COPPER RECOVERY IN A BENCH-SCALE CARRIER FACILITATED TUBULAR SUPPORTED LIQUID MEMBRANE SYSTEM

S. Makaka[#*], M. Aziz[*] and A. Nesbitt[*]

[*]Department of Chemical Engineering, Cape Peninsula University of Technology, Cape Town Campus, P.O.Box 652, Cape Town, 8000, South Africa

Abstract

The extraction of copper ions in a tubular supported liquid membrane using LIX 984N-C as a mobile carrier was studied, evaluating the effect of the feed characteristics (flowrate, density, viscosity) on the feed-side laminar layer of the membrane. A vertical counter-current, double pipe perspex bench-scale reactor consisting of a single hydrophobic PVDF tubular membrane mounted inside was used in all test work. The membrane was impregnated with LIX 984N-C and became the support for this organic transport medium. Dilute Copper solution passed through the centre pipe and sulphuric acid as strippant passed through the shell side. Copper was successfully transported from the feed-side to the strip-side and from the data obtained, a relationship between Schmidt, Reynolds and Sherwood number was achieved of $Sh = 8.4 \, Re^{0.6} \, Sc^{0.3}$.

Keywords*: Dimensionless numbers; Feed mass transfer coefficient (k_f); Transport; Supported liquid membrane; LIX984N-C.*

1. Introduction

Treatment of waste material from mining and mineral processing is gaining more and more importance because of increasing demand for high purity products and also because of increased environmental concerns [1]. This translates into incentives to develop new applications of membrane separation technology by scientists and engineers and to

develop new theories of mass transport and controlling mechanisms [1].

Extracting metals from ores requires a number of operations: some mechanical, physical, and physicochemical known as mineral beneficiation and some chemical known as extractive metallurgy [2].

Supported liquid membrane (SLM) extraction appears to show potential for the extraction of metal ions from wastewater process streams. An SLM is made up of an organic liquid, known as extractant absorbed in the pores of a membrane acting as a support. Mass transport in this system occurs by extracting the metal ions from the aqueous feed phase and releasing it into the aqueous strip phase, through the membrane. Both these steps occur in a single unit operation, which is an advantage of SLM's.

An extractant is dissolved in the organic membrane phase. It acts as a shuttle, extracting the metal ion from the feed phase and releasing it on the other side of the membrane. In this, extraction and stripping are performed in one single process step [3].

Although the phenomenon of SLM's is common in nature, to date no industrial application for SLMs has been reported in literature, [4].

The short comings of SLMs have been identified as the following; lack of membrane and reactant stability during general use, low rates of ion transport between phases, osmotic effects and the relatively high cost of the membrane support material. Therefore there is great scope for further investigation of SLMs, for the purposes of improving performance.

SLMs are classified according to different shapes and structures, i.e. flat sheets, tubular, hollow fibres, etc. Membrane characterization includes; mechanical strength ,chemical resistance e.g. pH range, compatibility with solvents, permeability to different species e.g. pure water permeability, gas permeability, average porosity and pore size distribution, etc.

Specifically for this study, tubular supported liquid membranes (TSLM) were used. The diameters of tubes range from 5mm to 25mm, with 12.5mm being the most common [1].

Advantages include turbulent flow, providing good membrane/solution contact and removing retentate film build-up, relatively easy cleaning, easy handling of suspended solids and viscous fluids and ability to replace or plug a failed tube during operation. The feed flow pattern is easy to characterize and therefore design and analysis based on fluid dynamic principles is possible. Tubular membrane modules can handle reasonably high transmembrane pressure. Disadvantages include high capital cost, low packing density, high pumping costs, and limited achievable concentrations [5].

The extraction of copper ions in a tubular supported liquid membrane of diameter 12 mm using LIX 984N-C as a mobile carrier was studied with the objective of evaluating the effectiveness of the system and modelling the ion flux, in terms of mass transfer coefficient as a function of traditional empirical dimensionless-number models.

2. Theory

SLM technology is, theoretically, one of

the most efficient membrane-based methods of separation. It does not use pressure or voltage, but is based on difference of chemical energy as a driving factor of the process [6]. Transport in this process occurs despite the large chemical potential gradient existing between the feed and the carrier in the membrane [7].

