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Theoretical Analysis of Copper-Ion Extraction through Hollow Fiber Supported Liquid Membranes

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ABSTRACT

An understanding of the extraction of metal ions through hollow fiber supported liquid membranes is important for the design of such systems. In this paper, copper-ion extraction through hollow fiber supported liquid membranes containing D2EHPA as a carrier agent is analyzed. Both a rigorous model and a simple model with varied permeation coefficients for the system are proposed. The once-through mode is first modeled and the parametric effects on the extraction rate are discussed. The recycling mode is then modeled. A comparison between the rigorous model and the simple model with varied/constant permeation coefficients is made. From the models it is found that the permeation coefficient is a function of copper ion concentration.

INTRODUCTION

Liquid membrane technology has attracted increasing attention for its potential in the field of separations, and it has been demonstrated to be an effective tool in many applications such as resource recovery, pollutants removal, and bioseparations. Liquid membrane extraction is a process for transporting a solute from a low concentration solution through a liquid membrane to a high concentration solution while maintaining high selectivity. An active chemical carrier is usually added into the liquid membrane to help the transport. In general, liquid membranes are either unsupported or supported. Unsupported liquid membranes are in the form of double emulsion drops and were first proposed by Li (1). Due to the great number of very small globules present in the system, liquid surfactant membranes have a large transport area with a thin membrane, hence there

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is a fast extraction rate for the solutes. But the complicated demulsification process for the recovery of concentrated solute as well as of membrane liquid makes commercialization of the liquid surfactant membrane process extremely difficult. In supported liquid membranes, the membrane is held in a porous structure which is usually a polymer membrane. The advantages of supported liquid membranes are: no demulsification problem, the process is simple, the extractant inventory is very small, and the extractant loss is also very small. Although low permeation rate and degradation of the liquid membranes are the weak points of supported liquid membranes, utilization of hollow fibers in liquid membrane technology has overcome the above drawbacks because a large membrane surface area is available and degraded membranes can be easily regenerated as reported by Teramoto and Tanimoto (2). Several experimental investigations (3–8) have been made for the extraction of various metal ions through hollow fiber supported liquid membranes (HFSLM). Although many models have been reported for flat-plate-type supported liquid membranes (9–15), models of the HFSLM system are considerably fewer. Teramoto and Tanimoto (2) proposed a permeation mechanism to describe the extraction process of copper ion through an HFSLM. Later, Danesi (16, 17) proposed a simple model for the once-through mode and recycling mode operations of HFSLM. In his model, a parameter, the so-called permeation coefficient, is adopted in the calculation of the permeation rate of copper ion through the membrane. This permeation coefficient is considered to be constant throughout the entire process.

In the present paper the system of a copper ion solution flowing through an HFSLM is examined theoretically. Both a rigorous model and a simple model with a varying permeation coefficient for the system are proposed. In addition, the once-through mode and the recycling mode are also discussed. A comparison between the rigorous model and the simple model with a varying/constant permeation coefficient is made.

REACTION MECHANISM

It has been shown that the reaction between copper ion and D2EHPA occurs at the membrane interfaces according to the following reaction equation (14, 15, 18):

$$\mathrm{Cu^{2+}} + 2\mathrm{(RH)_2} \rightleftharpoons \overline{\mathrm{CuR_2{\cdot}2RH}} + 2\mathrm{H^+} \tag{1}$$

$$(C + 2B \rightleftharpoons M + 2H)$$

And the forward and reverse reaction rates are expressed as:

$$\text{Forward reaction rate} = k_f[C\cdot B^2/H^2 - M/K_{ex}] \tag{2}$$

$$\text{Reverse reaction rate} = k_f[M/K_{ex} - C\cdot B^2/H^2] \tag{3}$$

in which k_f is the forward reaction rate and K_{ex} is the equilibrium constant.

PERMEATION MECHANISM

When an aqueous feed solution containing copper ions flows through the lumen of an HFSLM, the copper ions are continuously extracted by the carrier present in the membrane phase, causing the copper ion concentration of the feed solution to gradually decrease along the hollow fiber. The permeation mechanism of copper ions through the hollow fiber wall is schematically shown in Fig. 1. The permeation rate of each elementary step is described as follows.

Step 1. Due to the driving force of the concentration gradient, the copper ions in the aqueous feed solution permeate through an aqueous film formed along the hollow fiber wall and move toward the liquid membrane. The permeation rate of the copper ions can be expressed as

$$J_1 = k_w(C_1 - C_{1s})A_1/A_{av} \tag{4}$$

in which k_w is the mass transfer coefficient of copper ion in the aqueous solution and $A_{av} = (A_1 + A_2)/2$.

