Hydrodynamic Investigations on Heavy Metal Extraction in Membrane Extractors

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ABSTRACT

Extraction of heavy metals in membrane contactors was investigated theoretically in this study. Extraction of Cu^{2+} with a kerosene solution of di(2-ethylhexyl) phosphoric acid (D2EHPA) was studied. Simulations were performed using computational fluid dynamics of mass and momentum transfer in all subdomains of a circular membrane contactor. The membrane contactor consists of three sections: lumen, membrane and shell side. Conservation equations were derived for Cu^{2+} in the membrane contactor and solved numerically based on finite element method (FEM). With solving conservation equations, velocity, concentration and pressure distributions were obtained for solute. The simulation results showed that pressure drop is not appreciable in the membrane contactor. Furthermore, simulation results revealed that membrane contactors are efficient in the extraction of heavy metals.

Key words: Heavy metals, Extraction, Numerical simulation, Computational fluid dynamics.

INTRODUCTION

Extraction of heavy metals such as Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, and Cd^{2+} with organophosphorus extractants such as di(2-ethylhexyl)phosphoric acid (D2EHPA) is an important separation process in hydrometallurgical and waste water treatment processes[1]. Conventional metal extraction processes are carried out using equipments such as packed towers, mixer-settlers, etc. which try to maximize the contact area of two immiscible phases for mass transfer operation. These contactors have some disadvantages such as formation of stable emulsions, thereby inhibiting the phase separation and product recovery; avoid using liquids having similar densities and foaming. Additional limitations present in packed towers include loading requirements and flooding restrictions[2].

Membrane technology can overcome the drawbacks of conventional metal extraction processes. A membrane is a semi-permeable barrier between two phases. If one component of a mixture moves through the membrane faster than another mixture component, a separation can be accomplished. Dispersion-free metals extraction using microporous membrane contactors is being extensively studied. The types of microporous membranes used in membrane extraction studies include hydrophobic, hydrophilic, and composite membranes[3-7]. Mass transfer of metals extraction in membrane contactors can be analogous to the

heat transfer in heat exchangers. The contactors used in membrane extraction are different in design from ordinary heat exchangers, but in principle the only difference is the relative direction the two fluids move[3].

The current study, presents a numerical simulation using CFD of mass and momentum transfer in a membrane contactor for laminar flow conditions. Axial and radial diffusion are considered in the equations of mass transfer inside the fiber, through the membrane, and within the shell side of the contactor. The convection was also considered in both of the tube and shell sides. The aim of this simulation was to predict the concentration, pressure and velocity of solute component (Cu^{2+}) in the contactor.

Theory
Model equations

Fig. 1 shows a concentric circular membrane extractor with inserting a hydrophobic microporous permeable barrier to divide a circular tube into two subchannels conducting a double-flow operation. The feed phase containing aqueous solution of Cu^{2+} flows inside the inner tube (fiber) while the extractant solution flows counter-currently inside the shell side. Because of hydrophobicity of the membrane, the extractant-containing phase which is organic penetrates the membrane pores and wets them. An interface established at the pores mouth adjacent to the feed phase. At the interface, chemical reaction occurs between metal ion (Cu^{2+}) and organometallic complex is formed and diffuses through the membrane pores and transferred to the shell side. Therefore, the driving force in this process is concentration difference of solute.

The mass transfer model is built considering the following assumptions:
- Steady state and isothermal conditions
- Fully developed parabolic velocity profile inside fiber
- Laminar flow for two phases in the contactor
- The membrane is completely extraction-phase filled
- The complexing reaction occurs at the aqueous-membrane interface
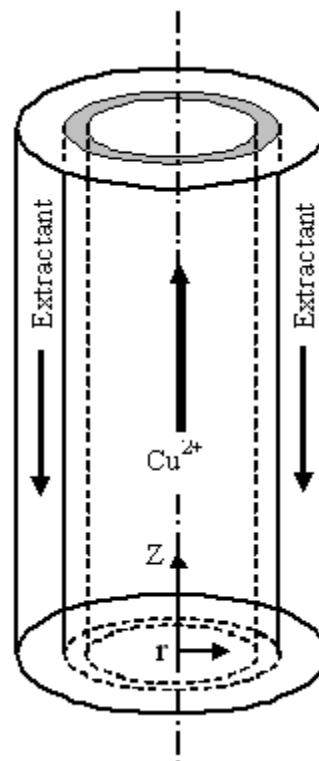- The chemical reaction is very fast and achieves equilibrium.

