# Optimization of Cu(II) Ion Extraction and Stripping through Liquid Membrane by Response Surface Methodology

Siu Hua Chang, Alif Azwan Abdul Wahab, Ayub Md Som

*Abstract*— **This study aimed to optimize the operating parameters of a liquid membrane for the maximum extraction and stripping of Cu(II) ions by using response surface methodology (RSM). The parameters considered for optimization include feed phase flowrate, membrane phase flowrate, extraction time and stripping time. The optimization was conducted by applying central composite design and the regression models were developed. The optimum conditions found for feed phase flowrate was 2.52 L/h, membrane phase flowrate was 2.69 L/h, extraction time was 5.15 h and stripping time was 23.36 h.**

*Index Terms*—**Optimization, liquid membrane, response surface methodology**

## I. Introduction

Cupric (Cu(II)) ion is ubiquitous in the environment. Cu(II)-containing wastewater is discharged by various industries such as electroplating, pulp and paper, print circuit board manufacturing, refinery and foundries [1,2]. A small concentration of Cu(II) will be beneficial to living organisms, otherwise it will cause serious threat to the lives such as Wilson's disease [1,3]. Several methods are available to remove and recover Cu(II) from wastewater such as absorption, coagulation-flocculation, chemical precipitation, ion-exchange and solvent extraction [4–6].

Recently, liquid membrane has drawn many attentions over other methods due to its effectiveness, high selectivity, energy saving, low cost, non-equilibrium mass transfer and operated in single step [7,8]. The efficiency of liquid membrane is affected by many operating parameters which can be optimized by response surface methodology (RSM). Response surface methodology is a statistical multivariate optimization technique which has been used extensively in numerous processes or systems. This is owing to its several outstanding features over the conventional univariate one-factor-at-a-time technique such as simultaneous optimization of several parameters, monitoring of interaction effect between parameters on the response, fewer experiments required and more economical. Some of the typical response surface designs used for optimization include 3-level factorial design, central composite design (CCD), Doehlert and Box-Behnken.

Manuscript received Dec 8, 2015; revised Dec 15, 2015. This work was supported in part by the Ministry of Higher Education of Malaysia under the Research Acculturation Grant Scheme.

S. H. Chang is with the Faculty of Chemical Engineering, UniversitiTeknologi MARA (UiTM) Malaysia, 13500 Permatang Pauh, Penang, Malaysia (phone: +604-382 2546; fax: +604-382 3292; e-mail: shchang@ppinang.uitm.edu.my).

A. A. A. Wahab is with the Faculty of Chemical Engineering, UniversitiTeknologi MARA (UiTM) Malaysia, 13500 Permatang Pauh, Penang, Malaysia (e-mail: shalalah_alz@yahoo.com.my).

A. M. Som is with the 3Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM) Malaysia, 40450 Shah Alam, Selangor, Malaysia (e-mail: ayub522@salam.uitm.edu.my).

In this work, a liquid membrane process was optimized for the maximum extraction and stripping of Cu(II) ions by using CCD which is one of the most widely used experimental designs in RSM. The parameters considered for optimization include feed phase flowrate, membrane phase flowrate, extraction time and stripping time. The optimization was conducted by applying a central composite design and the optimum condition was determined.

## II. Materials and Methods

### A. Materials

Some waste cooking oil was collected from local restaurant and filtered by using cheesecloth before use. Chemicals such as di-2-ethylhexylphosphate (D2EHPA) (>95% purity, Merck), tributylphosphate (TBP) (>99% purity, Merck), sodium sulphate (Na2SO4) (>99% purity, QRëC), copper sulphate pentahydrate (Cu2SO4.5H2O) (>99.6%, R&M chemical), Sodium acetate (CH3COONa) (>99% purity, QRëC), Acetic acid (CH3COOH) (>99% purity, Merck) and ( sulphuric acid (H2SO4) (>98% purity, Fisher Scientific) were analytical grade reagents which were used as received.

