J. Int. Environmental Application and Science, Vol. 15(4): 188-193 (2020)

Research Paper

Transport of Mercury in Bulk Liquid Membrane Using Calixarene Nitrile Derivative

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Received September 12, 2020; Accepted October 28, 2020

Abstract: Mercury is an important industrial metal and its wastes are very toxic to the environment. In the previous study, phthalonitrile substituted calix[4]arene (3) was synthesized and two-phase extraction properties toward the selected metal cations, such as Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+}, are reported. Extraction studies showed that it's selective for Hg^{2+} cation. Therefore, this ligand was used for Hg^{2+} transport in bulk liquid membrane (BLM) at the first time in this study. The experimental data showed that new phthalonitrile substituted calix[4]arene is a nice carrier for Hg^{2+} transport through bulk liquid membrane.

Keywords: *Calixarene, Heavy metal, Mercury, Bulk liquid membrane (BLM)*

Introduction

Mercury is a common environmental pollutant. It is one of the most used metals in the industry. It has a large of applications such as fluorescent lamps, catalysts, batteries (Katzung, 1987; Mendonça Fábrega & BorgesMansur, 2007). Mineral deposits and industrial wastes are the major mercury contamination sources. The removal and control of potentially hazardous heavy metals such as mercury, lead and cadmium from polluted waste and / or waste streams is unavoidable to prevent contamination of aquatic and continental ecosystems (Förstner & Wittmann, 2012).

Mercury can cause serious health problems. Mercury acts mainly on the nervous system (Lidsky and Schneider, 2003; Max Roundhill et al., 2009; Antonio & Leret, 2000). It causes neurological symptoms such as nervousness, memory loss, insomnia and depression (Mishra et al., 1998; Lin, 2008; Samanta & Bandyopadhyay, 2017, Qian, 2007). In recent years, there are various techniques have been developed for mercury removal such as, liquid-liquid extraction, ion exchange, electrolysis and precipitation.

The calix[4]arenes are an important member of supramolecular chemistry. Calixarenes are a class of cyclic phenols, linked by methylene groups. They have cylindrical shapes with various cavity sizes due to the presence of different numbers of phenols, and with heights that vary according to functional groups on the molecule (Neri et al., 2016; Güngör 2020). Calix[4]arene have most appropriate cavity for complex with metal cation (Gutsche, 2008).

The bulk liquid membrane (BLM) is the most important factor in the carrier molecule. Because, selectivity and effectiveness of liquid membrane transport depend on this carrier. Scientists has researched new selective and effective carriers in recently years (Ersoz, 2007). Phthalonitrile substituted calix[4]arene (3) (Şekil 1) have been reported as selective with a higher affinity toward mercury in the previously study. Therefore, it's investigated the transport of mercury in the BLM in this study.

Materials and Methods

Chemicals and procedure

Dichloromethane was used as organic solvent. The carrier (compound **3**) was synthesized according to the literature method (Güngör, 2018). Organic solution was prepared by dissolving compound **3** in dichloromethane. The concentration of compound **3** in the membrane solution was $1x10^{-3}$ M. Stock solutions of $1x10^{-5}$ M metal cations were used. The pH was fixed at 4.00 ± 0.01 during the measure.

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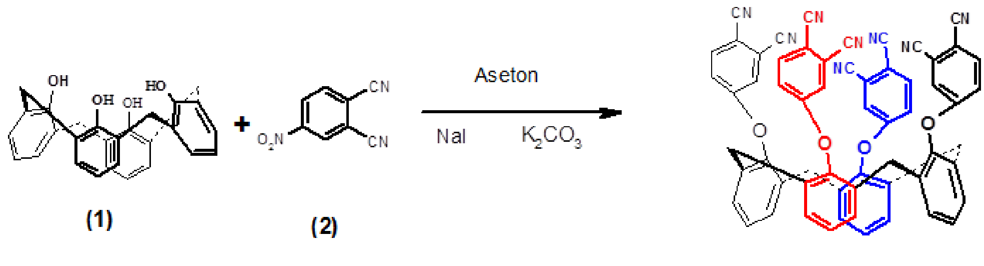


Figure 1. Synthesis of compound 3

Liquid membrane transport of Hg^{2+}

Liquid-liquid extraction studies of compound **3** were performed as previously reported. Figure 2 shows experimental setup (U-Type glass cell). The contact area between the aqua solution (donor and acceptor phase) and organic phase were 1.5 cm^2. The aqueous feed solution (7 cm^3) consisted of $Hg^{2+}2Pic^-$ ($1x10^{-5}$ M) adjusted to pH 4.0. The organic phase was stirred 170 rpm. The temperature of the U-Type glass cell contents was kept constant at 298K± 1.

