theory to the experiments. The value of PeB affected the initial change in outlet concentration; that is, the slope of the curve. The value of K_f mainly influenced the steady-state value. Thus, we were able to evaluate PeB and K_f independently. The calculated time courses agreed well with the experimental ones irrespective of the initial concentration of metal ions and of the feed rate of the polymer solution.

Figure 5 shows the relation between the concentration of metal ions recovered, c_{out} , and the average residence time, τ . As is expected from Eq. (6), c_{out} is proportional to τ irrespective of the hollow fiber membrane used, while the recovery rate (slope) was significantly dependent on the material of the hollow fibers used.

Relations between c_{out} and c_0 were examined. Figure 6 shows the results for the hollow fibers HF1 and HF2 with a 0.8-mm inner diameter when the average residence time is 259 seconds. The values of c_{out} were about 10 times as large as c_0 regardless of the membrane pore size of polyacrylonitrile hollow fibers. Figure 7 shows the results for the hollow fibers with a 1.4 mm inner diameter. The values of c_{out} for HF3 are about 20–30 times as large as c_0 when τ is 795 seconds, while the copper was recovered but not concentrated with the polysulfone membrane (HF4).

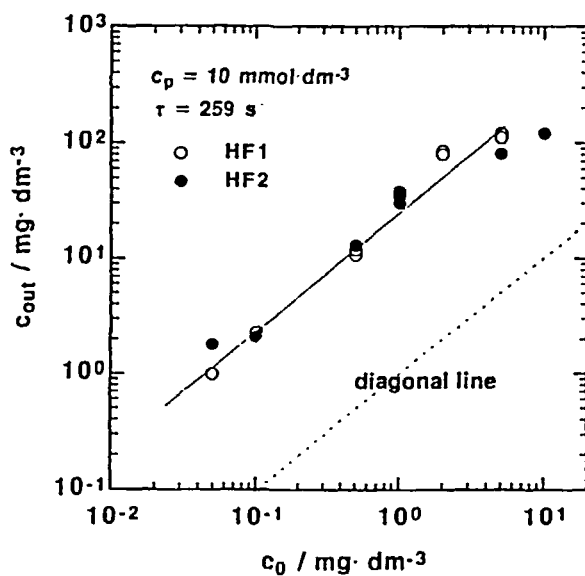


FIG. 6 Relationship between outlet concentration of metal ions and concentration of the sample solution.

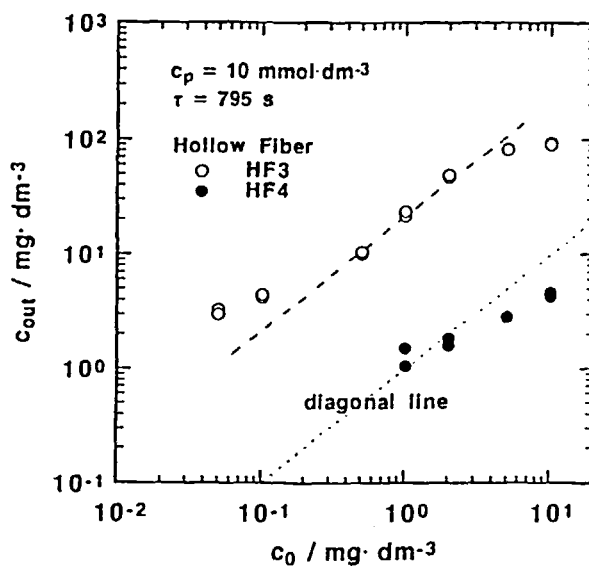


FIG. 7 Relationship between outlet concentration of metal ions and concentration of the sample solution.

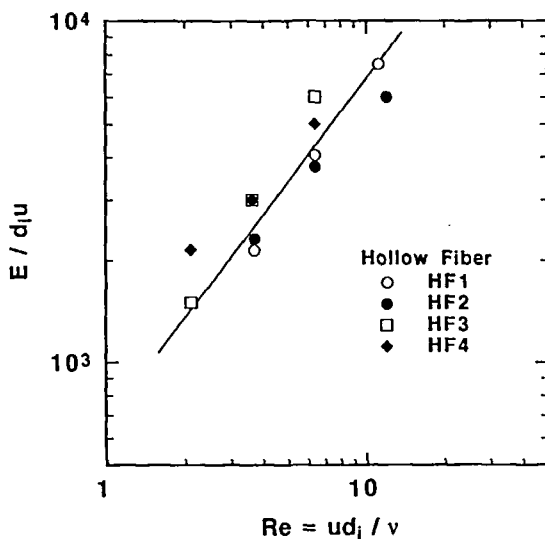


FIG. 8 Relationship between $E/u d_i$ and Reynolds number, $u d_i / \nu$.