### B. Methods

Figure 1 shows the schematic diagram of the liquid membrane system used in this work. It consists of three phases, namely, Cu(II)-containing aqueous phase (feed phase), H2SO4 aqueous phase (stripping phase) and waste cooking oil organic phase (membrane phase). Both of the feed and stripping aqueous phases are separated with a solid impermeable wall and layered on top by the organic membrane phase. The aqueous phase compartments are equipped with some specially-design tubes with holes that control the amount of organic membrane phase droplets released into the aqueous phases. During the operation, the membrane phase was pumped continuously into and out of

ISBN: 978-988-14047-6-3
ISSN: 2078-0958 (Print); ISSN: 2078-0966 (Online)

the system, while the feed phase and stripping phase were pumped into and out of the system at specific extraction and stripping times. Some samples of the feed and stripping phases were collected at the outlets of the system for chemical analysis with an inductively coupled plasma optical emission spectrometer (ICP-OES). The percent extraction (%E) of Cu(II) ions was determined by:

$$\%E = \frac{Cu_{i,aq} - Cu_{f,aq}}{Cu_{i,aq}} \times 100 \quad (1)$$

where $Cu_{i,aq}$ is the initial Cu(II) ion concentration in the aqueous phase and $Cu_{f,aq}$ is the final Cu(II) ion concentration in the aqueous phase after extraction, whereas the percent stripping (%S) of Cu(II) ions was given by:

$$\%S = \frac{Cu_{f,strip}}{Cu_{i,aq} - Cu_{f,aq}} \times 100 \quad (2)$$

where $Cu_{f,strip}$ is the final Cu(II) ion concentration in the stripping phase. All experiments were conducted at room temperature (25$^{o}$C).

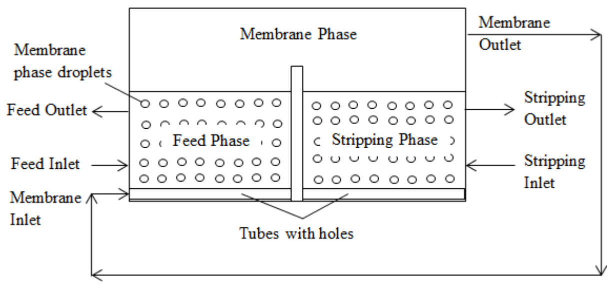


Fig. 1. Liquid membrane system used in this work

### C. Design of Experiment

*Central Composite Design*

CCD is one of the most widely used experimental designs for the first order and second order polynomial models [9]. It allows the researchers to find the ideal and reasonable information about experimental sequences for testing the lack of fit without involving the large amount of design points [9]. In this work, the parameters studied in three levels (−1, 0, 1) using the face-centered CCD are given in Table 1. The factorial points are coded to the (−1, 1) interval where the low and high levels are coded as −1 and 1, respectively, while the centre points are located at (0, 0).

TABLE I
PARAMETERS AND LEVELS USED IN THIS STUDY

| Parameters | Symbols | Low (-1) | Middle (0) | High (1) |
|---|---|---|---|---|
| Membrane flowrate (L/h) | A | 1.9 | 2.3 | 2.7 |
| Feed flowrate (L/h) | B | 1.6 | 2.7 | 3.8 |
| Extraction time (h) | C | 2 | 4 | 6 |
| Stripping time (h) | D | 4 | 14 | 24 |

## III. RESULTS AND DISCUSSION

### A. Design Matrix Used and Responses Measured

Table 2 shows the design matrix of CCD used and the average responses (%E and %S) measured in this work. It consists of a total of 29 runs which were conducted randomly to avoid the influence of the uncontrolled factors. All experiments were carried out under homogeneous condition in one block of measurement. The %E and the %S were found to vary from 11 – 88% and 3 – 51%, respectively.

