

Simultaneous Extraction and Stripping of Cu(II) from Aqueous Solutions through Soybean Oil-Based Bulk Liquid Membrane

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Abstract. This work aimed to investigate the simultaneous extraction and stripping of Cu(II) from aqueous solutions through a soybean oil-based bulk liquid membrane (SOBLM). The membrane phase used was soybean oil (diluent) loaded with di-2-ethylhexylphosphoric acid (carrier) and tributylphosphate (phase modifier), whereas the stripping phase was sulphuric acid (H₂SO₄) at various concentrations. Effects of stirring, strip to feed interface area (S:F) ratio, H₂SO₄ concentration and operating time on Cu(II) extraction and stripping through SOBLM were investigated. It was found that stirring affected the extraction process significantly but showed relatively smaller effect on the stripping process. The other parameters such as S:F ratio, H₂SO₄ concentration and operating time, however, were found to control the stripping process more than the extraction process. The highest extraction (98%) and stripping (86%) were achieved by using SOBLM with four stirrings for all phases, S:F ratio of 2.5:1 and 3 M H₂SO₄ as the stripping phase within 24 h of operating time.

Keywords: extraction, stripping, Cu(II), bulk liquid membrane, soybean oil, di-2-ethylhexylphosphoric acid

1. Introduction

Cupric ion (Cu(II)) is the most commonly found copper species in the environment and the most toxic form to living organisms [1]. Various techniques that can be applied to remove and recover Cu(II) from aqueous solutions include chemical precipitation, reverse osmosis, ion exchange, solvent extraction, membrane filtration and adsorption [2]. However, these techniques have their own inherent limitations such as less efficiency, sensitive operating conditions, production of secondary sludge, high capital and operating costs, and further the disposal is a costly affair [3]. Hence, more efficient and cost-effective removal and recovery methods are sought-after to overcome these difficulties.

Recently, liquid membrane has been given a considerable attention by a host of researchers in the removal and recovery of heavy metals from aqueous solutions. Some of the pronounced advantages of liquid membrane over the traditional separation and solid membrane techniques include the low capital and operating costs, low energy consumption, high concentration factors and high fluxes [4]. However, the conventional organic solvents used in liquid membrane systems are those of petroleum derivatives such as kerosene [4-5], benzene [6], dinitrile [7] and chlorinated organic solvents [8]. These solvents are usually toxic, flammable, volatile, non-biodegradable, non-renewable and expensive. Losses of these solvents into the waterways due to the poor membrane stability [2] would lead to a severe environmental problem to all living things. To overcome this problem, application of greener solvents such as vegetable oil-based organic solvents [9-10] to replace the conventional toxic organic solvents in liquid membrane is indispensable.

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Bulk liquid membrane (BLM) is among the simplest system to perform liquid membrane processes. In this work, simultaneous extraction (removal) and stripping (recovery) of Cu(II) from aqueous solutions was conducted through a soybean oil-based bulk liquid membrane (SOBLM). The membrane phase used was composed of soybean oil (diluent), di-2-ethylhexylphosphoric acid (D2EHPA) (carrier) and tributylphosphate (TBP) (phase modifier), whereas the stripping phase was sulphuric acid (H₂SO₄) at various concentrations. Effects of stirring, strip to feed interface area (S:F) ratio, H₂SO₄ concentration and operating time on Cu(II) extraction and stripping from aqueous solutions through SOBLM were investigated.

2. Materials and Methods

2.1. Materials

Soybean oil (Soon Soon Oil Mill Sdn. Bhd., Malaysia), copper sulphate pentahydrate (CuSO₄·5H₂O), D2EHPA, TBP, H₂SO₄, acetic acid (CH₃COOH), sodium acetate (CH₃COONa), sodium hydroxide (NaOH) and sodium sulphate (Na₂SO₄) (Merck, ≥ 99% purity) were used as received.