It has been suggested that the rate of mass transfer through SLM systems might be controlled by three resistances, i.e., the resistances through the feed-side and strip-side laminar layers in addition to diffusion through the membrane. It has been reported that in the specific case of transport resistances in the direct contact membrane distillation process using a flat sheet module, the controlling resistance to mass transport is found in the feed-side hydrodynamic- laminar layer [8].

In this study an empirical approach was used to model the mass transfer, i.e. the relationship between the different physical quantities e.g. viscosity density, flow rate, etc., and the mass transfer rate, was determined.

An increase in temperature of the feed will increase the mass transfer rate in the aqueous film at the feed and stripping phases and results in a decrease in viscosity of the liquid phases and the liquid membrane inside the support [9]. This will have a direct effect on the Schmidt number. The Sherwood number, Eq. (1) is typically correlated with the Reynolds number, Eq. (2) and Schmidt number, Eq. (3) with a logarithmic function, Eq. (4) .

The actual relationship is determined from experimental data.

$$Sh = \frac{k_f L}{D_{Cu}} \qquad ...(1)$$

$$Re = \frac{\rho L v}{\mu} \qquad ...(2)$$

$$Sc = \frac{\mu}{\rho D_{AB}} \qquad ...(3)$$

$$Sh = C \, Re^n \, Sc^m \qquad ...(4)$$

The logarithmic form of the empirical model relationship presented in Eq. (4) is assumed to be in effect in this system. It is noted that this model will only be effective if the mass transfer controlling mechanism is in the laminar hydrodynamic layer on the feed side of the membrane and proving this will have to be part of this test work.

An increase in the feed flow rate will increase the Reynolds number; and this will influence the mass transport across the membrane [9]. The Reynolds number of a flow strongly influences the velocity boundary layer characteristics and hence is likely to have a great impact on the mass transfer coefficient.

Diffusion of the metal ions from the bulk through the aqueous stagnant layer on the feed membrane side can be modelled using Fick's law shown by Eq. (5), whereby k_f represents the mass transfer coefficient on the feed-side of the membrane. From this mass transfer equation, the aqueous feed mass transfer coefficient (k_f) can be calculated:

$$N_{CU} = k_f \left(Cu^{2+}{}_{bulk} - Cu^{2+}{}_{surface} \right) \qquad ...(5)$$

3. Materials and methods

3.1 Kinetic test

The 20cm long tubular membrane module made of Polyvinyldene fluoride (PVDF) from Koch membrane systems was impregnated with a carrier consisting of an extractant (20% LIX 984N-C) supplied by Cognis Corporation, dissolved in an organic diluent, which in this test work was Kerosene (Kimix chemicals). As an extraction reagent, LIX984N has shown a good performance in solvent extraction circuits, with achieved copper recovery of 98% [10].

After impregnation using a vacuum desiccator for an hour, the membrane was then fixed inside the SLM reactor as shown in the experimental set up Fig. 1.

The feed was a synthetic solution of Copper Sulphate at a concentration of 100 ppm and the strip solution was a 25% sulphuric acid by mass. The total volume in the strip and feed phases was 200ml. The pH of the feed solution was kept constant at pH of 5 and an Automatic pH controller unit was used to control the pH at a desired value. Batch experiments were conducted. The runs were performed in duplicate so as to check the repeatability of the results.

Discrete flow rates and temperatures were chosen for each test varying between 30 and 120ml.min^{-1} and 21 and 50°C, as shown in the experimental matrix Table 1.
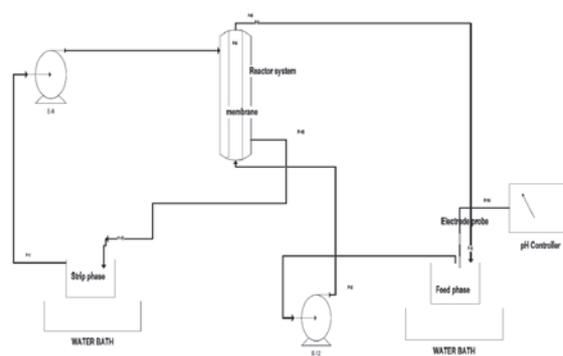

Fig. 1. The representation of the set-up used for the test work: Two water baths (Buchi 461), feed and strip solutions, pH controller pump and electrode probe (Hanna instruments), (E-8&E-12) two peristaltic pumps (Dune Engineering), membrane supporting system (Double pipe perspex bench scale reactor) and (P-9) PVDF tubular membrane (Koch membrane systems).