TABLE 1
DESIGN MATRIX OF CCD USED AND AVERAGE RESPONSES MEASURED

| Standard Order | Run | Blocks | Parameters* | | | | %E | %S |
|---|---|---|---|---|---|---|---|---|
| | | | A | B | C | D | | |
| 20 | 1 | 1 | 2.3 | 3.8 | 4 | 14 | 57 | 18 |
| 29 | 2 | 1 | 2.3 | 2.7 | 4 | 14 | 60 | 14 |
| 7 | 3 | 1 | 1.9 | 3.8 | 6 | 4 | 55 | 3 |
| 19 | 4 | 1 | 2.3 | 1.6 | 4 | 14 | 46 | 26 |
| 3 | 5 | 1 | 1.9 | 3.8 | 2 | 4 | 11 | 5 |
| 14 | 6 | 1 | 2.7 | 1.6 | 6 | 24 | 82 | 51 |
| 26 | 7 | 1 | 2.3 | 2.7 | 4 | 14 | 67 | 27 |
| 25 | 8 | 1 | 2.3 | 2.7 | 4 | 14 | 70 | 35 |
| 27 | 9 | 1 | 2.3 | 2.7 | 4 | 14 | 72 | 25 |
| 12 | 10 | 1 | 2.7 | 3.8 | 2 | 24 | 47 | 30 |
| 4 | 11 | 1 | 2.7 | 3.8 | 2 | 4 | 38 | 6 |
| 15 | 12 | 1 | 1.9 | 3.8 | 6 | 24 | 32 | 12 |
| 1 | 13 | 1 | 1.9 | 1.6 | 2 | 4 | 23 | 10 |
| 24 | 14 | 1 | 2.3 | 2.7 | 4 | 24 | 67 | 40 |
| 10 | 15 | 1 | 2.7 | 1.6 | 2 | 24 | 66 | 46 |
| 8 | 16 | 1 | 2.7 | 3.8 | 6 | 4 | 67 | 6 |
| 21 | 17 | 1 | 2.3 | 2.7 | 2 | 14 | 44 | 38 |
| 17 | 18 | 1 | 1.9 | 2.7 | 4 | 14 | 49 | 18 |
| 9 | 19 | 1 | 1.9 | 1.6 | 2 | 24 | 27 | 15 |
| 16 | 20 | 1 | 2.7 | 3.8 | 6 | 24 | 88 | 47 |
| 18 | 21 | 1 | 2.7 | 2.7 | 4 | 14 | 81 | 43 |
| 6 | 22 | 1 | 2.7 | 1.6 | 6 | 4 | 82 | 9 |
| 22 | 23 | 1 | 2.3 | 2.7 | 6 | 14 | 77 | 26 |
| 2 | 24 | 1 | 2.7 | 1.6 | 2 | 4 | 66 | 15 |
| 5 | 25 | 1 | 1.9 | 1.6 | 6 | 4 | 59 | 8 |
| 11 | 26 | 1 | 1.9 | 3.8 | 2 | 24 | 37 | 20 |
| 23 | 27 | 1 | 2.3 | 2.7 | 4 | 4 | 64 | 11 |
| 28 | 28 | 1 | 2.3 | 2.7 | 4 | 14 | 56 | 13 |
| 13 | 29 | 1 | 1.9 | 1.6 | 6 | 24 | 49 | 32 |

*A: Membrane flowrate, B: Feed flowrate, C: Extraction time, D: Stripping time

### *B. Reduced Regressions Models*

The reduced regression models for %E and %S determined at 5% significance levels are given as follows:

%E =65.50+12.80A+15.37C+4.14D-11.91B2-4.85AB-2.48AC+3.98BC+5.23BD (3)

%S = 29.46+6.35A-2.74B+13.10D-7.69B2+4.33 AD+3.55CD (4)

In Eqs. 3 and 4, the positive coefficients show the synergistic effects on the responses while the negative coefficients show their antagonistic effects. The adequacy of these models was assessed and they were found to be statistically adequate from analysis of variance. For %E model (Eq. 3), coefficient of determination ($R^2$) and adjusted $R^2$ ($R^2_{adj}$) of 0.9604 and 0.9100 were obtained, whereas for %S model (Eq. 4), $R^2$ and $R^2_{adj}$ of 0.9332 and 0.8482 were attained. The lack-of-fit of these models were also assessed and it was found to be insignificant.