Fig. 1: Concentric membrane contactor for extraction of Cu^{2+}

The main equation that describes the transfer of solute (Cu^{2+}) from aqueous phase to organic phase is continuity equation. This equation is derived from mass balance of solute in an element. The differential form of continuity equation for solute may be written as [8]:

$$\frac{\partial C_i}{\partial t} + \nabla \cdot (-D_i \nabla C_i + C_i V) = R_i \qquad ...(1)$$

where c_i denotes the concentration of solute (mole/m^3), D_i denotes its diffusion coefficient (m^2/s), V the velocity vector (m/s) and R_i denotes the reaction term (mol/m^3.s). The velocity vector can be expressed analytically or obtained by coupling a momentum balance to the equation system. This equation is also called convection and diffusion equation.

In the reaction term, arbitrary kinetic expressions of the reactants and products can be

introduced. The expression within the brackets represents the flux vector, where the first term describes the transport by diffusion and the second represents the convective flux:

$$N_i = -D_i \nabla C_i + C_i V \qquad ...(2)$$

where N_i is the mass flux vector (mol/m².s). The diffusion coefficient for the dissolved species accounts exclusively for the interaction between the solute and the solvent. In the Maxwell-Stefan convection-diffusion application mode, the interaction between the different dissolved species is also taken into account.

Equation (1) is the main equation of mass transfer. This equation should be solved numerically to obtain the concentration distribution of solute in the membrane contactor. To solve the continuity equation (Eq. 1), velocity distribution is needed. Velocity distribution is obtained by solving the momentum equation, i.e. Navier-Stokes equations. Therefore, the momentum and continuity equation should be coupled and solved simultaneously to obtain the concentration distribution of solute.

The Navier-Stokes equations describe flow in viscous fluids through momentum balances for each of the components of the momentum vector in all spatial dimensions. They also assume that the density and viscosity of the modeled fluid are constant, which gives rise to a continuity condition. The Navier-Stokes equations are defined by Equation 3. The momentum balances and continuity equation form a nonlinear system of equations with three and four coupled equations in 2D and 3D, respectively [8]:

$$\rho \frac{\partial V}{\partial t} - \nabla \cdot \eta (\nabla V + (\nabla V)^T) + \rho(V.\nabla)V + \nabla p = F$$
$$\nabla.V = 0 \qquad ...(3)$$

where η denotes the dynamic viscosity (kg/m.s), V the velocity vector (m/s), ρ the density of the fluid (kg/m³), p the pressure (Pa) and F is a body force term (N).

Boundary conditions for equations are listed in the Table1.

Table 1: Boundary conditions of mass transfer equations

Position	Tube	Membrane	Shell
z = 0 (Inlet)	$C_i = C_0$	Insulated	Convective flux
z = L (Outlet)	Convective flux	Insulated	C_i=0
r = R$_1$	$C_1 = C_2/m$	$C_2 = C_1$*m	
r = R$_2$	-	$C_2 = C_3$	$C_3 = C_2$
r = R$_3$	-	-	$\frac{\partial C_i}{\partial r} = 0$ (symmetry)

where m is partition coefficient of solute between aqueous phase and organic phase. Diffusion mechanism ($V = 0$) is assumed for mass transfer of solute within the membrane. The chemical reaction for all sections is assumed to be zero ($R_i = 0$).

