

# Kinetics of Cu (II) Transport through Bulk Liquid Membrane with Different Membrane Materials

Siu Hua Chang, Ayub Md Som, Jagannathan Krishnan

**Abstract**—The kinetics of Cu(II) transport through a bulk liquid membrane with different membrane materials was investigated in this work. Three types of membrane materials were used: fresh cooking oil, waste cooking oil and kerosene, each of which was mixed with di-2-ethylhexylphosphoric acid (carrier) and tributylphosphate (modifier). Kinetic models derived from the kinetic laws of two consecutive irreversible first-order reactions were used to study the facilitated transport of Cu(II) across the source, membrane and receiving phases of bulk liquid membrane. It was found that the transport kinetics of Cu(II) across the source phase was not affected by different types of membrane materials but decreased considerably when the membrane materials changed from kerosene, waste cooking oil to fresh cooking oil. The rate constants of Cu(II) removal and recovery processes through the bulk liquid membrane were also determined.

**Keywords**—Transport kinetics, Cu(II), bulk liquid membrane, waste cooking oil.

## I. INTRODUCTION

**L**IQUID membrane is a prospective separation technique due to its salient features such as simultaneous removal and recovery of solutes in a single unit, non-equilibrium solute transport, high selectivity, high recovery and low energy consumption [1]. There are many types of liquid membrane, among which, bulk liquid membrane (BLM) is the simplest type, easy to manipulate, while offering good membrane stability [2]. It has been used in various applications such as precious metal recovery [3], toxic metal [4], non-metal [5] and organic pollutant [6] removal from wastewater, and so forth.

Typical materials used to formulate the membrane phase of BLM are the petroleum-based organic solvents such as kerosene, hexane, heptane, toluene, and chloroform [2]. In spite of their efficiencies in many separation processes, these solvents are invariably poisonous and their disadvantages to human health and environment often far outweigh their advantages to the society. Therefore, green solvents like ionic liquid and vegetable oil have drawn significant interest of numerous researchers in recent years as the potential materials to replace the classical toxic solvents in formulating the membrane phase of BLM. For instance, Chakraborty and Bart [7] studied the transport of toluene across an ionic liquid-

based BLM, while Chang et al. [8] investigated the removal and recovery of heavy metals from wastewater through a vegetable oil-based BLM. Ionic liquid is generally considered 'green' because of its negligible vapor pressure and high boiling point [9]. Nevertheless, it has been reported by several researchers that ionic liquid tends to pose different degrees of toxicity to living organism [10] and its price is relatively more expensive than the conventional petroleum-based organic solvents [11].

As yet, all vegetable oils that have been used to formulate the membrane phase of liquid membrane are of pure and fresh (unused) ones, and the impure and waste (used) ones have not been reported yet. Therefore, in this work, different membrane materials like fresh cooking oil, waste cooking oil and kerosene were used to prepare the membrane phase of a BLM. The transport kinetics of Cu(II) through the BLM with different membrane materials were outlined and discussed.

## II. KINETIC MODELS

The kinetic models for the facilitated transport of solutes through BLM are derived from the kinetic laws of two consecutive irreversible first-order reactions. They are expressed as:

$$R_s = \exp(-k_1 t) \quad (1)$$

$$R_m = \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \quad (2)$$

$$R_r = 1 - \frac{1}{k_2 - k_1} [k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \quad (3)$$

where  $R_s$ ,  $R_m$  and  $R_r$  are the reduced solute concentrations in the source, membrane and receiving phases, respectively,  $k_1$  and  $k_2$  are the apparent first-order rate constants of the removal and recovery processes, and  $t$  is the time elapsed. The derivation and detailed explanation of these models can be found in Chang et al. [8].

## III. MATERIALS AND METHODS

### A. Materials

The fresh cooking oil was bought from a local department store, while the waste cooking oil was collected from a local restaurant. The former was used without further purification, whereas the latter was pretreated to remove solid particles and excessive water. Copper sulfate pentahydrate (R&M Chemicals,  $\geq 99.6\%$  purity), kerosene (Sigma-Aldrich,  $\geq 99\%$  purity), di-2-ethylhexylphosphoric acid (D2EHPA) (Acros Organics,  $\geq 99\%$  purity), tributylphosphate (TBP), acetic acid,

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sodium acetate, sodium hydroxide, sodium sulfate and sulfuric acid (Merck,  $\geq 99\%$  purity) were used as received.

### B. Experimental Setup

The experimental setup of BLM used in this work was as described in Chang et al. [8]. It consists of a rectangular glass vessel (160mm length x 90mm width x 100mm height) divided into two compartments by a 40 mm-height glass plate of thickness 2mm. The smaller compartment is filled with an aqueous source phase (500mg/L Cu(II) in acetate buffer solution of pH 4.46) while the bigger one with an aqueous receiving phase (1.5 M sulfuric acid solution), both of which are layered with an organic membrane phase (88 mM D2EHPA (carrier) and 60 mM TBP (modifier) dissolved in either fresh cooking oil, waste cooking oil or kerosene). Each of these phases is stirred at 150 rpm and the BLM vessel is placed in a water bath of which its temperature is maintained constant at 40°C.

