Kinetic Study of Cd(II) Ions Extraction Using Trioctylamine as Carrier in Bulk Liquid Membrane (BLM)

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ABSTRACT: *Simultaneous extraction and stripping of Cd(II) ions from aqueous solution by using bulk liquid membrane (BLM) was explored. This study was aimed to identify the conditions to achieve maximum Cd(II) ions removal and the reaction kinetics was thoroughly analysed. The membrane phase was made by using trioctylamine (TOA) and kerosene, as carrier and diluent, respectively. Meanwhile, the feed phase contained the targeted solute ($CdCl_2$) dissolved in a pH adjusted solution while ammonia was used as the stripping agent. To achieve maximum Cd(II) ions removal, the effect of carrier concentration, stirring speed as well as extraction time were studied. Experimental data obtained shows that 0.1 wt% TOA in kerosene, 400 rpm stirring speed and 4 h of extraction time resulted in highest removal of Cd(II) ions. Furthermore, it was identified that the extraction process across BLM prefers acidic condition (pH of 1). The capability of the system to extract Cd(II) ions from the feed phase was known by using dimensionless reduced concentration, R_f where the maximum removal of Cd(II) ions achieved was 0.0193 at the mentioned conditions. The reaction kinetics were investigated to identify the reaction rate constants for extraction reaction (k_1) and stripping reaction (k_2). The value of k_1 and k_2 were found to be 0.94 h^{-1} and 2.45 h^{-1}, respectively.*

Keywords: Bulk liquid membrane, BLM, Cd(II) extraction, kinetics, trioctylamine

1.   INTRODUCTION

Cadmium is a soft, bluish white metal that is very malleable with molecular weight of 112.414 g mol^{-1}. It can be easily oxidised in air and in acidic condition, it is soluble and forms ions. Cd(II) ions is the most common pollutant which has well-documented records on its bad effects to aquatic life and human beings, mainly due to its toxicity and carcinogenic properties.[1] Cd(II) is most often used in the manufacturing sectors such as electroplating, hydrometallurgy and dye synthesis. This type of heavy metal tends to accumulate in the environment as it is non-biodegradable.[2] As these sectors expand with time, a more effective and reliable method to reduce Cd(II) ions contamination is needed.

There are many options available in minimising Cd(II) ions concentration from aqueous solution. Reported techniques are filtration, flocculation, biological processes, solvent extraction, ions exchange and precipitation.[3–5] However, these techniques have drawbacks as some of them are energy intensive process besides generating secondary and highly toxic sludge. In addition, they are costly as well as unable to gain high removal of the metal ions. Liquid membrane technology was found to be an alternative method to remove metal ions from aqueous solution at lower cost and it uses minimal amount of solvent. In fact, the process consumes lower energy and can be easily operated.[6]

To date, there are three types of liquid membrane configurations namely emulsion, supported and bulk.[7–9] Each configuration offers significant advantages. For instance, the emulsion type allows high surface area to volume ratio while supported configuration offers better stability of the membrane.[7,10] On the other hand, bulk liquid membrane (BLM) is the simplest configuration among all.[11] All types of liquid membrane share the same solute transportation mode as they require the assistance of carrier to extract the targeted solute from the feed phase.[12] Liquid membrane combines stripping and extraction process in a single operation. In the context of Cd(II) ions removal via liquid membrane, the transport of Cd(II) ions from the feed solution could be assisted by TOA, D2EHPA, CYANEX 272 and LIX 984N as the carrier.[13–16] Figure 1 illustrates the mechanism of Cd(II) ions extraction through BLM containing TOA as carrier and OH^{-} as counter ions.[13] TOA diffuses from the bulk membrane phase to the feed membrane interface where it reacts with Cd(II) ions for protons exchange. This process resulted in the formation of carrier-solute complex. The Cd(II) carrier complex formed diffuses through the membrane to the stripping interface where ions are exchanged for Cd(II) by reacting with the counter ions. The carrier-solute complex will be broken down, leading to the stripping of Cd(II).[17] Following this is the carrier regeneration process that results in a new reaction cycle. The Cd(II) ions transport mechanism