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Numerical solution of model equations
The model equations related to shell, membrane and tube side with the appropriate boundary conditions were solved using COMSOL software, which uses finite element method (FEM) for numerical solutions of model equations. The finite element analysis is combined with adaptive meshing and error control using numerical solver of UMFPACK. This solver is an implicit time-stepping scheme, which is well suited for solving stiff and non-stiff non-linear boundary value problems. An
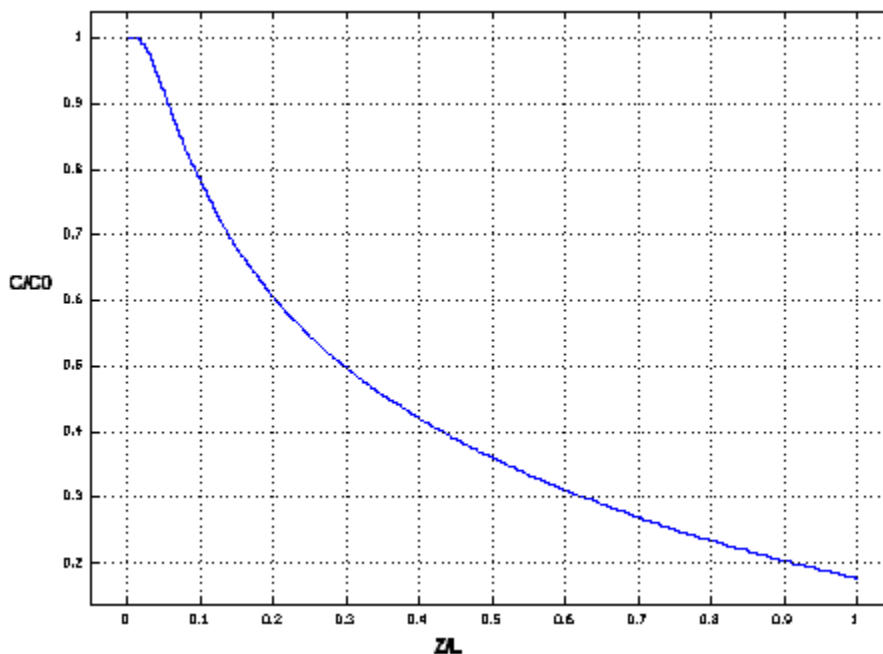
Fig. 2: Axial concentration distribution of solute in the extractor. Feed flow rate = 8E-8 m³/s, organic flow rate = 2E-7 m³/s, inlet concentration of solute = 8 mol/m³, Temperature = 298 K, Pressure = 1 atm

IBM-PC-Pentium4 (CPU speed is 2800 MHz) was used to solve the set of equations. The computational time for solving the set of equations was about 10 minutes.

RESULTS AND DISCUSSION

Concentration distribution of solute along the extractor

Fig. 2 presents the dimensionless concentration distribution (C/C_0) of solute in the tube side of the membrane extractor. The feed phase flows from one side of the contactor ($z = 0$) where the concentration of solute is the highest (C_0), whereas the organic phase (extractant) flows from the other side ($z = L$) where the concentration of solute is assumed to be zero. As the feed flows through the tube side, it moves to the membrane due to the concentration difference, and then it is swept by the moving extractant.

The extraction efficiency of solute which is defined the ratio of the solute transfer from the feed phase to extraction phase to total solute in the initial feed phase determined by using Eq. (4) as follows:
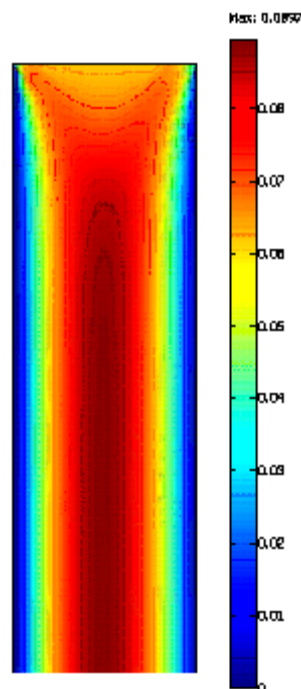