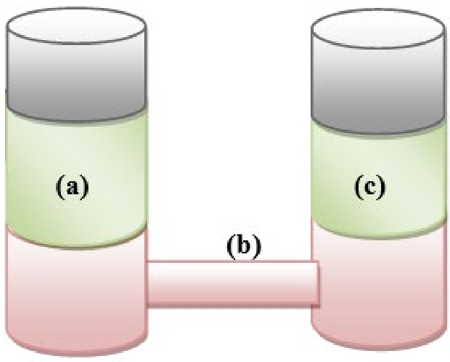


Figure 2. Experimental transport apparatus.

Results and Discussion

Metal cation (Co^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+} and Pb^{2+}) extraction study of Compound 3 was previously reported. Compound 3 was found to be selective against mercury. Therefore, compound **3** was used for Hg^{2+} transport in bulk liquid membrane (BLM) in this study.

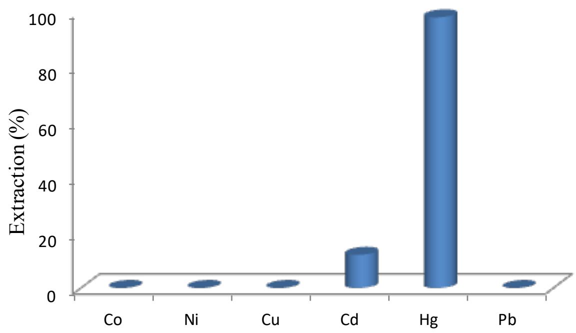


Figure 3. Extraction percentages of selected metal cations by compound **3**.

Regeneration of compound 3 and mercury

The efficiency of compound **3** can be confirmed with its reusability and regeneration. The activity of compound 3 can be confirmed with its reusability and regeneration. Therefore, experiments were carried out at different pH values. As a result, it was observed that approximately 85% mercury recovery could be achieved at pH 7. Mercury could be reused industrially after the evaporation of water. Simultaneously, compound **3** in dichloromethane that is free of mercury could be reused for extraction of mercury from contaminated water that is produced from industries. The regenerated carrier was used repeatedly for the amputation of mercury from aqueous environment and the total overall efficiency of regenerated carrier remained almost same as shown in Figure 4. This result shows the cyclical process of use and reuse of compound **3** as well as used mercury.

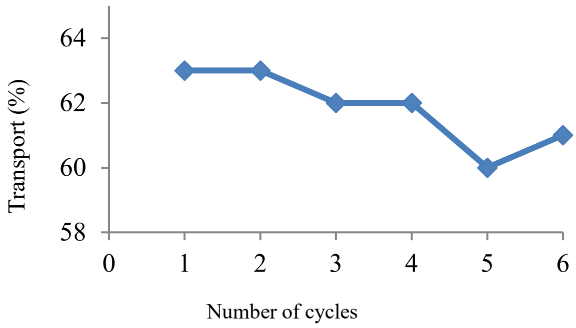


Figure 4. Efficiency of compound **3** after regeneration.

Transport of mercury in BLM

The compound **3** has selective and renewable properties against mercury ions. Therefore, the transport of mercury with compound **3** as a carrier in BLM was investigated. Figure 5 shows the ion transport mechanism. BLM has a significant role in separation science. BLM are used in many industries (*e.g.* wastewater treatment, biotechnology, pharmaceutical and environmental) because of economic advantages and efficiency. Mercury transport in BLM consists of two stages. In the first stage, mercury ion passes into the organic phase by forming a complex with compound **3**. The complex formed progresses in the organic phase and reaches the donor phase. In the second stage, the complex between the compound **3** and the mercury ion breaks down and the mercury ion passes to the donor phase. (Ersoz, 2007).

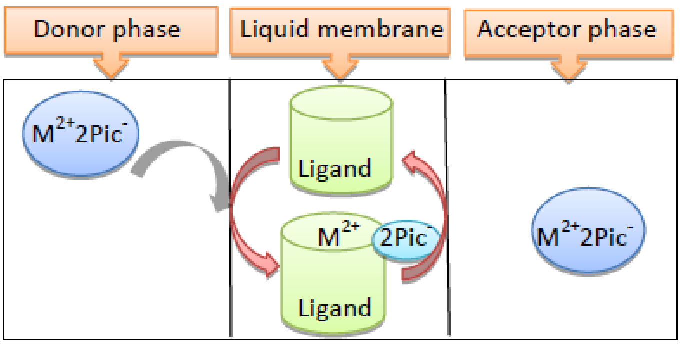


Figure 5. Transport mechanism in bulk liquid membrane

In the studies, the variation of Hg^{2+} concentration with time was directly measured in both acceptors (C_a) and the donor (C_d) divisions. The corresponding change of concentration in the membrane (C_m) can be getting from the material balance by considering reduced dimensionless concentrations.