is therefore a coupled counter ion transport, with Cd(II) and OH⁻ ions travelling in the opposite direction.[18] This mode of transportation is called as Type II Facilitated Transport.[17]
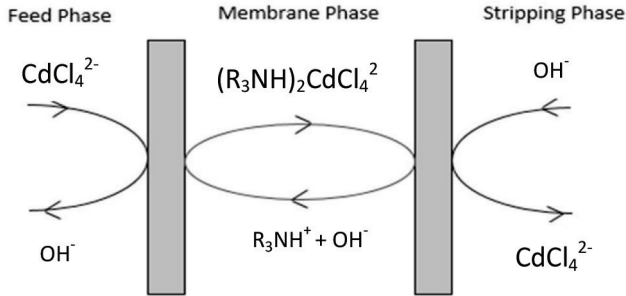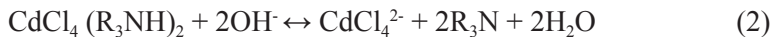

Figure 1: Facilitated counter transport of Cd(II) ions using TOA as carrier.

Known reactions equations that took place on the interfaces are as follows:[13]

$$CdCl_4^{2-} + 2R_3NH^+ \leftrightarrow CdCl_4(R_3NH)_2 \tag{1}$$

$$CdCl_4(R_3NH)_2 + 2OH^- \leftrightarrow CdCl_4^{2-} + 2R_3N + 2H_2O \tag{2}$$

The objective of this study is to obtain maximum Cd(II) ions removal by looking at the following parameters: carrier concentration, stirring speed and extraction time. The work will be followed by the analysis of kinetics data to determine the reaction rates constants for extraction and stripping reaction.

1.1 Theory

From the kinetic data, the reaction rate constant, k (h⁻¹) values will be determined. The kinetic behaviour gives first-order time differentiation that can be described as the equations as following:[17]

$$\frac{dR_f}{dt} = -k_1 R_f \tag{3}$$

$$\frac{dR_m}{dt} = k_1 R_f - k_2 R_m \tag{4}$$

$$\frac{dR_p}{dt} = k_2 R_m \tag{5}$$

Meanwhile, Equations 6, 7 and 8 are the results of integration of Equations 3, 4 and 5, respectively:

$$R_f = e^{-k_1 t} \tag{6}$$

$$R_m = \frac{k_1}{k_2 - k_1}[e^{-k_1 t} - e^{-k_2 t}] \tag{7}$$

$$R_p = 1 - \frac{1}{k_2 - k_1}[k_2 e^{-k_1 t} - k_1 e^{-k_2 t}] \tag{8}$$

The value of k_1 is the reaction rate constant for extraction reaction (on feed-membrane interface) and the value of k_2 is the rate constant for stripping reaction (on membrane-stripping interface). On the other hand, R_f, R_m and R_p represent dimensionless reduced concentrations of Cd(II) in the feed, membrane and stripping phase, respectively. They were calculated by taking the ratio of C_{ft}, C_{mt} and C_{pt} to the initial Cd(II) ions concentration in the feed phase. C_{ft}, C_{mt} and C_{pt} are the concentrations of Cd(II) ions in the feed, membrane and stripping phase at time t.

2.   EXPERIMENTAL

2.1   Chemicals

Table 1 provides the list of chemicals used in this study and their purposes. All solutions were prepared by using distilled water and the pH of the feed phase was adjusted to a desired value before any extraction process took place.

Table 1: Chemicals used and their function in the configuration of BLM.