Step 2. On reaching the internal interface of the membrane, the copper ions react with the carrier present in the membrane to form copper complexes. The formation rate of the copper complexes is

$$R_1 = k_f[C_{1s}\cdot B_{1s}^2/H_{1s}^2 - M_{1s}/K_{ex}]A_1/A_{av} \tag{5}$$

Step 3. The complexes formed at the internal interface then diffuse across the membrane toward the other side. By assuming a linear concentration profile in the membrane, the diffusion rate of the copper complexes in the membrane is expressed as

$$J_m = k_m(M_{1s} - M_{2s}) \tag{6}$$

in which K_m is the mass transfer coefficient of the copper metal complex in the membrane phase.

Step 4. On reaching the external interface, the copper ions are stripped from the copper complexes by the assistance of strong acid present in the internal phase. The stripping rate is

$$R_2 = k_f[M_{2s}/K_{ex} - C_{2s}\cdot B_{2s}^2/H_{2s}^2]A_2/A_{av} \tag{7}$$

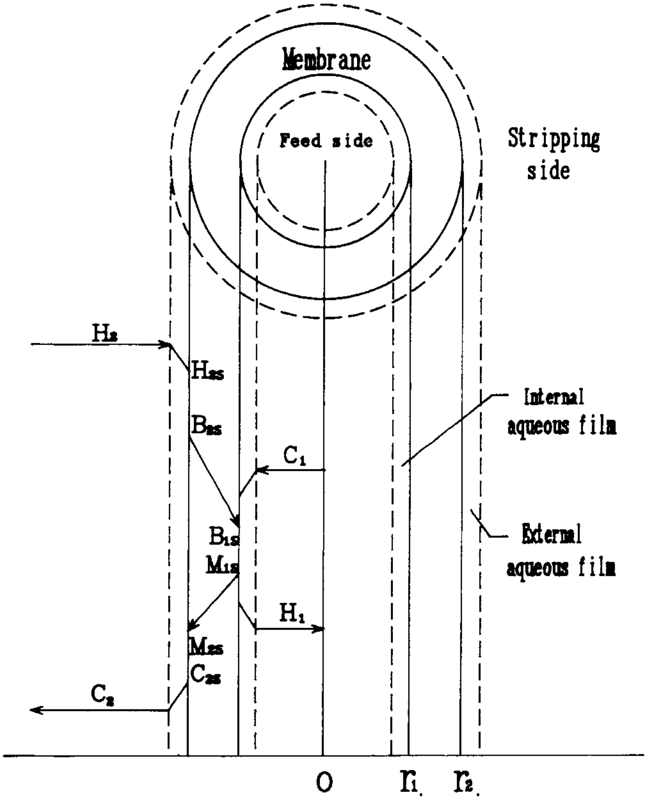

FIG. 1 Schematic diagram of permeation mechanism of copper ion extraction through hollow fiber wall.

Step 5. The stripped copper ions permeate through an aqueous film outside the hollow fiber and enter the stripping solution. The permeation rate is expressed as

$$J_2 = k_w(C_{2s} - C_2)A_2/A_{av} \tag{8}$$

At steady state, all the rates are equal, i.e.,

$$J_1 = R_1 = J_m = R_2 = J_2 = J \tag{9}$$

Additional constraints for the system are

$$2C_1 + H_1 = 2C_{1s} + H_{1s} = 2C_{10} + H_{10} \tag{10}$$

$$2C_2 + H_2 = 2C_{2s} + H_{2s} = H_{20} \tag{11}$$

$$2M_{1s} + B_{1s} = 2M_{2s} + B_{2s} = B_0 \tag{12}$$

Equations (3)–(12) are valid for any axial position in the hollow fiber, and hence J for any given position can be easily obtained by solving Eqs. (3) to (12) simultaneously.

ONCE-THROUGH MODE

For the once-through mode, the outlet concentration of copper ions at the exit of the hollow fiber can be obtained by making an overall material balance for the feed solution over the hollow fiber. Before deriving the governing equations, certain assumptions are needed in order to simplify the mathematics and the model development:

1. All physical and transport properties are constant during the entire extraction process operation.
2. Axial diffusion in the fiber lumen is neglected.
3. Except in the aqueous film which forms along the fiber wall, the concentration profile of copper ions in the fiber lumen is flat at any axial position.
4. The system is at steady-state operation.

Based on these assumptions, a material balance equation for the copper ions of the feed solution over an element section may be formulated as follows:

$$-Q_1 \frac{dC_1}{dx} = J_x \pi (r_1 + r_2) \tag{13}$$

The boundary conditions for Eq. (13) at $x = 0$ are

$$C_1 = C_{10} \quad \text{and} \quad H_1 = H_{10} \tag{14}$$

Combining with the mechanism equations, Eq. (13) can be numerically integrated from inlet to outlet of the hollow fiber to obtain the outlet concentration of the copper ion.