$$R_d = \frac{C_d}{C_o},\ R_m = \frac{C_m}{C_o}, R_a = \frac{C_a}{C_o} \tag{2}$$

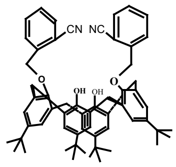
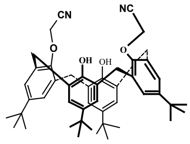
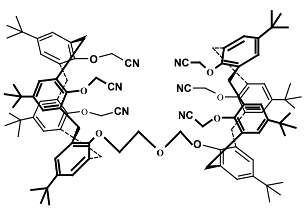
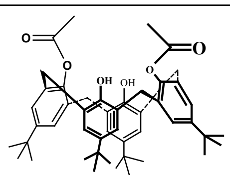
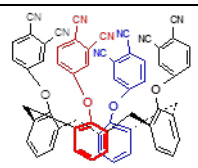
Where, the material equilibrates with respect to reduce dimensionless concentrations can be written as Ra + Rd + Rm = 1.

At zero time and at time intervals, samples (2 mL) were withdrawn from donor phase and acceptor phase. The change in concentration of Hg^{2+} was determined by a UV-Vis spectrometer.

Afterwards, it was added to both sides of the membrane solutions immediately to maintain a constant volume in the solutions.

The transport of mercury is based on mass transfer between donor phase and donor–membrane phase interfaces (Ersoz, 2007). The diffusion of mercury along the diffusion layer in the immediate vicinity of the aqueous-membrane interface is due to complex between Hg^{2+} and functional group of compound **3**. The concentration of Hg^{2+} in donor phase was decreased mono-exponentially with time, while increased exponentially in acceptor phase. Figure 6 show the time dependence of the reduced concentration of Hg^{2+} transported in the donor and the acceptor phase under optimal experimental conditions. The compound **3** showed faster transport percentage than calix[4]arene derivatives which using in previous studies (Gungor *et al*., 2005; Tabakci et al., 2013; Memon & Yilmaz, 2002; Memon et al., 2002; Gubbuk et al., 2010; Memon & Yilmaz, 2000;). In addition to, stirring speed of the membrane was slower than previously studies. Compaison of transport performance of new compound for mercury with previously reported studies is given (Table 1).

Table 1. Comparison of transport performance of compound **3** for mercury with previously reported studies.

Ref	Solvent	Stirring Rate (rpm)	Temperature (K)	Time (min.)	Percentage of mercury carried to the acceptor phase (%)
	$CHCl_3$	200	298	500	60
	$CHCl_3$	500	298	600	65
	$CHCl_3$	500	298	600	60
	$CHCl_3$	500	298	600	63
	CH_2Cl_2	**170**	298	**300**	63

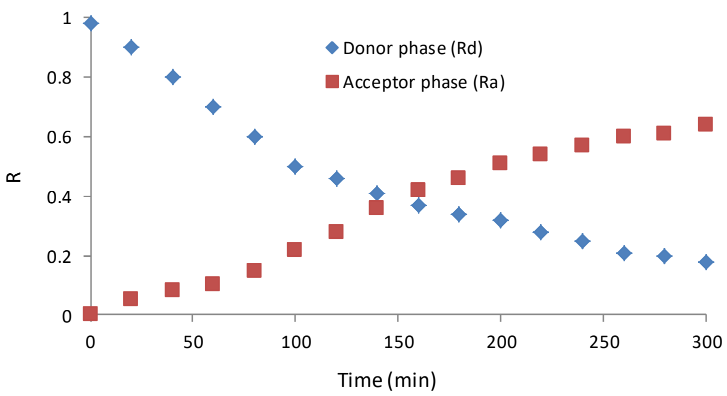


Figure 6. Time evolution of reduce concentration of $Hg^{2+}2Pic^{-}$ transported in donor and acceptor phases in BLM.

Conclusion

This study has been reported that calixarene bearing phthalonitrile groups which are ideal carrier towards Hg^{2+} in liquid-liquid extraction systems. Firstly, liquid–liquid solvent extraction was used to evaluate the extraction capacity of the compound **3** towards selected metal ions. Compound **3** separated mercury in a high selectivity. Furthermore, this compound **3** can complex with Hg^{2+} at pH 4 while decomplex at pH 7. These results show that compound **3** may be useful as potential carrier for BLM. Therefore, the transport of Hg2 + with compound 3 as a carrier in BLM has been investigated. Transport studies showed that compound **3** has a higher transport speed than the calix [4] arene derivatives, which reported in previous studies (Table 1). It is also seen that mercury transport percentage is higher than aliphatic nitrile groups compared to aromatic nitrile groups.

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