2.2. Methods

Fig. 1 shows the experimental rigs (Rigs 1, 2 and 3) of SOBLM used in this work. They are cubical glass containers divided into two compartments by a 40 mm-height flat vertical wall. One compartment is filled with an aqueous feed (F) phase while another one with an aqueous strip (S) phase. These aqueous phases are layered with a membrane (M) phase. The flat vertical wall is placed at specific positions so that it gives S:F ratios of 1:1, 2.5:1 and 1:2.5 to Rigs 1, 2 and 3, respectively. The F phase contained 500 mg/L of initial concentration of Cu(II) which was prepared by dissolving an appropriate amount of CuSO₄·5H₂O in 0.1 M acetate buffer solution with pH 4.46 and loaded with 250 mM Na₂SO₄, whereas the S phase was H₂SO₄ at various concentrations (1.5-6.0 M). The M phase, on the other hand, was prepared by mixing soybean oil with 85 mM D2EHPA and 60 mM TBP. Initially, effect of stirring on Cu(II) extraction and stripping was investigated using Rig 1 by stirring some or all its phases at 100 rpm (Fig. 2). A blank test where no stirring was applied to any phases was also conducted. The best stirring condition was then used to investigate the effect of S:F ratio on Cu(II) extraction and stripping using Rigs 2 and 3 (Fig. 1). All experiments to investigate the effects of stirring and S:F ratio employed 1.5 M H₂SO₄ as the S phase and were conducted for 5 hours throughout. Lastly, effects of H₂SO₄ concentration (1.5, 3, 4, 6 M) and operating time (1, 3, 7, 9, 11 and 24 h) on Cu(II) extraction and stripping were investigated by using the selected rig.

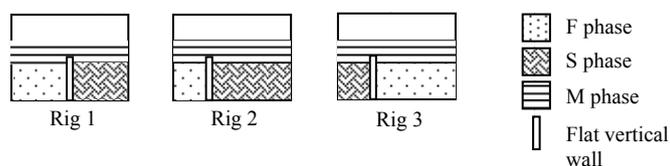


Fig. 1: Experimental rigs of SOBLM used in this work

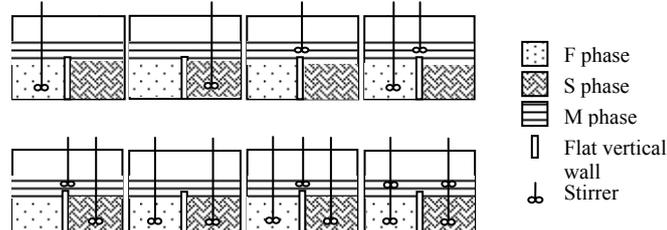


Fig. 2: Different stirring conditions studied with Rig 1

During the course of experiments, samples (0.5 mL) of F and S phases were analyzed for Cu(II) concentration by a flame atomic absorption spectrophotometer (Perkin Elmer, AA-400) after appropriate filtration and dilution. The percentage extraction (%E) of Cu(II) was then calculated according to:

$$\%E = \frac{[Cu]_{o,F} - [Cu]_{f,F}}{[Cu]_{o,F}} \times 100\% \quad (1)$$

where [Cu]_{o,F} and [Cu]_{f,F} are the initial and final Cu(II) concentrations in the F phase, respectively. The percentage of stripping (%S) of Cu(II) was given by:

$$\%S = \frac{[Cu]_{f,S}}{[Cu]_{0,F} - [Cu]_{f,F}} \times 100\% \quad (2)$$

where $[Cu]_{f,S}$ is the final Cu(II) concentration in the S phase. The initial concentration of Cu(II) in both the M and S phase was assumed zero. All experiments were carried out in duplicate or triplicate at room temperature (25°C) and the relative standard deviation between replicate samples within an experiment range was less than 2%.