### *C. Determination of Optimum Operating Condition*

The response surface plots of %E revealed that %E were influenced greatly by feed phase flowrate, membrane phase flowrate and extraction time, while those of %S showed that %S were affected by membrane phase flowrate, stripping and extraction times. The optimum conditions of the involved parameters which yielded the maximum values of two of the responses with desirability close to 1 is shown in the Table 3. The predicted responses of %E of 90.2% and %S of 52.6% are also presented. The former was found to differ by 3.61% from the actual response of %E (86.6%) while the latter varied by 0.11% from the actual response of %S (52.5%). Hence, it can be concluded that the reduced regression models of %E and %S were sufficient to estimate the responses in the working range studied.

TABLE 3

OPTIMUM OPERATING CONDITION OF LIQUID MEMBRANE

| Feed flowrate (L/h) | Membrane flowrate (L/h) | Extraction time (h) | Stripping time (h) | Predicted %E | Predicted %S | Desirability |
|---|---|---|---|---|---|---|
| 2.51 | 2.69 | 5.15 | 23.36 | 90.2 | 52.6 | 1 |

## IV. CONCLUSION

This work was conducted to optimize the operating parameters of a liquid membrane system by using a central composite design in response surface methodology. Four operating parameters, namely, feed phase flowrate, membrane phase flowrate, extraction time and stripping time were optimized for the maximum extraction and stripping of Cu(II) ions. Regression models of percent extraction (%E) and percent stripping (%S) were developed and they were found to be statistically adequate within the working range studied. The optimum operating conditions at maximum %E (90.2%) and %S (52.6%) were determined as 2.52 L/h, membrane phase flowrate as 2.69 L/h, extraction time as 5.15 h and stripping time as 23.36 h.

ACKNOWLEDGMENT

The author would like to acknowledge the research grant provided by the Ministry of Higher Education of Malaysia under the Research Acculturation Grant Scheme (Project reference number: RAGS/2013/UITM/TK05/11; Project code: 600-RMI/RAGS 5/3 (80/2013)).

## REFERENCES

[1] S.H. Chang, T.T. Teng and I. Norli, "Cu(II) transport through soybean oil-based bulk liquid membrane: Kinetic study," Chemical Engineering Journal, vol. 173, no. 2, pp. 352–360, Sep. 2011.

[2] S.H. Chang, T.T. Teng and N. Ismail, "Extraction of Cu(II) from aqueous solutions by vegetable oil-based organic solvents," *Journal of Hazardous Materials*, vol. 181, no. 1-3, pp. 868–72, Sep. 2010.

[3] F. Bulcke, P. Santofimia-Castaño, A. Gonzalez-Mateos and R. Dringen, "Modulation of copper accumulation and copper-induced toxicity by antioxidants and copper chelators in cultured primary brain astrocytes," *Journal of Trace Elements in Medicine and Biology*, vol. 32, pp. 168–176, Oct 2015.

[4] S.H. Chang, T.T. Teng, N. Ismail and A. F. M. Alkarkhi, "Selection of design parameters and optimization of operating parameters of soybean oil-based bulk liquid membrane from Cu(II) removal and recovery from aqueous solutions," *Journal of Hazardous Materials*, vol. 190, no. 1-3, pp. 197-204, Jun 2011.

[5] Y.V. Nancharaiah, S. Venkata Mohan and P.N.L. Lens, "Metals removal and recovery in bioelectrochemical systems: A review," *Bioresource Technology*, vol. 195, pp. 102–114, Nov. 2015.

[6] M. Bilal, J.A. Shah, T. Ashfaq, S.M.H. Gardazi, A.A. Tahir, A. Pervez, et al., Waste biomass adsorbents for copper removal from industrial wastewater – a review, *Journal of Hazardous Materials*, vol. 263, part 2, 322–333, Dec. 2013.

[7] S.H. Chang, Types of bulk liquid membrane and its membrane resistance in heavy metal removal and recovery from wastewater, Desalination and Water Treatment, to be published, 2015.

[8] S.H. Chang, Vegetable oil as organic solvent for wastewater treatment in liquid membrane processes, *Desalination and Water Treatment*, vol. 52, no. 1-3, 88–101, 2014.

[9] S.H. Chang, T.T. Teng and N. Ismail, Optimization of Cu(II) extraction from aqueous solutions by soybean-oil-based organic solvent using response surface methodology, *Water, Air, & Soil Pollution*, vol. 217, pp. 567–576, May 2010.