Table 1. Experimental matrix

Temperature ⟶	21.0 deg	30.0 deg	40.0 deg	50.0 deg	
Flow rates ↓					
30 ml/min	8.9	11	13.4	16	**Reynold's No.**
40 ml/min	11.9	14.6	17.8	21.3	
50ml/min	14.8	18.3	22.3	26.6	
60 ml/min	17.8	21.9	26.7	31.9	
70 ml/min	20.8	25.6	31.2	37.3	
80 ml/min	23.7	29.2	35.6	42.6	
90 ml/min	26.7	32.9	40.1	47.9	
100 ml/min	29.7	36.5	44.5	53.2	
120 ml/min	35.6	43.8	53.4	63.9	
Schmidt No.	**198.8**	**161.3**	**132.4**	**110.7**	

The associated Reynolds and Schmidt numbers are also given in Table 1.

Samples were drawn from the feed and strip solutions at least every hour for the entire duration of the run. The concentration of copper in each sample was determined by Atomic Absorption Spectrophotometer.

4. Results and discussion

4.1 Copper extraction

As expected, the copper concentration in the feed solution decreased during each run as shown in Fig. 2. At the lowest flow rate, i.e. 30ml.min^{-1}, the smallest drop in copper concentration was recorded i.e. 45%, implying that the lowest amount of copper was extracted under these circumstances, while at higher flow rates, the copper concentration in the feed decreased by approximately 65%. This would indicate a strong correlation between the rate of extraction and flow rate, which is strong evidence that assuming a laminar layer controlling mechanism is treasonable. Despite taking 50 hours for each run, it appeared that equilibrium was not reached.

The copper reports to the stripping side as

expected and a selection of results are given in Fig. 3 (the first 5 hours). The mass balances were found to be satisfactory giving an average accuracy of within 6% with a standard deviation of 6.4.
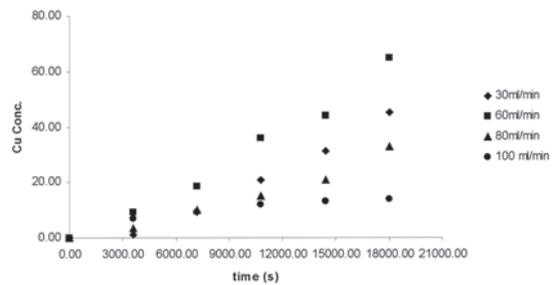

Fig. 3. Copper ions increase on the strip phase (5hrs)

4.2 Mass transfer coefficient on the feed side of the membrane

In Fig. 4, the values of the mass transfer coefficients, calculated using Eq. (5) applied to the feed side of the membrane are shown. The coefficient was calculated from measured data sampled in the first hour of each run, assuming the concentration of the copper at the liquid membrane interface to be zero. As the slope of concentration versus
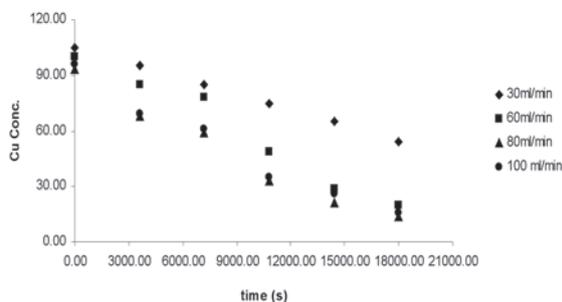

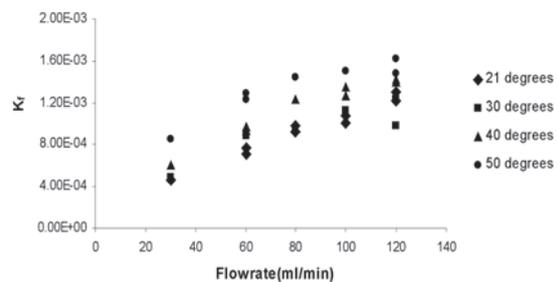*Fig. 2. Copper ions decrease on the feed phase (5hrs)*

Fig. 4. Mass transfer coefficient vs. Feed flowrate

time, remained relatively constant during this phase, this approach was assumed reasonable.