The parameters which will affect the copper ion extraction are copper ion concentration (C_0), carrier concentration (B_0), and hydrogen ion concentrations in both side solutions (H_1 and H_2, respectively). The values of the parameters used for the investigation are summarized in Table 1. To describe the degree of copper-ion extraction, the term "removal efficiency" is introduced; it is defined as the percentage of copper ion removed from the feed solution.

(a) Effect of C_0

Figure 2 shows the relationship between copper-ion removal efficiency and initial copper-ion concentration for different hollow fiber lengths. As

TABLE 1
Values of the Parameters Used in the Model Calculation

C_{10}	$= 500$ ppm	V_f	$= 2.0$ L
B_0	$= 1.5 \times 10^{-5}$ mol/L	K_{ex}	$= 1.8 \times 10^{-3}$
H_1	$= 1.5 \times 10^{-5}$ mol/L	k_f	$= 1.8 \times 10^{-6}$ cm
H_2	$= 0.25$ mol/L	k_w	$= 1.0 \times 10^{-3}$ cm/s
Q_f	$= 10.0$ mL/s	k_m	$= 0.76 \times 10^{-5}$ cm/s

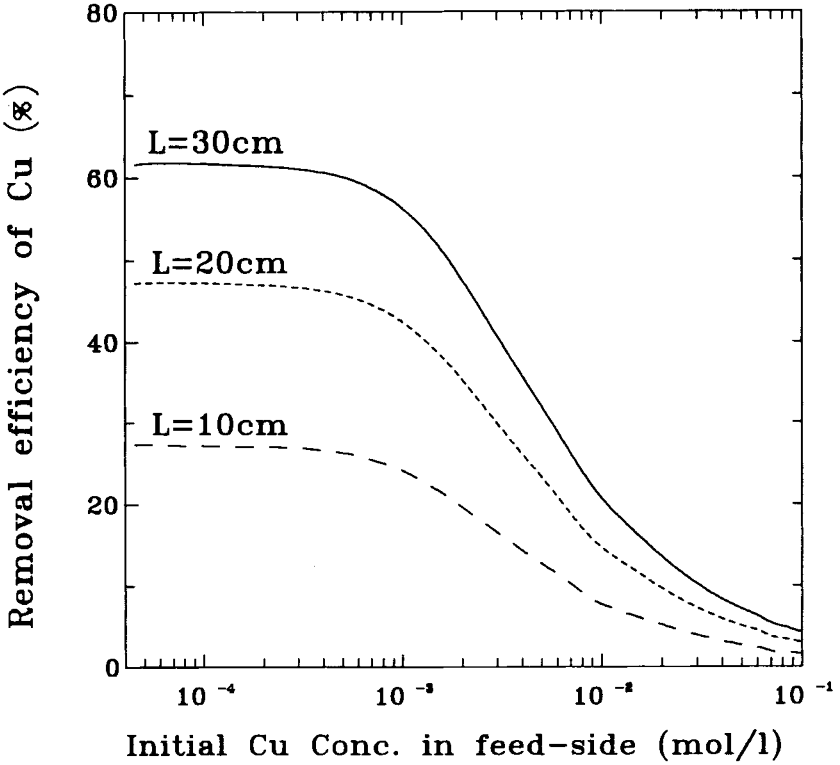

FIG. 2 Effect of C_0 on the removal efficiency.

can be seen from this figure, at lower copper-ion concentrations with C_0 less than 10^{-3} mol/L, the removal efficiency remains almost unchanged. However, when C_0 increases from the 10^{-3} mol/L level, the removal efficiency decreases sharply.

(b) Effect of B_0

Lower carrier concentrations give quite limited extraction results because they provide less transport capability for the copper-ion complex. Figure 3 shows that for an effective extraction, the carrier concentration must retain a certain level, say, 5 mol/L. However, any further increase in carrier concentration may decrease the removal efficiency due to a remarkable increase in the viscosity of the liquid membrane which inhibits copper complex diffusion.