Chemicals	Role
TOA, supplied by Merck	Carrier
Ammonia solution 28% (NH_4OH)	Stripping agent
Commercial grade kerosene	Diluent
Cadmium chloride ($CdCl_2$), supplied by Sigma Aldrich	Solute in feed phase
Hydrochloric acid 37% (HCl) Sodium hydroxide (NaOH)	Feed phase pH adjustment

2.2   Cd(II) Ions Extraction Using BLM

The feed phase was prepared by dissolving 50 ppm of $CdCl_2$ in a pH adjusted solution. On the other hand, the membrane phase was prepared by dissolving TOA at varying concentrations (0.025 wt% to 0.25 wt%) in kerosene. As for the stripping phase, 50 ml of ammonia solution was used as stripping agent at concentration of 1.0 M. The system was stirred for 4 h at room temperature at varying speed;

100 rpm to 800 rpm. The volume ratio of feed to membrane to stripping phase was kept constant at 2:1:1. The setup is illustrated in Figure 2.
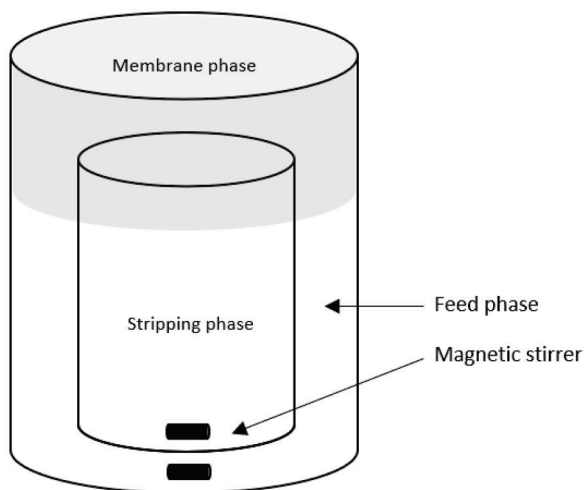

Figure 2. Apparatus setup for BLM.

2.3   Cd(II) Ions Concentration Measurement

Once the extraction process ended, the feed and stripping phase solution was taken out to determine the concentration of Cd(II) ions in each phase. Inductive Coupled Plasma Mass Spectrometry, ICP-MS (PerkinElmer) Optima 800J was used to measure Cd(II) ions concentration in all samples at 228.802 µm wavelength. Meanwhile, the concentration of Cd(II) ions in the membrane phase was calculated by using mass balance. The concentration data obtained was used to calculate the ratio of dimensionless reduced concentration and they were denoted as R_f, R_m and R_p, referring to ratio in feed, membrane and stripping phase, respectively.

2.4   Kinetic Study of Cd(II) Ions Extraction and Stripping

The experiment was carried out at extraction time ranging from 1 h to 12 h. The speed was kept constant at 400 rpm at initial concentration of 50 ppm of $CdCl_2$ in an acidic solution. HCl was used to adjust the pH of the feed to 1 before the extraction process took place. The TOA concentration in membrane phase was kept constant at 0.1 wt% while the remaining is kerosene. The final concentration of Cd(II) ions was analysed and the kinetic data was established.

