

# Bulk Liquid Membrane (BLM) for Cd(II) Ions Removal using Trioctylamine (TOA) as Carrier

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## Abstract

The extraction of Cd(II) ions by using bulk liquid membrane (BLM) was investigated in this current study. Similar to liquid-liquid extraction, BLM was used to enhance the process via Type II Facilitated Transport. BLM consists of membrane phase which made up of carrier (Trioctylamine, TOA) dissolved in kerosene, feed phase CdCl<sub>2</sub> dissolve in HCl solution and ammonia solution as the stripping phase. The aim of this study is to identify the condition for the ideal concentration of carrier (Trioctylamine) in the membrane phase as well as the stirring speed and extraction time. Experimental data obtained shows that the optimum conditions are; 0.1 wt% TOA in kerosene, 400 rpm and 4 hours. Extraction of Cd(II) ions across BLM prefers acidic condition at pH of 1. Maximum removal of Cd(II) at 96.26% was achieved at this condition. The study was followed by determination of reaction rates ( $k_1$ ,  $k_2$ ) and flux (J) of Cd(II) extraction across BLM. It was found that  $k_1$ ,  $k_2$  and J were 0.94 h<sup>-1</sup>, 2.45 h<sup>-1</sup> and 0.671 h<sup>-1</sup> respectively.

**Keywords:** Bulk liquid membrane (BLM); Cd(II) extraction; reaction rates constant; flux; Trioctylamine (TOA)

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## 1. Introduction

Cd(II) is a soft, bluish white metal which is very malleable with molecular weight of 112.414 g/mol. It can be easily oxidized in air and in acidic condition, it is soluble. 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 (Ahmad et al., 2015) and carcinogenic property (Chen et al., 2016). 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 due to its non-biodegradable property (Wu et al., 2006). Therefore, before releasing them into the environment, their concentrations should be minimized to achieve the permissible level, thus many techniques were proposed to achieve this objective.

Existing technique for Cd(II) removal from aqueous solutions are filtration, flocculation, biological processes, solvent extraction (Černá, 1995), ions exchange (Ahmed et al., 1998), and precipitation (Mahmood et al., 2011). However, these processes have drawbacks as they are energy intensive process, production of secondary sludge and highly toxic sludge, high cost, as well as incomplete removal of the metal.

Over the recent years, liquid membrane technology has gained attention among the researchers as an alternative to remove metal cations from aqueous solution at low capital costs, by using minimal amount of solvent, lower energy consumption, easy operation and high selectivity (Kislik, 2015). To date, there are three types of liquid membrane configurations named emulsion (ELM) (Ahmad et al., 2011), supported (SLM) (Muthuraman & Teng, 2009) and bulk liquid membrane (BLM) (Chang, 2014). Each of this configuration offers significant advantages for instance, the emulsion allows high surface area to volume ratio (Ahmad et al., 2011) while supported offers better stability of the membrane (Malik et al., 2011), whereas bulk liquid membrane is the simplest configuration among all (Mateescu et al., 2013).

However, these three types of liquid membrane shared the same solute transportation mode. They require the assistance of carrier to extract the targeted solute from the feed phase (Marino & Figoli, 2015). Liquid membrane combines stripping and extraction process in a single operation. In the context of Cd(II) removal via bulk liquid membrane, the transport of Cd(II) ions from chloride solution could be assisted by TOA (Kumbasar, 2009),

D2EHPA (Hajarabeevi et al., 2009), CYANEX 272 (Swain et al., 2007) and LIX 984N (Yang & Fane, 1999) as the carrier. Fig. 1 illustrates the mechanism of Cd(II) ions extraction through bulk liquid membrane containing TOA as carrier and OH<sup>-</sup> as counter ions. TOA diffuses from the bulk membrane phase to the feed membrane interface where it reacts with Cd(II) 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 protons are exchanged for Cd(II) ions by reacting with the stripping agent (ammonia solution). The carrier-solute complex will be broken down thus, leading to the stripping of Cd(II) in that stripping phase (León et al., 2016). Following this process is the carrier regeneration, resulting in a new separation cycle. The Cd(II) transport mechanism is therefore a coupled counter ion transport mechanism, with Cd(II) and OH<sup>-</sup> travelling in the opposite direction (Leon & Guzmán, 2008). This mode of transportation is called Type II Facilitated Transport (León et al., 2016).