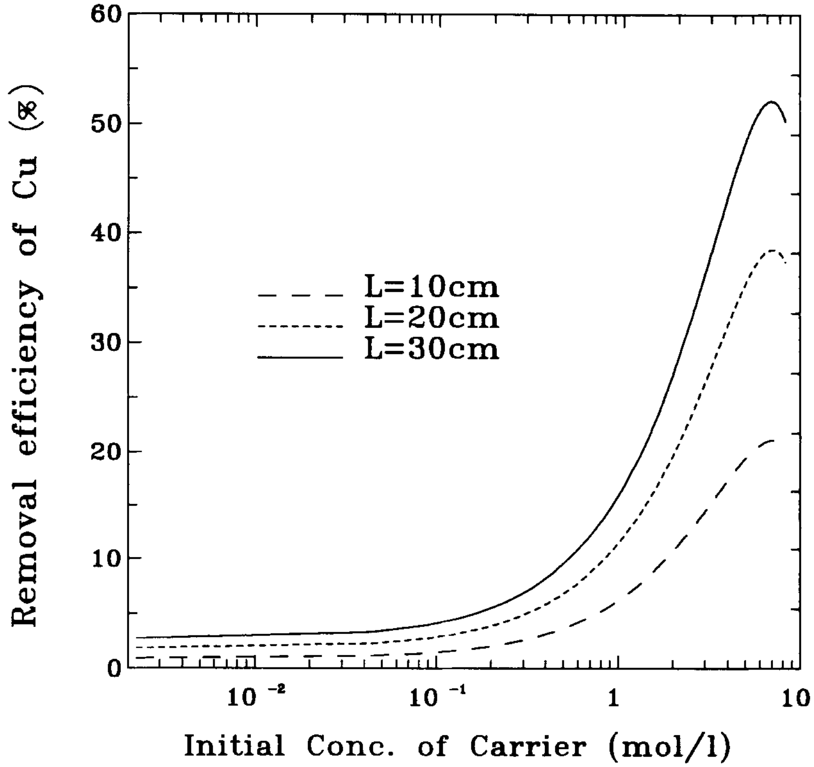

FIG. 3 Effect of B_0 on the removal efficiency.

(c) Effect of H_1

The effect of H_1 on the removal efficiency is shown in Fig. 4. Decreasing H_1 will certainly increase the removal efficiency. This is mainly because decreasing H_1 will increase the copper complex formation rate. Hence, low H_1 is favorable for copper extraction. However, when H_1 is lower than 10^{-3} mol/L, the copper complex formation rate becomes so fast that it no longer has a key role for extraction. Thus, the removal efficiency is independent of H_1 in the lower H_1 region.

(d) Effect of H_2

A high H_2 value is favored for extraction since it will increase the stripping reaction rate. Figure 5 shows that when H_2 increases from 10^{-3} to 0.1 mol/L, the removal efficiency increases dramatically. This is mainly

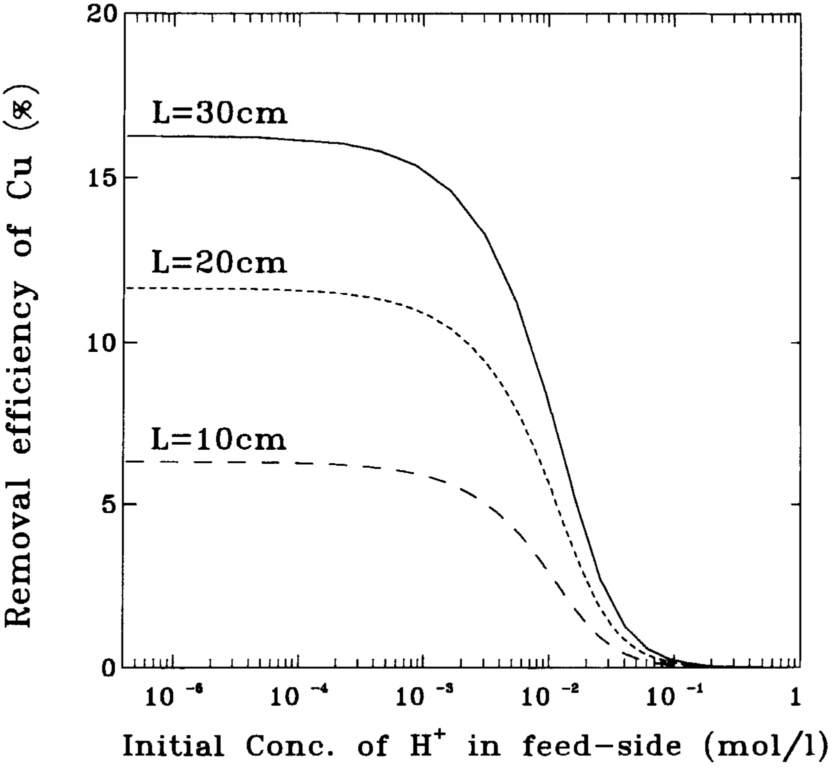

FIG. 4 Effect of H_1 on the removal efficiency.