3. RESULTS AND DISCUSSION

3.1 Effect of External Feed Phase pH

To determine the effect of pH in the feed phase on the dimensionless reduced concentration, R_f, the pH was varied from 1 to 13. The profile of R_f against external phase pH is shown in Figure 3. It can be seen from the figure that the high pH value (>5) causes the R_f to increase significantly. The lowest R_f with a value of 0.0374 was obtained at a low pH value which is 1. This is mainly due to chemical ions speciation, owing to the fact that, the reaction of Cd(II) ions extraction with the carrier requires the ions to exist in the anionic form ($CdCl_4^{2-}$).[19] This ionic species was not formed neither in neutral nor basic medium. This phenomenon limits the capability of the extraction process at higher pH even though the system was loaded with carrier. As the pH increases surpassing the neutral, the absence of any Cd(II) ions species were reported and it is highly likely for Cd(II) precipitate to be formed.
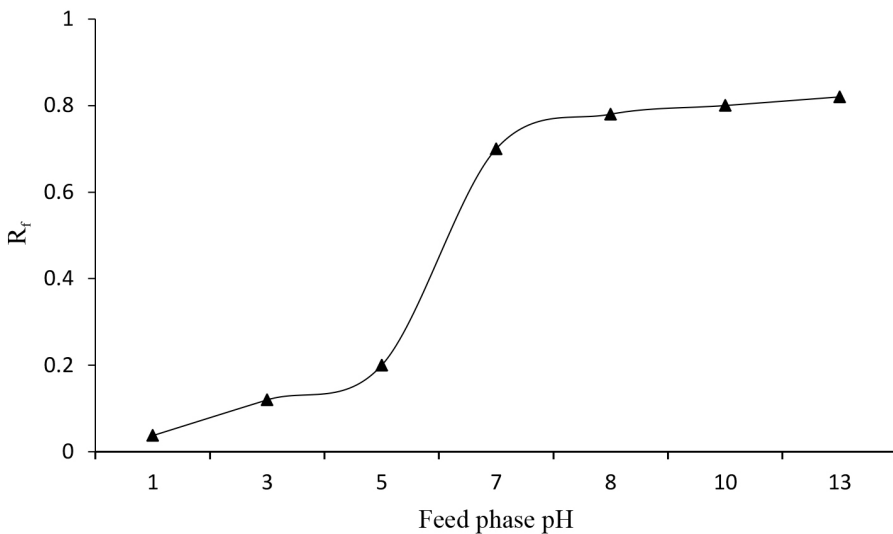

Figure 3: Effect of feed phase pH on R_f. Experimental conditions are 500 rpm stirring speed, 0.1 wt% TOA, and 4 h extraction time.

3.2 Effect of Carrier Concentration

Data provided in Figure 4 illustrates the effect of carrier (TOA) concentration on the extraction capability of the system. The data reveals that the transport of Cd(II) ions across the membrane phase were affected by the concentration of TOA.

From the data provided, increment of TOA concentration from 0.025 wt% to 0.1 wt% increases the efficiency significantly. This phenomenon is highly possible to be caused by sufficient amount of carrier existed in the system. Figure 4 shows that further increment of carrier concentration in the membrane over 0.1 wt% decreases the Cd(II) removal efficiency.
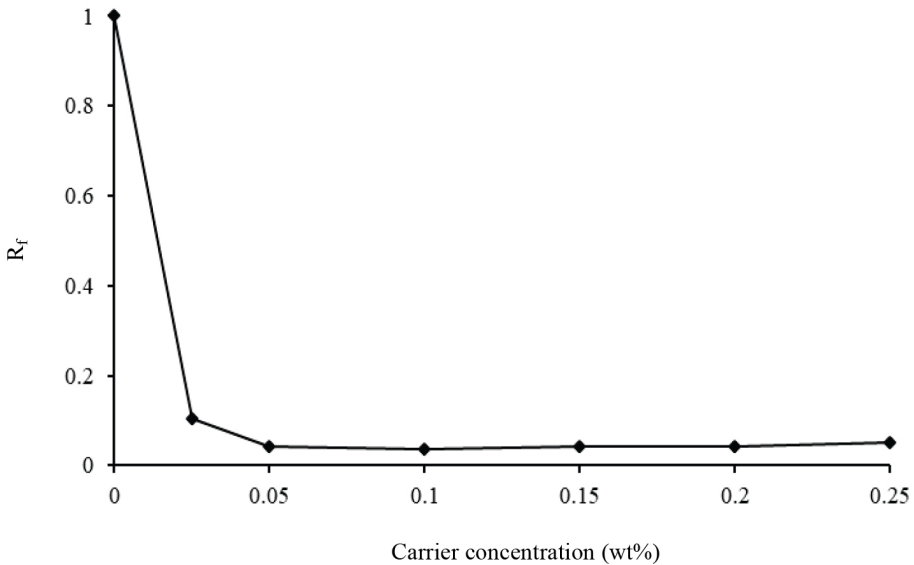

Figure 4:   Effect of carrier concentration on R_f. Experimental conditions are 500 rpm stirring speed, 4 h extraction time, and feed phase pH of 1.