3. Results and Discussion

3.1. Effect of stirring

Fig. 3 shows the %E and %S obtained at different stirring conditions with Rig 1. For cases with no stirring ({1}) and one stirring for the S phase ({3}), the %E achieved is about 30% only. The low %E leads to no stripping observed in these cases. For the rest of the cases ({2}, {4}, {5}, {6}, {7}, {8} and {9}) studied, %E of more than 80% are recorded. This implies that stirring of either the F, M, or all phases inclined to improve the transport of Cu(II) from the F into M phases by minimizing the boundary layers in the aqueous and organic phases [11]. In spite of the great improvement of %E observed in these cases, the corresponding %S achieved are, however, much lower, which are about 10% only. This indicates that the stripping process was not controlled by the hydrodynamic conditions. Nevertheless, it should be noted that stirring of M phase affects the %S appreciably. If the M phase is stirred ({4}, {5}, {6}, {8} and {9}), a substantial amount of Cu(II) is stripped, with %S of about 10%. When the M phase is not stirred ({1}, {2}, {3} and {7}), however, extremely low or zero %S is observed. These findings could be explained by the viscous soybean oil-based organic solvent which was used as the M phase in this work. Apparently, stirring of M phase increased its fluidity and, thus, enhanced the transport of Cu(II) from the M into S phases. The best stirring condition, i.e. four stirrings for all phases ({9}), which achieved %E of over 90% and %S of over 10% was selected for further studies.

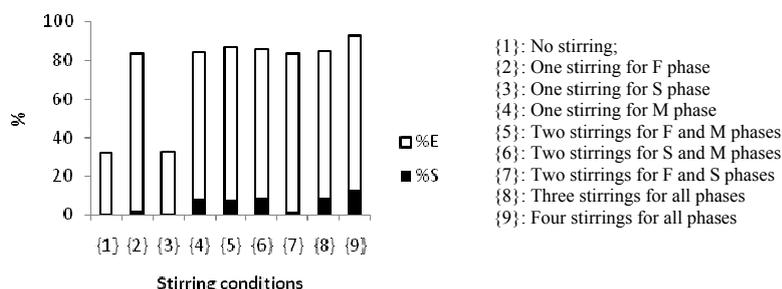


Fig. 3: %E and %S obtained at different stirring conditions using Rig 1

3.2. Effect of S:F ratio

Fig. 4 shows the %E and %S obtained at different S:F ratios with four stirrings for all phases. It is found that %E of more than 90% is achieved by S:F ratios of 1:1 and 2.5:1 while less than 80% is achieved by S:F ratio of 1:2.5. This implies that the bigger S:F ratio (2.5:1) did not affect the %E much compared with 1:1 S:F ratio, but inclined to reduce it when the smaller S:F ratio (1:2.5) was used. The smaller S:F ratio (1:2.5) means a greater volume of F phase and, hence, a lower %E is achieved within the same operating time. On the other hand, the highest %S (~20%) is obtained at S:F ratio of 2.5:1 while the lowest %S (<10%) at S:F ratio of 1:2.5. The higher %S achieved at S:F ratio of 2.5:1 was attributed to the larger M/S interfacial area available for the transport of Cu(II) from the M into S phases. Hence, the S:F ratio of 2.5:1 was selected for further studies.