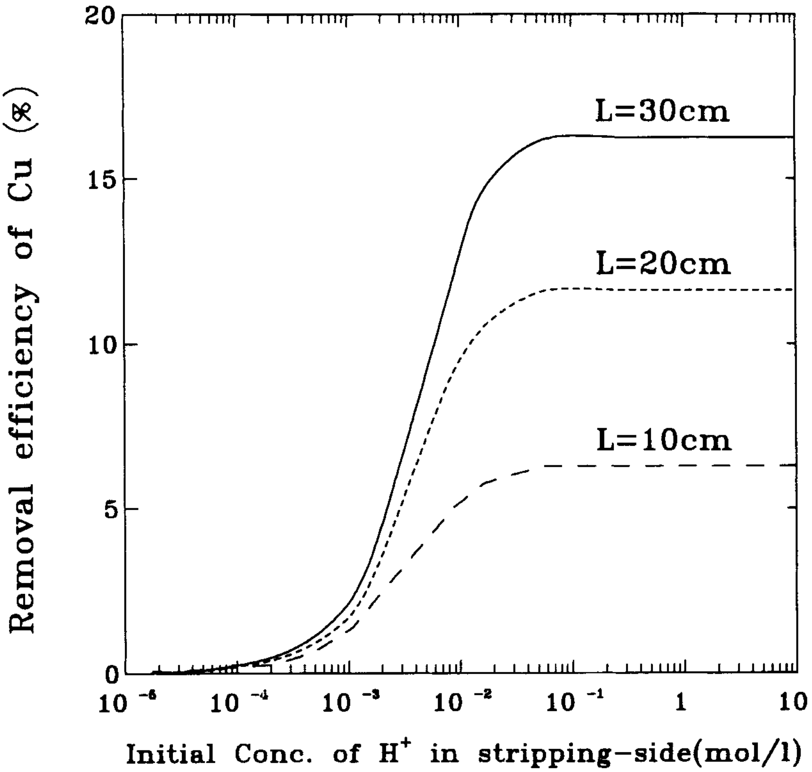

FIG. 5 Effect of H_2 on the removal efficiency.

because increasing H_2 increases the stripping rate and hence keeps the copper complex concentration near the interface on the stripping side at a low level, and this is favorable for complex diffusion from the feed side to the stripping side. Hence, for efficient extraction, H_2 should be greater than 0.1 mol/L.

RECYCLING MODE

For the recycling mode, both feed solution and stripping solution are recycled, as shown in Fig. 6. To model the recycling mode, Danesi in 1984 proposed a simple model with a constant permeation coefficient. In this study, both a rigorous model and a simple model with a varied permeation coefficient are developed.

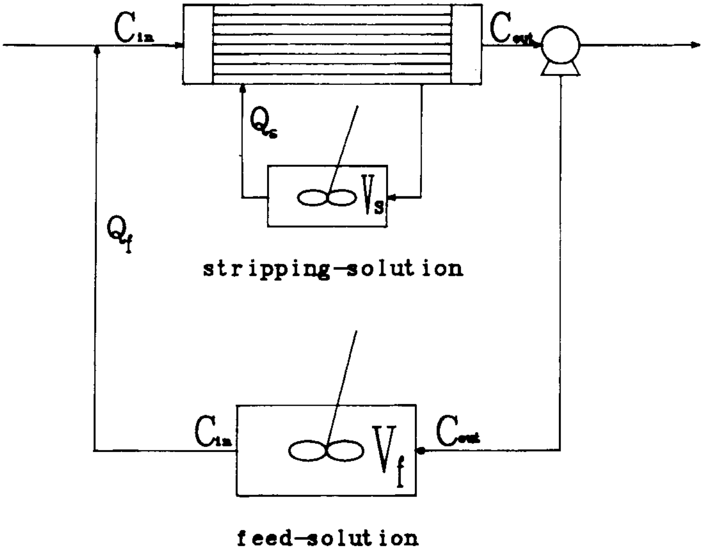

FIG. 6 Recycling mode operation.

(a) Rigorous Recycle Model

For the rigorous recycle model, the exiting copper-ion concentration from the hollow fiber for each cycle was obtained by calculating the copper-ion concentration step by step axially starting from the inlet of the hollow fiber, and the copper-ion concentration in the stirred feed tank was then calculated based on this outlet concentration. Referring to Fig. 6, the following material balance equation can be formulated for the feed-stirred tank:

$$-V_f \frac{dC_{in}}{dt} = Q_f(C_{in} - C_{out}) \tag{15}$$

Since C_{out} in this equation can be calculated from the mechanism and once-through mode equations (Eqs. 4–14) for each cycle path, the time course of C_{in} can then be easily obtained by simultaneously solving Eq. (15) and Eqs. (4)–(14).