Low viscosity of the membrane phase at higher carrier concentration eased the stirring process.[20] This phenomenon resulted in high surface area for extraction process and shorter time is needed for Cd(II) ions to be transferred into the membrane phase. In fact, shorter path was created for solute diffusion process. Based on Figure 4, any increment of the carrier concentration beyond 0.1 wt% does not benefit the system significantly. This is due to the fact that, the number of moles of TOA present is said to be sufficient to extract Cd(II) ions in the feed phase. TOA concentration of 0.1 wt% was selected in this experiment.

3.3   Effect of Stirring Speed

Data of dimensionless reduced concentrations, R_f as a function of stirring speed is presented in Figure 5. The extraction was conducted by using constant TOA concentration (0.1 wt%) at different speed of stirring; 100 rpm to 800 rpm. As the stirring speed increases, shear provided from the stirrer during stirring reduces

the membrane globules size, hence providing high interfacial area per volume ratio for extraction process. Increment of Cd(II) ions extraction is a result of this condition.[21] It can be explained that faster stirring speed decreased the external mass transfer resistance.[22] This increment enhanced the external mass transfer coefficient thus more cadmium was extracted into the membrane phase. However, further increment of the stirring speed did not increase the extraction capability significantly. This is highly possible due to the equilibrium achieved and the capacity of the membrane to extract Cd(II) ions has become insignificant due to the concentration gradient. A stirring speed of 400 rpm was selected to extract maximum Cd(II) ions removal where the R_f recorded is 0.0193.
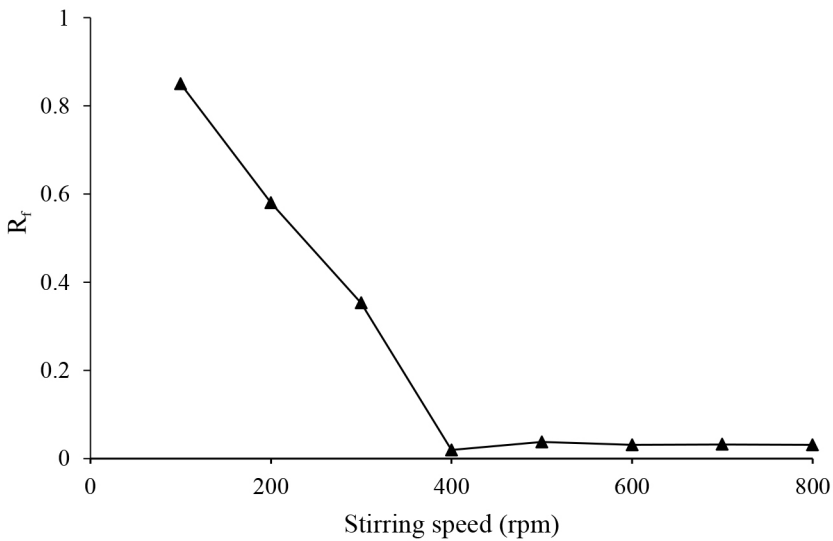

Figure 5:   Effect of stirring speed on R_f. Experimental conditions are 0.1 wt% TOA, 4 h extraction time, and feed phase pH of 1.

