

CHAPTER II

LITERLATURE REVIEWS

Membrane for the separation and concentration of metal ions have received considerable study throughout the past three decade due to characteristics such as ease of operation, energy and selectivity advantages and low cost operations factor. Membrane extraction process using hollow fibers are of particular interest because of their versatility.

The permeation rates through supported liquid membranes were calculated by Plucinski and Nitsch(1988). The system composed of zinc(aq)-dithizone-carbon tetrachloride. The experimental were performed in a stirred cell. To describe the mass transfer through supported liquid membrane the general step model was used, and calculation were performed using standard programs to solve the system of equation and for numerical integration. A good agreement between experimental and calculated results was obtained. This indicates that the transport of metal ions through supported liquid membrane can be calculated on the basis of a good knowledge of liquid-liquid extraction (kinetic and equilibria parameters) and hydrodynamics of the apparatus(mass transfer coefficient).

A carrier- mediated liquid membrane process to transport copper for the purpose of regenerating etching and plating baths in a printed wiring has been studied. Copper is transported from the alkaline etching solution to the acid plating bath through a solid supported liquid membrane consist of solution of a β -diketone in kerosene. A copper flux of $3.2 \mu\text{g}\cdot\text{cm}^2\cdot\text{sec}^{-1}$ has been obtain with a 50 % solution of β -diketone(LIX 54-100) supported by thin ($25 \mu\text{m}$) microporous polypropylene film. A study of the effect of process variable including aqueous stirring rate, reactant concentrations and membrane thickness indicates that diffusion of copper carrier complex across the membrane is the permeation rate controlling process at sufficiently high stirring rate and copper feed

concentration. The equilibrium distribution relationship between the feed solution and the membrane appears to be nonlinear for carrier concentrations above 40 %. Independent measurements using well characterized, track etched membrane have qualitatively verified the inverse relationship between concentration and diffusivity of the copper carrier complex, but are not accurate enough to quantitatively support the simple membrane diffusion mode. The selectivity of the membrane for copper is at least on the order of 10^2 with respect to nickel, zinc and tin (O'Hara and Bohrer(1989)).

Hann et al. (1989) presented a mass transfer model for the extraction of copper ions with LIX 84 that may easily be extended to describe the extraction of other metal ions. The effect of the hydrogen and copper ions concentrations on the copper flux through the membrane was measured for the diffusion and for a reaction-limited case to determine the rate parameters in the mass transfer model. The regeneration of the liquid ion exchanger (carrier) was found to be slow compare with the formation of the chelate complex. It is shown that using the proposed mass transfer model can simulate the extraction experiments.

Dispersion free solvent extraction from an actual process stream has been studied using microporous hydrophobic polypropylene hollow fiber membrane modules. Simultaneous extraction of two solute species from the same stream has been investigated using different hollow fiber modules with different packing fractions, surface areas and membrane types. Very high solute recoveries have been achieved in modules only 15 cm long. Mass transfer performances of a single module and module in series have been characterized. For tube side controlled extraction, mass transfer correlations are valid for variety of modules suggesting easy scale-up. Experimentally obtained height of transfer unit (HTU) values as low as 3 cm suggest new perspectives in contacting equipment. A long term extraction study using a prototype module indicated no performance deterioration over 64 days. Alternate design strategies for extraction from a large scale stream have been analyzed(Prasad and Sirkar, 1990).

Shiau and Chen (1993) studied theoretical analysis of copper-ion extraction through hollow fiber supported liquid membrane by used Bis(2-ethylhexyl) phosphoric acid (D2EHPA) as a carrier agent. Both rigorous model and simple model with varied permeation coefficient for system are proposed. The once-through and the recycle mode were studied. From this study found that both models gave the closed experimental data and concluded that simple model can use in this system. From the model it is found that the permeation coefficient is function of copper ion concentration. The rate-controlling steps are permeation through the membrane and the aqueous film of solution.

Juang (1993) studied permeation and separation of zinc and copper by supported liquid membrane containing D2EHPA dissolved in kerosene as a mobile carrier. A permeation model was present taking into account the aqueous film diffusion of metal ions toward and out of the membrane and the membrane diffusion of D2EHPA and its metal complexes. It was found that the calculated permeation rates were in good agreement with the measured results. Higher selectivity in the separation of zinc and copper was obtained when the diffusion resistance in the membrane phase was dominant.