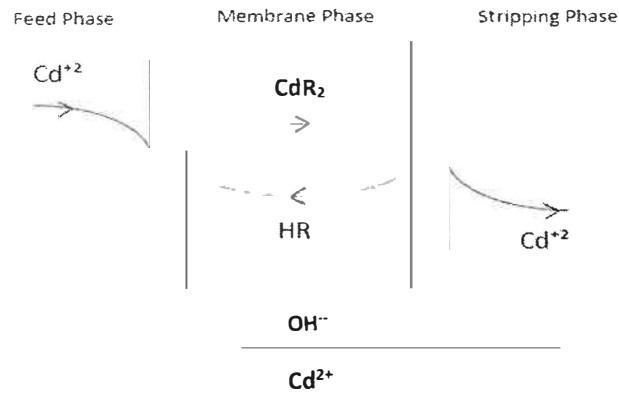


Fig. 1. Facilitated counter transport of Cd(II) ions using Trioctylamine (TOA) as carrier and H<sup>+</sup> as counter ions.

The objective of this study is to find the ideal carrier concentration and stirring speed in membrane phase for selective separation of Cd(II). The study will be followed by the establishment of kinetics study for Cd(II) extraction across BLM, as well as determining the reaction rates  $k$  ( $\text{h}^{-1}$ ) together with flux,  $J$  ( $\text{h}^{-1}$ ). This data for the reactions that took place on the feed-membrane interface and membrane-stripping interface.

### 1.1 Theory

From the kinetic data, the reaction rate constant,  $k$  ( $\text{h}^{-1}$ ) value will be determined thus, the flux,  $J$  ( $\text{h}^{-1}$ ). The kinetic behavior gives first-order time differentiation can be described as the equation below:

$$\frac{dR_f}{dt} = -k_1 R_f = J_{f/m} \quad (1)$$

$$\frac{dR_m}{dt} = k_1 R_f - k_2 R_m \quad (2)$$

$$\frac{dR_p}{dt} = -k_2 R_m = J_{m/p} \quad (3)$$

Integration from those equations give:

$$R_f = \exp(-k_1 t) \quad (4)$$

$$R_m = \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \quad (5)$$

$$R_p = 1 - \frac{1}{k_2 - k_1} [k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \quad (6)$$

The value of  $k_1$  is the rate constant for extraction (feed) and value of  $k_2$  is the rate constant for stripping process. Maximum flux ( $J_{max}$ ) is for the counter transport of Cd(II) using different parameter. On the other hand,  $R_f$  represents dimensionless reduced concentrations of Cd(II) in the feed phase is denoted as  $C_{f}/C_0$  while  $R_m$  represents in the membrane phase give the equation  $R_m = C_{m}/C_0$  and  $R_p = C_{pt}/C_0$  that  $R_p$  as in stripping phase.

These equations showed that the time dependence of  $R_f$  is monoexponential and the time dependence of both  $R_m$  and  $R_p$  is bioexponentiated. The known equation for the formation of Cd(II) carrier complex.



## 2. Methodology

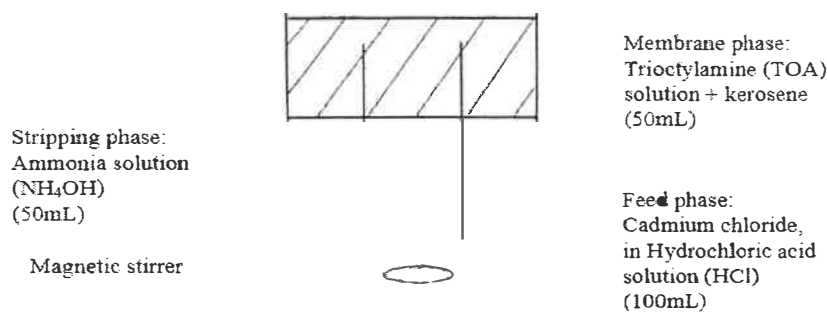


Fig. 2. The apparatus device set up for bulk liquid membrane

### 2.1 Chemicals

In this study, the chemicals used were Trioctylamine, TOA (Merck), cadmium chloride (Sigma Aldrich), hydrochloric acid 37% (QReC), commercial grade kerosene and ammonia solution 28% (QReC). All solutions were prepared using distilled water. Hydrochloric acid, HCl and Sodium Hydroxide, NaOH were used to adjust the pH of the feed phase.