3.4   Reaction Kinetics

Figure 6 shows model curves of R_f, R_m and R_p for Cd(II) extraction as the reaction progress. The data plotted was calculated from Equations 6, 7 and 8. R_f was found to decrease monoexponentially, while R_p follows an increasing sigmoidal type curve and R_m presented bell-shaped curve.[18] The concentration of Cd(II) ions in feed phase decreases as function of time while its concentration in the stripping phase showed the opposite trend. The data obtained proves that Cd(II) ions was extracted from feed and was stripped in the stripping phase.
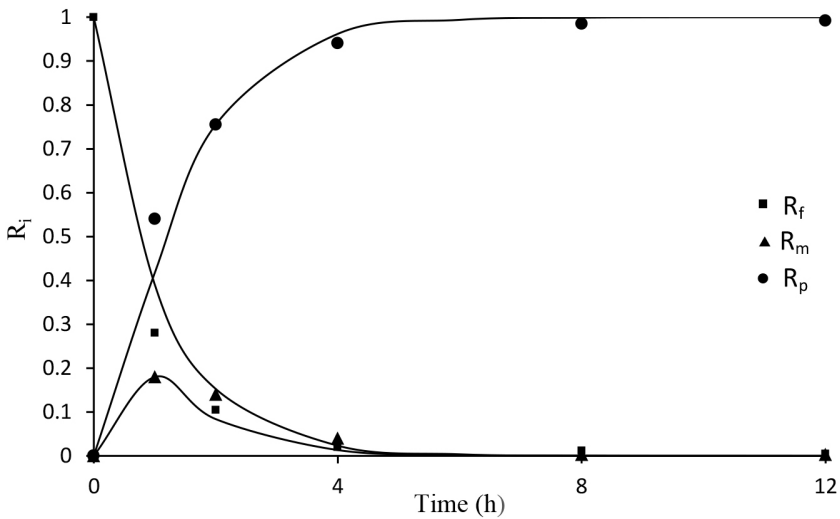
Figure 6:   Effect of time on Cd(II) removal efficiency. Experimental conditions are 0.1 wt% TOA, 4 h extraction time, and feed phase pH of 1.

Table 2:   Reaction rate constants for extraction (k_1) and stripping (k_2) reaction of Cd(II) ions through BLM.

Rate constants	Experimental data (h^{-1})
k_1	0.940
k_{2m}	2.589
k_{2p}	2.410
k_2 (average value)	2.450

The predicted model line was plotted by using k_1 and k_2 (average value) as tabulated in Table 2. The value of k_1 was directly obtained by iteration from Equation 6 until it introduced a constant value. An initial value of k_2 was later identified. k_{2m} and k_{2p} were known via fittings of Equations 7 and 8. The average value of k_2 was calculated by taking the mean of the reaction rate constants for reactions that occurred to extract and strip the Cd(II) ions. From the plot, the experimental data were found to be well fitted with the models shown in Equations 6, 7 and 8, where the R^2 values were found to be 0.986, 0.972 and 0.985 for data of R_f, R_m and R_p, respectively. It is highly possible due to the fact that TOA is a highly efficient carrier and in this study at 0.1 wt%.[24] This mechanism has been used to describe the transport of ions through BLM which Cd(II) ions transport obeys the kinetic laws.[23]

4.   CONCLUSION

An extraction system for Cd(II) ions through BLM system containing TOA as carrier was studied. The study suggested that the extraction of Cd(II) ions across BLM prefers acidic condition at pH of 1. The results also prove that the capability of Cd(II) ions extraction in BLM system is strongly influenced by the carrier concentration, stirring speed and also extraction time. The highest removal efficiency of Cd(II) was obtained by using 0.1 wt% of TOA concentration at stirring speed of 400 rpm. As for the extraction time, a comparative kinetic study of the Cd(II) transport through BLM were analysed by means of a kinetic model and the rate constants of the reactions were determined by numerical analysis of experimental results with k_1 value of 0.94 h^{-1}, and average value of k_2 is 2.450 h^{-1}. The model and experimental data were observed to have good agreement, hence revealing that TOA is capable to extract Cd(II) ions form an aqueous solution.

5.   ACKNOWLEDGEMENTS

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