Yun et al. (1993) studied removal of toxic heavy metal from aqueous waste streams by using hollow fiber supported liquid membrane. Toxic heavy metals studied were copper and chromium (VI). Each metal individually removed in separation once through experiments from a synthetic wastewater by organic extractant flowing in the shell side countercurrent to wastewater in the fiber module. The organic extractant used for copper was LIX84 dilute in n-heptane, and for chromium extraction was tri-n-octylamine (TOA) dilute in xylene. A mathematical model was developed to predict the extending of copper extraction from the aqueous synthetic wastewater. The equilibrium constant for copper was determined to be 1.7 from experimental partitioning data. The experimental data on copper extraction are described well by the model if the forward interfacial chemical reaction rate constant is 9.0×10^{-6} cm/s.

Yi and Tavlarides(1995) presented a numerical model to evaluate the dynamic behavior of mass transfer in the hollow fiber supported liquid membrane for metal ion removal from aqueous stream. The analysis that considers the effects of axial-flow velocity on the radial pressure difference across the membrane wall permits the specification of this operation of this operating parameter to avoid expression of impregnated carrier from the membrane and to prevent membrane wall rupture. The model account for effects of boundary layer mass transfer and kinetic rate resistance at the interfaces on membrane flux. The performance of different size membrane modules was estimated for two operating modes of a module: one for the flow of feed solution inside the membrane tube and the stripping solution flow in the annular region and the other for the flow of stripping solution inside the membrane tube and feed solution flow in the annular region of the module. A case system evaluated is copper ion extraction from acidic solutions using 2-hydroxy-5-nonylacetophenone oxime impregnated in α -alumina silica ceramic membranes. The performances of membrane module depend on the sizes and operating method. In these calculations, the operation condition of no-pressure difference across the membrane was imposed on the design. This condition is achieved by adjusting the ratio of the flow velocities of the feed and stripping solutions within the inside and annular regions of the modules.

Modeling and simulation of membrane process for recovery of Cr(VI) with aliquat 336 are presented by Alonso and Pantelides (1996). The simulation of this process was carried out using the gPROMS process modeling system. This software package provides a high-level language for the declarative description of mathematical models of unit operation. The mathematical models used may involve mixed sets of nonlinear integral, partial and ordinary differential and algebraic equation. Therefore both distributed and lumped units operation may be described. Steady state simulations of a single extraction membrane module were carried out for both the cocurrent and countercurrent cases. Models have been developed for both single-function and dual-function membrane modules, and these have been combined to model entire separation process carrying out simultaneous extraction and stripping of Cr(VI) from aqueous

solutions. Limited validation of the models developed has been carried out using experimental data already reported.

The efficiency of hollow fiber modules for chemical extraction are studied by Daiminger et al (1996). The system composed of Me_{aq} /bis(2-ethylhexyl) phosphate (DEPA) in isododecane. It was possible to achieve 2 – 4 orders of magnitude decrease of metal concentration in the aqueous phase by extraction in a single-pass flow mode. The necessary values of mass transfer coefficient were calculated using correlations existing in the literature, which were checked experimentally. The obtained results of extraction were compare with those for a pulsed sieve-plate column and an ideal mixer-settler cascade. It is possible to achieve similar extraction results in a short densely packed HFM compare to extraction column of 6 m length. This can be related to the high interfacial area and short diffusion paths, which prevail over the disadvantages of laminar flow. Preliminary experiments on reextraction show the possibility of thousandfold enrichment of zinc starting from 100 mg/L wastewater. This, together with chemical variability of solvent extraction should favor the HFM extraction against the classical solid ion exchanger.

Itsara (1998) studied the performance of extraction of copper ion from an extremely dilute solution with hollow fiber supported liquid membranes. Various factors affecting this extraction system were studied, viz. the concentrations of extractant in membrane phase in the range below 25 V/V%, the types of extractant between D2EHPA, LIX84-I and LIX 860-I, the concentrations of copper ion in feed solution in the range of 1 ppm to 100 ppm, flow patterns of feed solution in tube side and in shell side of hollow fiber supported liquid membranes, pH of feed solution controlled with buffer solution, and circulation of strip solution. Kerosene was used as an organic solution while 0.1 mol/l sulfuric acid was used as a strip solution. From the experiments, the ability of copper ion transportation was increased when concentration of extractant was increased. LIX-type extractant showed better performance than D2EHPA. Copper ion transportation was increased as concentration of copper ion in feed solution was increased. Flow pattern of feed solution in tube side and in shell side of hollow fiber module had no influence in

the performance of the system. Copper ion transportation was increased when pH of feed solution was kept at 5 by buffer solution. The copper ion transportation could be occurred appropriately by using small amount of strip solution in circulation mode.