(b) Simple Recycle Model with Varied Permeation Coefficient

For the simple recycle model, the hollow fiber is considered to be a single unit. An averaged copper-ion concentration (based on inlet and outlet concentrations) is used to calculate the total amount of copper ions extracted through the hollow fiber wall. This is a reasonable approach since the copper-ion concentration along the hollow fiber is close to a linear profile. By making a material balance over the hollow fiber for the copper ion of the feed solution, the following equation holds:

$$Q_f(C_{in} - C_{out}) = PA\left(\frac{C_{in} + C_{out}}{2}\right) \tag{16}$$

in which P is the permeation coefficient of copper ion through the membrane and A is the total permeation area. By simultaneously solving Eqs. (15) and (16), one can easily obtain the time course of the copper-ion concentration in the feed-stirred tank. However, before solving the equations, it should be determined if P is a function of the copper-ion concentration. Since the right side of Eq. (16) is equal to the total extraction of copper ions when the feed solution flows through the hollow fiber lumen, the following equation holds:

$$PA\,\frac{C_{in} + C_{out}}{2} = \frac{A}{L}\int_0^L J_x\,dx$$

or

$$P = \frac{2}{L(C_{in} + C_{out})}\int_0^L J_x\,dx \tag{17}$$

For any given C_{in}, J_x and C_{out} can be calculated by using Eqs. (4)–(14). By substituting these two values into Eq. (17), a relationship between P and C_{in} can be obtained. Based on the conditions given in this study, it is found that P and C_0 have close to a linear relationship. Therefore, P in Eq. (16) can be defined as

$$P = P_0C_{in}/C_0 \tag{18}$$

in which P_0 is the permeation coefficient when the inlet copper-ion concentration (C_{in}) is equal to C_0. P_0 can be calculated by using the once-through model equations. Substituting Eq. (18) into Eq. (16) yields

$$Q_f(C_{in} - C_{out}) = \frac{A}{2}\,P_0\,\frac{C_{in}}{C_0}\,(C_{in} + C_{out}) \tag{19}$$

Rearranging Eq. (19):

$$C_{out} = \frac{\phi C_0 - C_{in}}{\phi C_0 + C_{in}}\,C_{in} \tag{20}$$

in which $\phi = 2Q_f/AP_0$. By substituting Eq. (20) into Eq. (15), an analytical solution can be obtained for C_{in} as a function of time:

$$\ln\left(\frac{C_{in}}{C_0}\right) - \phi\left(\frac{1 - C_{in}/C_0}{C_{in}/C_0}\right) = -\frac{2Q_f}{V_f}t \tag{21}$$

(c) Simple Recycle Model with Constant Permeation Coefficient (Danesi's model)

For the constant permeation coefficient (P_0) which was used by Danesi in his simple recycle model, Eq. (20) becomes

$$C_{out} = \frac{\phi - 1}{\phi + 1}C_{in} \tag{22}$$

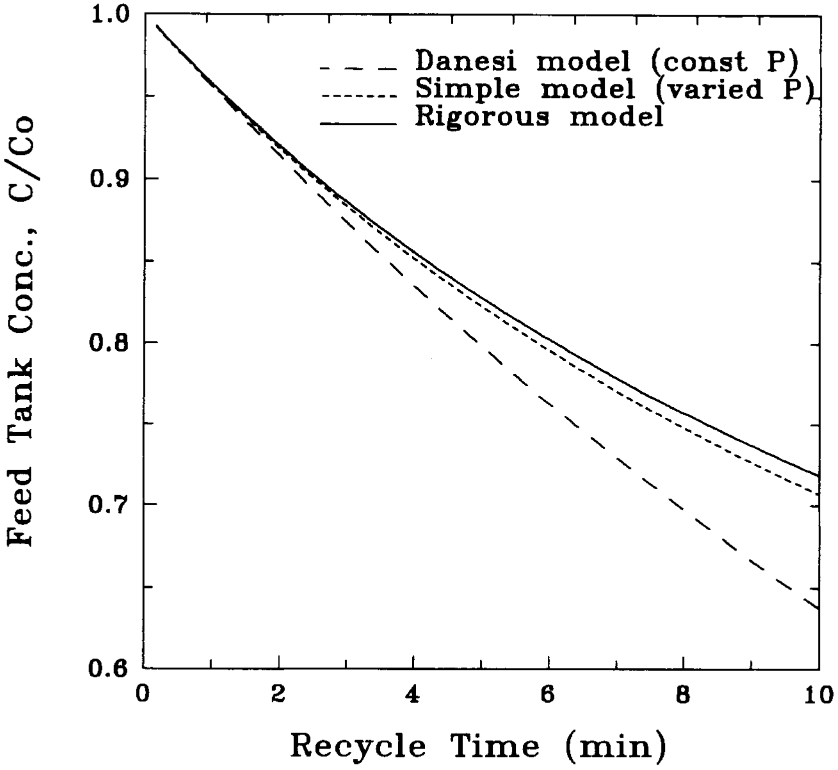

FIG. 7 Comparison of rigorous model and simple models with/without constant permeation coefficient.