It can be observed that the mass transfer coefficient appears to increase with increasing flow-rate, once again indicating that the laminar layer has a strong effect on the mechanism of mass transfer. In addition we observe that generally speaking the mass transfer coefficient improves with increasing temperature.

4.3. The empirical model

The Reynold's and the Schmidt's number were calculated from the parameters of the system and are shown in Table 1. The Sherwood number was calculated using the mass transfer coefficient obtained through Eq.(5). A traditional log-log relationship between the dimensionless numbers was assumed to determine the model parameters through a curve fitting process. The final model is given in Eq. (6).

$$Sh = 8.4\,\mathrm{Re}^{0.6}\,Sc^{0.3} \qquad ...(6)$$

Figure 5 compares the model prediction to the measured data. A parity line has also been
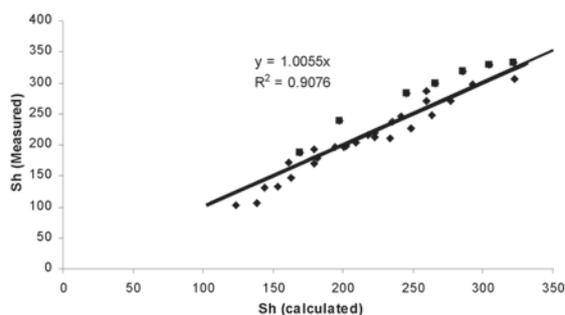

Fig. 5. The Sherwood no. Measured vs. Calculated

introduced. A linear regression fit of the data achieved an R^2 correlation of 0.907 which falls directly on the parity line for this data and gives a slope of 1.01.

5. Conclusion

From the results of this study it can be seen that copper ions can be extracted by this system especially considering that, many of the tests were repeated and very similar results obtained on each occasion.

In the Reynolds regime investigated in this test work, it would appear that the liquid flow rate on the feed side has a substantial effect on the mass transfer coefficient. More specifically, at a higher flow rate of 120 ml.min^{-1} and at a lower flow rate of 30 ml.min^{-1} at 2°C as shown in Fig. 4, the mass transfer coefficient lies between 1.22x10^{-3} and 4.65x10^{-4} cm.s^{-1}.

Temperature also appears to have an effect, at high feed solution temperature of 50°C the mass transfer coefficient on the feed side of the membrane lies between 1.63x10^{-3} and 8.54x10^{-4} cm.s^{-1}.

A credible and repeatable relationship between the Sherwood, Schmidt and Reynolds numbers was achieved as witnessed by the goodness of fit in Fig. 5.

As seen in other TSLM studies the achieved mass transfer coefficients are extremely low when compared with other mass transfer unit operations.

Acknowledgements

Nomenclature

D_{cu} - diffusion coefficient ($m^2.s^{-1}$)
N_{cu} - mass flux of copper (mol. $m^{-2}.s^{-1}$)
k_f - aqueous mass transfer coefficient ($cm.s^{-1}$)
L - length of the membrane (m)
v - velocity of the fluid ($m.s^{-1}$)
t - time (s)
Sh - Sherwood number
Re - Reynolds number
Sc - Schmidt number

Greek symbols

ρ - fluid density ($g.cm^{-3}$)
μ - fluid viscosity (Pa.s)

Subscripts

i - inner
o - outer
f - feed side
s - strip side

Abbreviations

PVDF - Polyvinyldene difluoride
SLM - Supported liquid membrane
TSLM - Tubular Supported Liquid Membrane
Cu - Copper

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