The modeling of mass transfer rates of metal ions across supported membrane were reported by Elhassadi and Do (1999). The model equations were tested using experimental data reported in the literature and produce in this work. It was found that uranium(VI) and thorium(IV) can be selectively separated and concentrated using supported liquid membrane. Depending on the way the liquid membrane are designed, the selectivity toward a specific metal can be predetermined. The effect of the ratio of the effective diffusivity to bulk diffusivity in free solutions was found to behave with the same characteristic of systems of preferentially adsorbed solutes. The two methods used for evaluating the parameters of the system were found to give good estimates of the parameters and to agree quite reasonably with each other. The nonlinear regression technique simulated many dynamic experimental results quite closely.

Szpakowska and Nagy (1999) studied the transport of copper(II) ion through liquid membrane in various experimental conditions. The results obtained are analyzed by using the concepts and methods of chemical kinetics. This approach allowed kinetic equations to be established which are sufficiently general to account for a large variety of transport kinetics (steady or nonsteady, first or zeroth order, diffusion or reaction controlled, reversible or irreversible), to identify clearly the rate-determining steps and to propose a detailed mechanism at the molecular level.

El Aamrani FZ, Kumar Aand Sastre AM studied the facilitated transport of Cu-II from chloride media through a flat-sheet supported liquid membrane (FSSLM) is investigated, using thiourea derivatives as ionophores, as a function of hydrodynamic conditions, concentration of copper ($1-3 \times 10^{-7}$ mol cm⁻³) and H⁺ (pH 0.1-2.5) in the feed solution, structure of carrier, carrier concentration ($0.7-3 \times 10^{-5}$ mol cm⁻³) in the membrane, strippant in receiving phase and support characteristics. A model is presented that describes the transport mechanism, consisting of diffusion through a feed aqueous

diffusion layer, a fast interfacial chemical reaction, and diffusion of carrier and its metal complex through the organic membrane. The organic membrane diffusional resistance ($\Delta(o)$) and aqueous diffusional resistance ($\Delta(a)$) were calculated from the proposed model, and their values were $107 \times 10^2 \text{ s cm}^{-1}$ and 625 s cm^{-1} , respectively. It was observed that the Cu-II flux across the membrane tends to reach a plateau at a high concentration of Cu-II or a low concentration of H^+ owing to carrier saturation within the membrane, leading to a diffusion-controlled process. The values of the apparent diffusion coefficient ($D(o(a))$) and limiting metal flux $J(\text{lim})$ were calculated from the limiting conditions and found to be $2.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $1.4 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$, respectively. The values of the bulk diffusion coefficient ($D(o, D-b)$) and diffusion coefficient ($D(o)$) calculated from the model were $2.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $1.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The polymeric microporous solid support, Durapore, was selected throughout the study as it gave the best performance.

Kumar and Sastre (2000) proposed modeling and mass transfer of separation and concentration of gold(I) from aqueous cyanide media by using hollow fiber supported liquid membrane. The organic extractant was N,N-bis(2-ethylhexyl) guanidine (LIX79). The model valid for recycle mode. The model is presented which describes the transport mechanism, indicating different rate-controlling steps. The validity of this model was evaluated with experimental data and found to tie in well with theoretical values. The effect of exceed cyanide in the feed up to 1000 ppm did not affect the recovery of gold.

The extraction of Cu(II) from an equimolar EDTA ethylenediaminetetraacetic acid (EDTA) solution across microporous hollow fibers to an organic phase containing Aliquat 336 (a quaternary amine) was studied by Ruy-Shin and I-Pyng Huang (2000). A mass transfer model was proposed considering aqueous layer diffusion, membrane diffusion and organic layer diffusion on the basis of a good knowledge of extraction chemistry and the transport properties of the relevant geometry. Close agreement between the measured and modeled results is obtained (average SD, 12 %). On the basis of the fractional resistance of each diffusion step, the present hollow fiber extraction process is

found to be combined and governed by aqueous layer and membrane diffusion. The resistance resulting from the organic layer diffusion is negligibly small.

Kasem (2000) studied and optimized the efficiency of copper ion extraction in the one, two and three stages hollow fiber supported liquid membrane system by using computer program. This research simulated and optimized the parameter that affects copper ion extraction. From the simulated results it was found that the average relative error of this model was 6.9 %. The efficiency of copper ion extraction in the two and three stages hollow fiber membrane system increased at least 2-3 times more than the efficiency of single stage extraction system.