As seen in Figs. 5 and 7, the recovery rate of metal ions using the hollow fiber polysulfone membrane is very low. The reason for this is not clear, but the polysulfone membrane is more hydrophobic than the polyacrylonitrile membranes.

Axial Dispersion Coefficient

As described above, the values of PeB were determined so they would match the calculated time courses of the outlet concentration of the recovered metal ions with experimental ones. As shown in Fig. 8, $E/u d_i$ was grossly proportional to the Reynolds number, $u d_i / \nu$, in analogy with the following theoretical relationship by Taylor (8):

$$E/u d_i = (u d_i / \nu)(\nu/D)/192 \quad (9)$$

However, the values of E were about two order of magnitude higher than the theoretical values estimated using the kinematic viscosity, $\nu = 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$, and the diffusion coefficient of the solution, $D = 1.5 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$. The difference seems to arise from the fact that a large portion of the poly-

mer-metal complexes may be formed in the vicinity of the hollow fiber wall, and they flow along the wall without distributing homogeneously over the cross-area of the bore of the fiber.

Overall Mass-Transfer Coefficient

Figure 9 shows the overall mass-transfer coefficients determined as mentioned above. Since K_f was not a strong function of u in the experimental range, the assumption (see above) that the lumen-film resistance could be neglected was valid. A similar tendency was observed in gas absorption systems having higher solubility or faster reaction rates (1). The film resistance at the outside surface of the fiber may be negligible because the recovery rate of metal ions was scarcely affected by stirring speeds over 500–600 rpm. Therefore, the diffusional resistance in the microporous membrane seems to be predominant.

The values of K_f obtained with polyacrylonitrile membranes are of the $10^{-5} \text{ m}\cdot\text{s}^{-1}$ order of magnitude, and close to those for SO_2 absorption with microporous hollow fiber devices (nonwetted mode in Ref. 2), while the

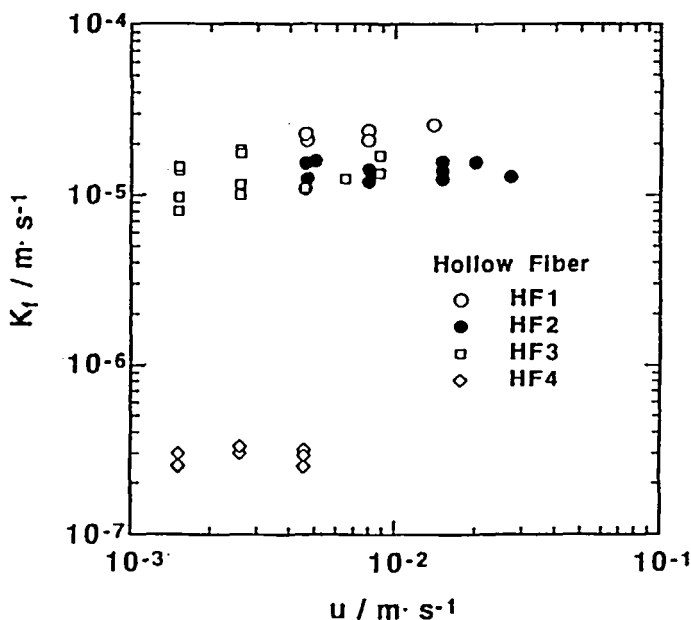


FIG. 9 Relationship between overall mass-transfer coefficient and linear velocity of the chelating polymer solution.

K_f values for the polysulfone membrane were much less than those for the polyacrylonitrile membranes. The results show that the permeation rate of metal ions through the membrane was significantly affected by the material of the hollow fibers used, but the reason is not clear.

CONCLUSIONS

To determine the process of recovering metal ions from dilute solution using a water-soluble chelating polymer and a microporous hollow fiber membrane, the mass transfer of metal ions through a hollow fiber membrane was studied by a transient method.

The time course of the outlet concentration of the metal ions recovered was analyzed based on a one-dimensional axial dispersion model. The model simulations agreed well with the experimental results. Thus, the overall mass-transfer coefficient and axial dispersion coefficient were determined in order to fit the calculated time courses of the outlet concentration to the experimental ones.

The mass-transfer coefficient was slightly affected by the flow rate of the polymer solution, but depended significantly on the material of the hollow fibers used. The high values of the overall mass-transfer coefficients, $10^{-5} \text{ m}\cdot\text{s}^{-1}$ order of magnitude, were obtained using polyacrylonitrile hollow fiber membranes.