### 2.2 Cd(II) Extraction

The feed phase was prepared using BLM by dissolving 50ppm  $CdCl_2$  in 1M of HCl solution. On the other hand, the membrane phase was prepared by dissolving TOA at varying weight (0.1 to 0.6 wt%) in kerosene. As for the stripping phase, ammonia solution ( $NH_4OH$ ) was used as stripping agent at concentration of 1M and volume of 50mL. All the solutions in the system stirred for 4 hours by magnetic stirrer at room temperature at varying speed 300rpm to 800rpm. The ratio of feed to membrane to stripping phase was kept constant at 2:1:1.

### 2.3 Cd(II) Ions Concentration Measurement

Inductively coupled Plasma Mass Spectrometry, ICP-MS (PerkinElmer) Optima 800J at 228.802 $\mu$ m wavelength was used to measure Cd(II) ions concentration in all samples. The final concentration of each phase was calculated as ratio of dimensionless reduced concentration, to its initial concentration and were denoted as  $R_f$ ,  $R_m$ ,  $R_s$  for feed, membrane and stripping respectively.

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

The kinetic study was conducted by using dimensionless as mentioned in Section 1.1. Cd(II) ions concentration in the membrane phase was established from the material balance.  $R_f$ ,  $R_m$  and  $R_s$  were dimensionless reduced concentration for feed, membrane and stripping phase respectively.

The experiment was carried out at various extraction time, ranging from 1 to 12 hours. The speed was kept constant at 400 rpm at initial concentration of 50 ppm of  $CdCl_2$  in 1M of HCl. The TOA concentration in membrane phase was kept constant at 0.1 wt% and the remaining is kerosene. The final concentrations of Cd(II) was analysed and the kinetic data was established.

## 3.0 Results and discussion

### 3.1 Cd(II) Ions Speciation

To determine the effect of pH in the feed phase on the removal efficiency of Cd(II), the pH was varied from 1 until 13. The profile of  $R_f$  against external phase pH is shown in Fig. 3. It can be seen from the graph that the increase in pH value caused the Cd(II) removal efficiency,  $R_f$  to decrease significantly especially at pH beyond neutral. The highest point of Cd(II) removal efficiency,  $R_f$  with a value of 90% was obtained at a low pH value which is 1. It shows that, at higher pH value, it does not give desirable effect on the removal of Cd(II) ions. Thus, limiting the capability of the extraction system when loaded with carrier. This is mainly due to chemical ions speciation (Crea et al., 2013). As the pH goes beyond neutral, the absence of any Cd(II) ions species were reported, only Cd(II) precipitate were to be found.

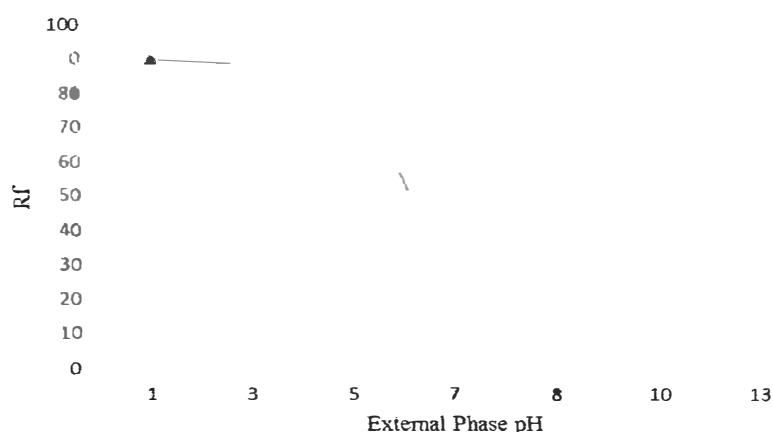


Fig. 3. Cd(II) Removal Efficiency with different pH value

### 3.2 Effect of carrier concentration

As seen in Fig. 4, the transport efficiency of Cd (II) is highly dependent on the concentration of carrier in the organic phase. The results have shown that the selectivity and the transport of metal cations were affected by the concentration of TOA (Krammer et al., 2011). 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. Fig. 4 shows that further increment of carrier concentration in the membrane over 0.1 wt% decreases the Cd (II) removal efficiency. With increasing concentration of carrier in the membrane phase, extraction increases and the maximum percentage of removal efficiency was obtained at carrier concentration of 0.1 wt%.