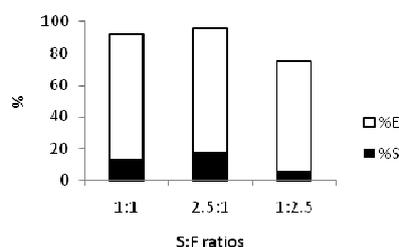


Fig. 4: %E and %S obtained at different S:F ratios

3.3. Effect of H₂SO₄ concentration

The strength of S phase, which varies with its concentration, is one of the important factors that determine the transport efficiency of metal ions through a liquid membrane. If metal complexes in the M phase are not stripped completely, the M phase would become saturated and this decreases the transport rate of metal ions through the liquid membrane [11]. Fig. 5 shows the %E and %S obtained by using different concentrations of H₂SO₄ as the S phase. In general, the %E of about or more than 90% are achieved throughout all the different H₂SO₄ concentrations studied. The %S, on the other hand, presents a maximum where it increases from 1.5 to 3 M and then decreases thereafter. This indicates that the extraction process was not, but the stripping process was, controlled by the concentration of H₂SO₄ in the S phase. The presence of H₂SO₄ aids in the stripping of Cu(II) by a cation exchange process between its protons from the S phase and Cu(II) from the M phase [12]. Hence, the rise of %S from 1.5 to 3 M H₂SO₄ concentrations was deduced from the increase of proton in the S phase for Cu(II) stripping. The reduction of %S beyond 3 M H₂SO₄, on the other hand, could be caused by the saturation of driving force for diffusion through SOBLM due to the increase of proton at the M/S interface [11]. The maximum %S of approximately 30% was achieved at 3 M H₂SO₄ and, thus, was used as the S phase for further studies.

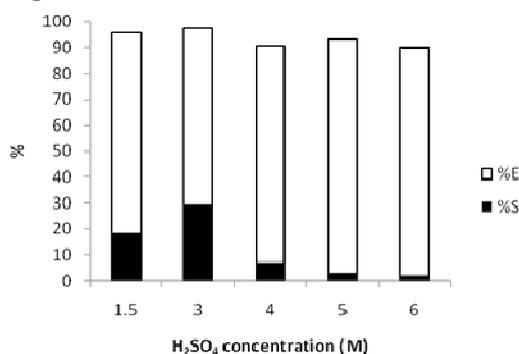


Fig. 5: %E and %S obtained by using different H₂SO₄ concentrations as the S phase

3.4. Effect of operating time

Fig. 6 shows the %E and %S obtained at different operating times. It is found that more than 70% of Cu(II) is extracted in the first hour and this increases to over 90% in 5 h. A slow increment of %E is observed thereafter until it reaches about 98% in 24 hours. Cu(II) stripping, on the other hand, proceeds at a much slower rate than the extraction process. In the first hour, only about 10% of Cu(II) is stripped. This is followed by a steady increment of about 10% of stripping in the subsequent time intervals up to 7 hours. The %S continues to increase from then on until it reaches 86% in 24 h. Since the stripping process happened at a much slower rate than the extraction process, a substantial amount of Cu(II) was accumulated in the M phase. The slow stripping rate could be deduced from the long transportation path [13] and the high viscous M phase used that may encumber the transport of Cu(II) through SOBLM [14]. Given the trend of graph (Fig. 6) obtained, it is predicted that the %S will continue to increase beyond 24 h.

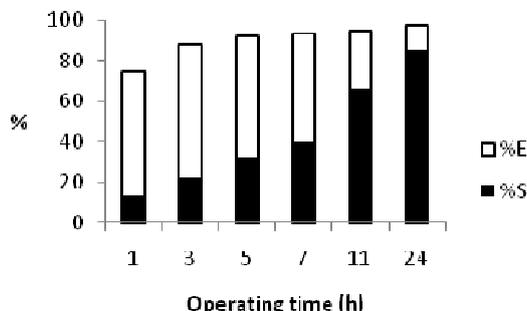


Fig. 6: %E and %S obtained at different operating times

4. Conclusion

Investigation of the effects of various parameters such as stirring, strip to feed interface area ratio, H₂SO₄ concentration and operating time revealed that they were influential to the extraction and stripping processes of Cu(II) through SOBLM. The extraction process was improved by stirring of either the feed, membrane, or

all phases, while the stripping was enhanced by stirring of the membrane phase, applying a high strip to feed interface area ratio (2.5:1), using a moderately high concentration (3 M) of H₂SO₄ as the stripping phase, and by running the process for an extended period of time (24 h). It was found that high extraction (98%) and stripping (86%) of Cu(II) could be achieved by using SOBLM with four stirrings for all phases, S:F ratio of 2.5:1, and 3 M H₂SO₄ as the stripping phase, as well as that operates for 24 h.

5. Acknowledgements

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6. References

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