### C. Experimental Procedures and Regression Analysis

During the course of experiment, some samples of source and receiving phases of BLM were collected periodically for Cu(II) concentration determination by using a flame atomic absorption spectrophotometer (Perkin Elmer, AA-400) after appropriate filtration and dilution. The corresponding concentrations of Cu(II) in the M phase were calculated from material balance by assuming that there was no loss of Cu(II) to the surroundings and both the initial Cu(II) concentrations in membrane and receiving phases were zero. All experiments were carried out in duplicate or triplicate and the relative standard deviation between replicate samples within an experiment range was less than 2%. The rate constants of Cu(II) removal ( $k_1$ ) and recovery ( $k_2$ ) processes in BLM were determined by performing a non-linear regression analysis on (1)–(3) using the SOLVER function of Microsoft Excel program (Microsoft Office 2013).

## IV. RESULTS AND DISCUSSION

### A. Effect of Membrane Materials on Transport Kinetics of Cu(II) across Source Phase

Fig. 1 shows the time evolution of reduced Cu(II) concentration across the source phase ( $R_s$ ) of BLM when different membrane materials were used. Both the experiment data and their corresponding fits are shown. All fits were found to have high coefficient of determination ( $R^2$ ), i.e.  $>0.98$ , with a small deviation of  $<0.3\%$  from their respective values of adjusted  $R^2$ . The latter, coupled with the small standard error of residuals (SER) ( $\leq 0.03$ ) obtained, indicate the adequacy of the kinetic models (Eq. 1-3) in fitting the experiment data. Meanwhile, the small values of 95% confidence interval (CI), i.e.  $\leq \pm 0.1$ , obtained for all the fits signify the reliability of the fitted parameters. As shown in Fig. 1,  $R_s$  decreases exponentially with time for all types of membrane materials studied and they do not change appreciably among different types of membrane materials used. This suggests an insignificant effect of membrane materials on the transport kinetics of Cu(II) across the source

phase of BLM, with a  $k_1$  value of approximately  $2.5 \text{ h}^{-1}$  obtained from (1) for all types of membrane materials. This is reasonable since Cu(II) was transported across the same source phase of BLM regardless of the type of membrane materials used.

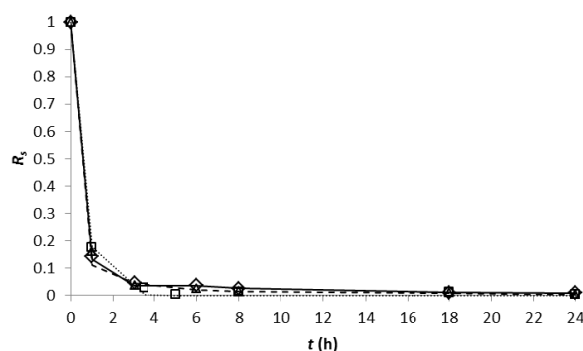


Fig. 1 Time evolution of  $R_s$  for Cu(II) through fresh cooking oil- (experiment data:  $\diamond$ , fit: —), waste cooking oil- (experiment data:  $\Delta$ , fit: ---) and kerosene-based (experiment data:  $\square$ , fit: ----) BLM

### B. Effect of Membrane Materials on Transport Kinetics of Cu(II) across Membrane Phase

Fig. 2 shows the time evolution of reduced Cu(II) concentration across the membrane phase ( $R_m$ ) of BLM when different membrane materials were used. All experiment data were fitted adequately ( $R^2 \geq 0.97$ , adjusted  $R^2 \geq 0.97$  and  $SER \leq 0.05$ ) and the reliability of the fitted parameters was verified (95% CI  $\leq \pm 0.1$ ). As shown in Fig. 2,  $R_m$  is a bell-shaped curve with its peak tilts to one side for all types of membrane materials studied. Unlike the  $R_s$  curves in Fig. 1,  $R_m$  curves vary considerably among different types of membrane materials used. They grow from narrow and low to broad and high peaks when the membrane materials were changed from kerosene, waste cooking oil to fresh cooking oil. This implies that Cu(II) tends to accumulate more in the membrane phase of BLM when fresh and waste cooking oils were used as the membrane materials. This could be attributed to the much higher viscosity of cooking oil ( $>40 \text{ cP @ } 25^\circ\text{C}$  [8]) than that of kerosene ( $1.64 \text{ cP @ } 25^\circ\text{C}$  [8]) which inhibited the diffusion of Cu(II) across the membrane phase. Between the fresh and waste cooking oils, the latter tends to show a narrower and lower peak, and that means less Cu(II) was accumulated in the membrane phase. This could be deduced from the improved fluidity of the waste cooking oil due to change in its composition (higher free fatty acids, glycerol and water contents) as a result of oxidation, hydrolytic and cracking reactions that take place during frying [12]. The  $k_2$  values obtained from (2) were  $0.35 \text{ h}^{-1}$  for kerosene,  $0.30 \text{ h}^{-1}$  for waste cooking oil and  $0.25 \text{ h}^{-1}$  for fresh cooking oil.