Substituting this into Eq. (15) yields

$$\ln\left(\frac{C_{\mathrm{in}}}{C_0}\right) = -\frac{2Q_{\mathrm{f}}}{V_{\mathrm{f}}}\frac{1}{\phi + 1}t \tag{23}$$

Apparently Eq. (23) differs from Eq. (21). Figure 7 is a comparison of the two simple recycle models with the rigorous recycle model. The simple recycle model with a varied permeation coefficient has only a 1% deviation from the rigorous recycle model for a recycle time of 10 minutes, while Danesi's recycle model deviates more than 10% for the same extraction time. This is because Danesi's model does not take into consideration P as a function of copper-ion concentration.

For the recycling mode operation, the circulation rate of the feed solution is an important parameter for copper-ion extraction. Figure 8 shows

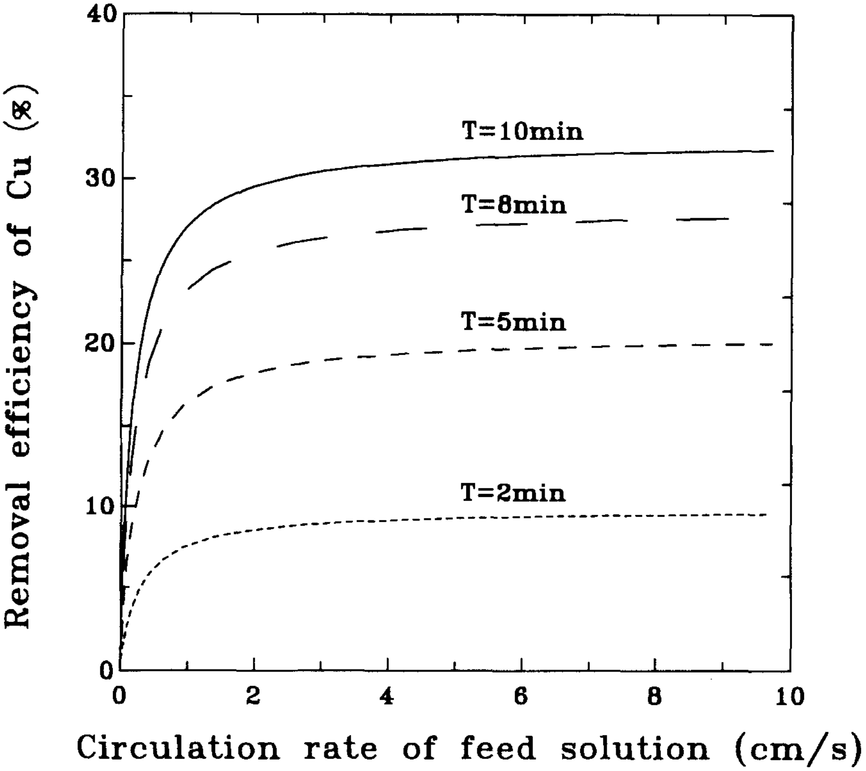

FIG. 8 Effect of circulation rate on the removal efficiency for the recycling mode.

the effect of the feed solution circulation rate on the copper-ion removal efficiency. As the circulation rate increases from 0 to 2 cm/s, the removal efficiency also increases due to the larger mass transfer coefficient and, consequently, the faster extraction rate. However, when the linear velocity of the feed solution is greater than 2 cm/s, the influence of this parameter on the removal efficiency is quite small.

RATE-CONTROLLING STEP

For a flat plate supported liquid membrane, several authors have pointed out the relative importance of chemical reaction control and diffusion controls through the aqueous film and the membrane for metal ions extraction. For a hollow fiber supported liquid membrane, the system also consists of similar permeation resistances: aqueous film diffusion resistances, chemical reaction resistances, and membrane diffusion resistance.

To determine the controlling step for the recycling-mode operation of a hollow fiber liquid membrane system, the following special cases are discussed.

Case 1. Chemical reaction resistances are neglected. Under this condition, both aqueous film diffusion resistances and membrane diffusion resistance are rate-controlling steps and Eqs. (5) and (7) become equilibrium equations, i.e.,

$$K_{ex} = M_{1s}\cdot H_{1s}/C_{1s}\cdot B_{1s}^2 \tag{24}$$

$$K_{ex} = M_{2s}\cdot H_{2s}/C_{2s}\cdot B_{2s}^2 \tag{25}$$

Case 2. Aqueous film diffusion resistances are neglected. Under this condition, both chemical reactions and membrane diffusion are the rate-controlling steps, and $C_{1s} = C_1$, $H_{1s} = H_1$, $C_{2s} = C_2$, $H_{2s} = H_2$. Equations (5) and (7) become

$$R_1 = k_f[C_1\cdot B_{1s}^2/H_1^2 - M_{1s}/K_{ex}]A_1/A_{av} \tag{26}$$

$$R_2 = k_f[M_{2s}/K_{ex} - C_2\cdot B_{2s}^2/H_2^2]A_2/A_{av} \tag{27}$$

Case 3. Membrane diffusion resistance is neglected. Under this condition, both aqueous film diffusions and chemical reactions are the rate-controlling steps, and $M_{2s} = M_{1s}$, $B_{2s} = B_{1s}$. Equation (7) becomes

$$R_2 = k_f[M_{1s}/K_{ex} - C_{2s}\cdot B_{1s}^2/H_{2s}^2]A_2/A_{av} \tag{28}$$

Figure 9 is a comparison of the three cases with the general case which takes all three resistances into consideration. As can be seen from this figure, Case 1 is quite close to the general case. Since Case 1 neglects