Fig. 3: Velocity field in the shell side of extractor. Feed flow rate = 8E-8 m³/s, organic flow rate = 2E-7 m³/s, inlet concentration of solute = 8 mol/m³, Temperature = 298 K, Pressure = 1 atm

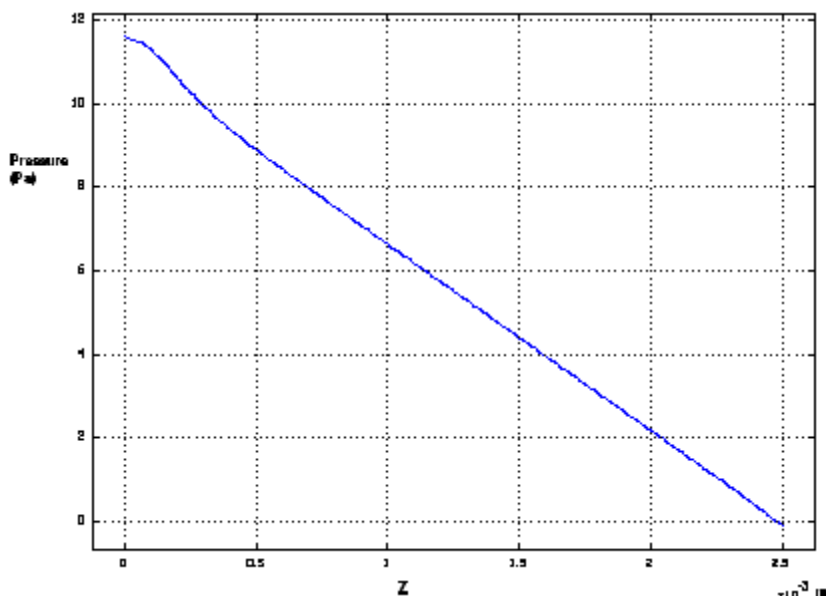**Fig. 4: Pressure distribution in the shell side of extractor. Feed flow rate = 8E-8 m³/s, organic flow rate = 2E-7 m³/s, inlet concentration of solute = 8 mol/m³, Temperature = 298 K, Pressure = 1 atm**

$$K = \frac{Q_{Feed}(C_{inlet} - C_{outlet})}{Q_{Feed}C_{inlet}} \qquad ...(4)$$

Where K is extraction efficiency of solute and Q is volumetric flow rate. The extraction efficiency for solute is calculated 85.8 for extraction of Cu^{2+} using membrane extractor. The extraction efficiency could be enhanced with increasing organic phase flow rate and decreasing feed flow rate because decreasing feed flow rate increases residence time of solute in the contactor.

Velocity field in the extractor

The velocity field in the shell side of membrane extractor is illustrated in the figure 3.

The velocity profile in the shell side of membrane contactor was simulated by solving the Navier-Stokes equations. Fig. 3 shows velocity profile in the shell side, in which extractant flows. The velocity profile is almost parabolic with a mean velocity increasing with membrane length because of continuous fluid permeation.

Pressure distribution along the extractor

Pressure distribution in the shell side of extractor is shown in the figure 4. As it is shown, pressure decreases along the membrane contactor. Figure 4 reveals that pressure drop is not appreciable in these contactors.

CONCLUSIONS

Extraction of heavy metals in membrane contactors was investigated theoretically in this study. Extraction of Cu^{2+} with a kerosene solution of di(2-ethylhexyl) phosphoric acid (D2EHPA) was studied. Simulations were performed using computational fluid dynamics of mass and momentum transfer in all subdomains of a circular membrane contactor. The membrane contactor consists of three sections: lumen, membrane and shell side. Conservation equations were derived for Cu^{2+} in the membrane contactor and solved numerically based on finite element method (FEM). With solving conservation equations, velocity, concentration and pressure distributions were obtained for solute. The simulation results showed that pressure drop is not appreciable in the membrane contactor. Furthermore, simulation results revealed that membrane contactors are efficient in the extraction of heavy metals.

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