APPENDIX

When Eq. (6) is Laplace-transformed and rearranged using the initial conditions, then

$$E \frac{\partial^2 \tilde{c}}{\partial z^2} - u \frac{\partial \tilde{c}}{\partial z} - s\tilde{c} + \frac{4K_f c_0/d_i}{s} = 0 \quad (\text{A-1})$$

where \tilde{c} and s denote the Laplace transform of c and the Laplace transform variable, respectively.

Substituting $z = xZ$ into Eq. (A-1) reduces it to

$$\frac{\partial^2 \tilde{c}}{\partial x^2} - \text{PeB} \frac{\partial \tilde{c}}{\partial x} - \text{PeB}\tau \tilde{c} + \text{PeB}\tau \frac{4K_f c_0/d_i}{s} = 0 \quad (\text{A-2})$$

where $\text{PeB} = uZ/E$, and τ is the average residence time defined as $\tau = Z/u$.

Applying the boundary conditions to the solution of Eq. (A-2) gives the following equation:

$$s\tilde{c} = -\frac{4K_f c_0/d_i}{s} \exp[(\text{PeB}/2)\{1 - \sqrt{1 + 4\tau s/\text{PeB}}\}x] \quad (\text{A-3})$$

$$+ \frac{4K_f c_0/d_i}{s}$$

In applying the inverse Laplace transformation to Eq. (A-3), the following equations are derived:

$$L^{-1}[s\tilde{c}] = \frac{dc}{dt} = \frac{1}{\tau} \frac{dc}{d\theta}$$

$$= (4/d_i)K_f c_0 \left[1 - \frac{1}{2} \exp(x \cdot \text{PeB}/2) \left[\exp(x \cdot \text{PeB}/2) \operatorname{erfc} \left\{ \frac{\sqrt{\text{PeB}}}{2} \left(\frac{x}{\sqrt{\theta}} + \sqrt{\theta} \right) \right\} + \exp(-x \cdot \text{PeB}/2) \operatorname{erfc} \left\{ \frac{\sqrt{\text{PeB}}}{2} \left(\frac{x}{\sqrt{\theta}} - \sqrt{\theta} \right) \right\} \right] \right]$$

$$= (4/d_i)K_f c_0 \left[1 - \frac{1}{2} \left[\exp(x \cdot \text{PeB}) \operatorname{erfc} \left\{ \frac{\sqrt{\text{PeB}}}{2} \left(\frac{x}{\sqrt{\theta}} + \sqrt{\theta} \right) \right\} + \operatorname{erfc} \left\{ \frac{\sqrt{\text{PeB}}}{2} \left(\frac{x}{\sqrt{\theta}} - \sqrt{\theta} \right) \right\} \right] \right]$$

$$(\text{A-4})$$

where θ is the dimensionless time defined as $\theta = t/\tau$, and erfc denotes the complementary error function.

Integrating Eq. (A-4) with respect to θ for $x = 1$ gives the time course of the concentration change at the outlet of the fiber.

SYMBOLS

c	concentration in the polymer solution flowing in the lumen ($\text{mol} \cdot \text{dm}^{-3}$)
c_f	concentration of free metal ions in polymer solution ($\text{mol} \cdot \text{dm}^{-3}$)
c_0	initial or sample concentration ($\text{mol} \cdot \text{dm}^{-3}$)
\tilde{c}	Laplace transform of c ($\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}$)
c_{out}	outlet concentration of metal ions recovered ($\text{mol} \cdot \text{dm}^{-3}$)
c_p	concentration of chelating polymer ($\text{mol} \cdot \text{dm}^{-3}$)
D	diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$)
d_i	inner diameter of hollow fiber (m)
E	axial dispersion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$)

H_n	function defined by Eq. (3) (—)
J_0	Bessel function of the first kind (—)
K_f	overall mass-transfer coefficient ($\text{m}\cdot\text{s}^{-1}$)
PeB	Bodenstein number defined by $Z\cdot u/E$ (—)
r	radial distance (m)
r_i	inner radius of hollow fiber (m)
r_o	outer radius of hollow fiber (m)
s	Laplace transform variable (s^{-1})
t	time (s)
u	average linear velocity ($\text{m}\cdot\text{s}^{-1}$)
U_0	function defined by Eq. (2) (—)
x	dimensionless axial distance defined by $x = z/Z$ (—)
Y_0	Bessel function of the second kind (—)
z	axial distance (m)
Z	length of hollow fiber (m)

Greek

α_n	constant defined by Eq. (4) (—)
ν	kinematic viscosity ($\text{m}^2\cdot\text{s}^{-1}$)
θ	dimensionless time defined by t/τ (—)
τ	average residence time defined by Z/u (s)

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