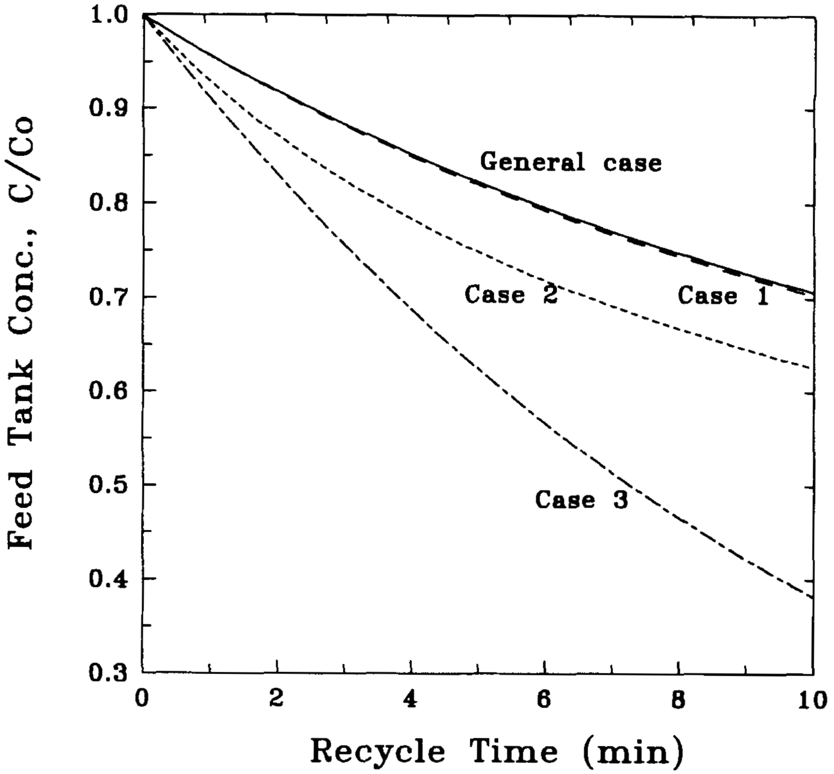

FIG. 9 Comparison of three special cases.

only the resistances of chemical reactions occurring at both interfaces, this result indicates that the reaction rates are fast enough and the resistances are negligible. On the other hand, Case 3 presents the largest deviation from the general case. Since the chemical reaction resistances are negligible, as is evident from Case 1, and since Case 3 neglects the resistance of membrane diffusion, the result of Case 3 indicates that membrane diffusion is a rate-controlling step. Similarly, the result of Case 2 indicates that aqueous film diffusion is also a rate-controlling step. In other word, both membrane diffusion and aqueous film diffusion are rate-controlling steps, with membrane diffusion being more important.

CONCLUSION

A theoretical analysis of copper-ion extraction through a hollow fiber supported liquid membrane containing D2EHPA is made in this study.

Models for both once-through mode and recycling mode operations are developed. For the recycling mode, both a rigorous model and a simple model with a varied permeation coefficient are proposed. The results of the simple model are quite close to the rigorous model, indicating that the simple model can be adopted for system performance calculation. According to the model analysis, the permeation coefficient is a function of the copper-ion concentration. The analysis also found that both membrane diffusion and aqueous film diffusion are rate-controlling steps.

NOTATION

A	total mass transfer area of hollow fiber (cm^2)
B	carrier concentration (mol/L)
C	copper ion concentration (mol/L)
H	hydrogen ion concentration (mol/L)
J	copper permeation rate (mol/cm^2/min)
K_{ex}	equilibrium constant
k_{f}	forward reaction rate constant (cm/min)
k_{m}	mass transfer coefficient of copper complex in the membrane phase (cm/min)
k_{w}	copper ion mass transfer coefficient in aqueous solution (cm/min)
L	hollow fiber length (cm)
M	concentration of copper complex (mol/L)
P	permeation coefficient (cm/min)
Q_{f}	volumetric flow rate of feed solution (L/min)
R	reaction rate (mol/cm^2/min)
r	radius of hollow fiber (cm)
t	time (min)
V_{f}	liquid volume of feed solution in stirred tank (L)

Subscripts

1	feed aqueous phase
2	stripping phase
0	initial condition
s	at interface

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