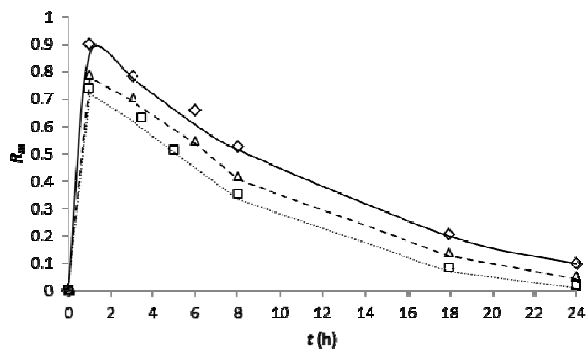


Fig. 2 Time evolution of  $R_m$  for Cu(II) through fresh cooking oil- (experiment data:  $\diamond$ , fit: —), waste cooking oil- (experiment data:  $\Delta$ , fit: ---) and kerosene-based (experiment data:  $\square$ , fit:  $\bullet\bullet\bullet$ ) BLM

### C. Effect of Membrane Materials on Transport Kinetics of Cu(II) across Receiving Phase

Fig. 3 shows the time evolution of reduced Cu(II) concentration across the receiving phase ( $R_r$ ) of BLM when different membrane materials were used. All experiment data were fitted adequately ( $R^2 \geq 0.98$ , adjusted  $R^2 \geq 0.98$  and  $SER \leq 0.05$ ) and the reliability of the fitted parameters was verified ( $95\% \text{ CI} \leq \pm 0.1$ ). As shown in Fig. 3,  $R_r$  exhibits a sigmoid increment curve for all types of membrane materials used. They evolve from sharp to relatively flat curves when the membrane materials were changed from kerosene, waste cooking oil to fresh cooking oil. This denotes that the amount of Cu(II) accumulated in the receiving phase increased from kerosene, waste cooking oil to fresh cooking oil. Although the same receiving phase of BLM was used for all types of membrane materials studied, the variation in the transport kinetics of Cu(II) across the preceding membrane phase had led to the different rates of Cu(II) transport across the receiving phase. The  $k_2$  values obtained from (3) were  $0.31 \text{ h}^{-1}$  for kerosene,  $0.27 \text{ h}^{-1}$  for waste cooking oil and  $0.21 \text{ h}^{-1}$  for fresh cooking oil. By taking the average of the  $k_2$  values obtained from both (2) and (3), the overall  $k_2$  values were  $0.33 \text{ h}^{-1}$  for kerosene,  $0.29 \text{ h}^{-1}$  for waste cooking oil and  $0.23 \text{ h}^{-1}$  for fresh cooking oil. These findings are compatible with those of Chang et al. [8].

### V. CONCLUSION

Effect of membrane materials on the transport kinetics of Cu(II) across a bulk liquid membrane was investigated. The different membrane materials studied were fresh cooking oil, waste cooking oil and kerosene. It was found that different membrane materials did not affect the transport kinetics of Cu(II) across the source phase of BLM. However, the transport kinetics of Cu(II) across both the membrane and receiving phases of BLM were influenced significantly by the types of membrane materials used where it decreased from kerosene, waste cooking oil to fresh cooking oil. Between fresh and waste cooking oils, the latter showed a higher rate of Cu(II) transport across both the membrane and receiving

phases of BLM. This may be attributed to the improved fluidity of waste cooking oil due to the change in its composition (higher free fatty acids, glycerol and water contents) as a result of oxidation, hydrolytic and cracking reactions that take place during frying. A  $k_1$  value of about  $2.5 \text{ h}^{-1}$  was obtained for all types of membrane materials studied, whereas the overall  $k_2$  values obtained were  $0.33 \text{ h}^{-1}$  for kerosene,  $0.29 \text{ h}^{-1}$  for waste cooking oil and  $0.23 \text{ h}^{-1}$  for fresh cooking oil.

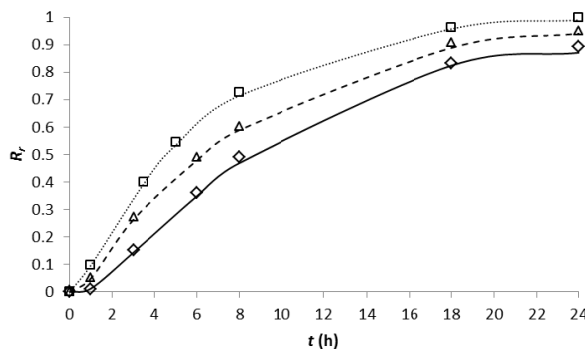


Fig. 3 Time evolution of  $R_r$  for Cu(II) through fresh cooking oil- (experiment data:  $\diamond$ , fit: —), waste cooking oil- (experiment data:  $\Delta$ , fit: ---) and kerosene-based (experiment data:  $\square$ , fit:  $\bullet\bullet\bullet$ ) BLM

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