The removal efficiency was calculated to demonstrate the transfer of Cd (II) cations from the feed phase into the stripping phase. In the systems with 0.1 wt% TOA, highest percentage of 96.26% removal efficiency were obtained. As the concentration of carrier increase further, the viscosity of the membrane phase solution decreases thus, the stirring process will be easier (Burmester et al., 1992). Therefore, this will increase the surface area provided and shorter time taken for Cd(II) ions to be transferred into the membrane globules (Ahmad et al., 2015).

In fact, shorter path were provided for solute diffusion. When the concentration is increased to more than 0.1 wt%, the number of moles of TOA are sufficient to extract all Cd(II) ions in the feed phase. The optimum TOA concentration selected experiment is 0.1 wt%.

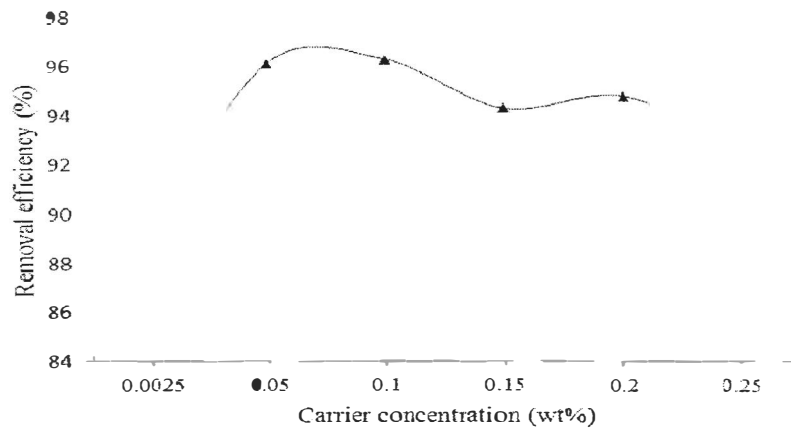


Fig. 4. Effect of carrier concentration on Cd(II) removal efficiency

### 3.3 Effect of Stirring Speed

Fig. 5, presented data of  $R_f$  as a function of stirring speed. The extraction was conducted by using constant TOA concentration (0.1 wt%) at different speed of stirring; 300rpm to 800rpm. As the stirring speed increases, shear provided from the impeller during stirring reduces the membrane globules size, hence providing high interfacial area per volume ratio extraction process, hence increase the amount of Cd(II) ions extracted into the membrane phase (Ahmad et al., 2017). It can be explained that accelerating stirring speed resulted in decrease of external mass transfer resistance (Hausmann et al., 2004). This increment enhanced the external mass transfer coefficient thus more cadmium was extracted into the membrane. However, further increment of the stirring speed does not increase the removal efficiency significantly. This is highly possible due to the equilibrium achieved and the capacity of the membrane to extract Cd(II) ions has become insignificant (Tuzun et al., 2005) due to the concentration gradient. The optimum stirring speed of the process for the Cd(II) ions extracted from the feed phase to membrane phase is 400rpm.

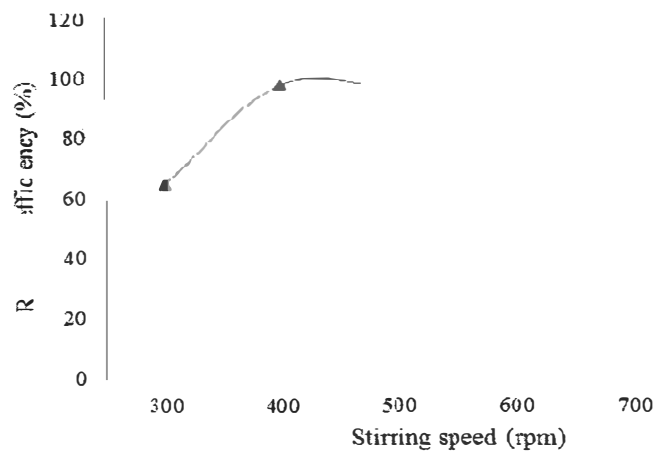


Fig. 5. Effect of stirring speed on Cd(II) removal efficiency