The facilitated co transport of silver and copper in acidic thiourea medium through a supported liquid membrane made of a flat sheet polypropylene membrane support containing dibenzo-18-crown-6 as a carrier was studied. The permeability factors increased with increasing carrier concentration reaching a limiting value at greater than 1 mM. The calculation of the diffusion coefficients in membranes showed a lower diffusivity of DB18C6 complexes for copper than for silver. Both permeability and diffusion factors increase with the pH of the feed phase reaching a plateau at pH = 1. An increase of temperature from 25 to 55° C drastically decrease the permeability and diffusion factors due to an evaporation of the organic phase from the membrane support. The diffusivity was significantly higher using a Cegard 2500 support with respect to Cegard 2400 and 2402 and Accurel PP. A theoretical model, applied elsewhere in the case of Donnan dialysis, has been applied for the first time to the case of facilitated transport, which has permitted evaluation of the effect of the diffusion of the carrier metal thiourea complexes inside the membrane support.

Su-Hsia Lin and Ruey-Shin Juang (2002) studied the simultaneous extraction recovery of free Cu^{2+} ions and ethylenediaminetetraacetic acid(EDTA) chelated anions from chloride solutions into a stripping HCl solution with a mixture of LIX64N and aliquat 336 in two hollow fiber modules. A kinetic model is presented that considers possible mass transfer steps, including aqueous layer diffusion, interfacial chemical

reaction, membrane diffusion and organic layer diffusion. In particular, the effects of the preferential extraction of one metallic species and the mutual interaction of the two extractants were also corrected in this model on the basis of the results for individual extraction systems. The calculated time profiles of the total Cu(II) concentrations were in reasonable agreement with the experimental data. Finally, the rate controlling mechanism of such nondispersive extraction processes were quantitatively in term of a comparison of the resistance of each mass transfer.

The separation of copper and zinc from an aqueous sulphate media by supported liquid membrane (SLM) using di-2-ethyl hexyl phosphoric acid (TOPS-99) as mobile carrier has been studied by Sarangi K and Das RP(2002). Celgard-2500, a microporous polypropylene film, was used as the solid support for the liquid membrane. A plate and frame type of cell was used for the experiment. The effects of different parameters such as flow rate, pH of feed solution, TOPS-99 concentration in the membrane phase and acid concentration in strip solution on separation of copper and zinc were studied. It was observed that flow rate of 100 mL/min (velocity 85.7 m/h) was sufficient to reduce the resistances due to the aqueous boundary layer. Zinc was permeated in a pH region 1.5-5.0, while copper permeation started at pH 3.0. At pH 2.5, the co-permeation of copper with zinc was negligible, and a high separation factor was achieved at this pH.

The extraction of Zn^{2+} and Cu^{2+} in a hollow fiber membrane module with a kerosene solution of di(2-ethylhexyl)phosphoric acid (D2EHPA) was studied by Juang RS, Huang HL (2003). Experiments were performed at different aqueous metal concentrations (0.78-15.7 mol/m³), pH 2-6, and organic D2EHPA concentrations (25-100 mol/m³). A mass transfer model was presented that considers aqueous layer diffusion, membrane diffusion, and organic layer diffusion. The calculated time profiles of aqueous metal concentrations agreed reasonably with the measured data (standard deviation, 9%) based on a good knowledge of the chemistry of extraction reactions and the transport properties of the relevant geometry. By comparing the relative resistance of each diffusion step, the extraction of Zn^{2+} was predominantly governed by aqueous layer diffusion; however, the diffusion in aqueous layer, membrane, and organic layer all

played a certain role for the extraction of Cu^{2+} . The changes of rate-controlling steps with time during the experiments were also evaluated.

Molinari R. et al. (2004) studied copper(II) removal and recovery from wastewater, e.g., washing water of contaminated soils, was investigated by using a new chelant, the molecule 2-hydroxy-5-dodecylbenzaldehyde (2H5DBA), never used before as a ligand for metal ions. This material was designed and synthesized by improving a method reported in the literature, obtaining a very high yield (80 vs 19%). Process selectivity and supported liquid membrane (SLM) viability were studied. The operating conditions and selectivity of the process were found by means of L-L extraction tests performed at different carrier concentrations (10, 30, and 50% v/v) using kerosene as the solvent. At 50% v/v carrier concentration and pH 5, the selectivities of Cu^{2+} separation vs Ni^{2+} , Zn^{2+} , and Mn^{2+} were 4.25, 315.0, and 280.0, respectively. The carrier concentration had a strong influence on the viability of the SLM process: indeed, by increasing the concentration of the carrier, the operating pH could be decreased, thereby avoiding copper precipitation in the feed phase. The enrichment factor of Cu^{2+} in the strip ($[\text{Cu}^{2+}]_{\text{strip}}/[\text{Cu}^{2+}]_{\text{feed}})(\text{final})$ was 23.5.



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