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An investigation of Calix[4]arene nitrile for mercury(II) treatment in HFSLM application

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ABSTRACT

The transport of mercury ions (Hg^{2+}) through hollow fiber supported liquid membrane was examined using the extractant Calix[4]arene nitrile. Optimum condition was achieved using 4.5 pH of feed solution, 0.004 M of Calix[4]arene nitrile as extractant, de-ionized water as stripping solution and an operating temperature of 313 K. Percentages of extraction and stripping of mercury(II) ions obtained reached 99.5% and 97.5%, respectively. The stability of the liquid membrane was investigated and showed stable performance over 24 h. After treatment, mercury(II) ions from petroleum produced water in feed solution was found to be below the legislation limit of 5 ppb.

1. Introduction

Mercury (Hg) and its compounds, especially methyl mercury, are toxic components that can harm the environment and bio-living even in small quantities. Mercury can be absorbed through skin, respiratory and gastro-intestinal tissues [1,2] and poses a tendency to concentrate within the living bodies [3].

Membrane technology has attracted the attention of many researchers for metal removal and wastewater treatment [4]. Several studies have shown that hollow fiber supported liquid membrane (HFSLM) is an effective method for separating a very low concentration of metal ions from various aqueous solutions. This method allows for both simultaneous extraction and stripping processes of target ions in one single-step operation, with high selectivity [5,6]. Many advantages of HFSLM over traditional methods include lower energy consumption, lower capital and operating costs and less solvent used [7]. HFSLM has a high surface area per unit volume that contributes to the adequate rates of separation for industrial purposes [8,9]. It has many applications in industries, such as in chemical, food and pharmaceutical processing [8,10–12]. Hollow fiber modules can be connected in parallel or in series for a larger capacity [13]. Therefore, HFSLM can be suitably used as a secondary method in order to effectively manage trace metal ions.

Recent studies have investigated the use of HFSLM for separating various trace metal ions from aqueous solutions [14] or wastewater [15]. Fontàs et al. [16] for example, separated Hg(II) from Cd(II) and Pb(II) in nitrate media at 2 pH. *N*-benzoyl-*N*,*N*-diheptadecylthiourea was used as an extractant and 0.3 M thiourea was used as the stripping solution and resulted in high separation of mercury. Mafu et al. [15] studied the extraction of arsenic(III) from wastewater via HFSLM. The results showed that 50% of arsenic (III) was removed using *n*-undecane and di-*n*-hexyl ether mixtures (3:1%v/v) as the liquid membrane. The stripping solution used was H_2SO_4. Guell et al. [14] separated Cr(VI) at a low concentration from different aqueous matrices via HFSLM using Aliquat 336 as the extractant. 0.5 M HNO_3 was used as the stripping solution. The results demonstrated high efficiency in removing Cr(VI) from different aqueous samples. Previous success in the separation of mercury ions are summarized in Table 1.

In this work, Calix[4]arene nitrile was deployed as mercury(II) ions extractant. Calix[4]arenes is used in various applications such as purification, chromatography, catalysis, enzyme mimics, ion selective electrodes, phase transfer and transport across the liquid membranes. A variety of Calix[*n*]arene derivatives is known for its effective use in the selective removal of metal ions from wastewater [26,27]. Calix[4]arene nitrile has the capacity to capture Hg^{2+} in weak acid condition and thereby can form mercury complex ions. The complex ions are in co-ordination bond

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Nomenclature

r_i Inner radius of the hollow fiber (cm)
r_o Outer radius of the hollow fiber (cm)
t Time (s)
T Temperature (K)
ε Porosity of hollow fiber (%)
τ Tortuosity factor membrane (−)

which is reasonably strong but not too hard for a neutral-based stripping solution to break the bond.

This study was set up to identify key parameters that influence the performance of extraction and recovery of Hg^{2+} from petroleum produced water. The effects of experimental parameters such as pH in feed solution, compositions of feed solution, concentration of extractant, flow rate of both feed and stripping solutions and temperature were investigated.The removal threshold for this study was targeted to be less than 5 ppb which is the permissible discharge limit of industrial wastewater imposed by the government regulator in the Kingdom of Thailand [28].

2. Theory

2.1. Transport of mercury(II) ions across the liquid membrane phase

In the HFSLM system, both feed and stripping solutions are fed into the tube and shell sides of the hollow fibers, respectively. Both solutions are separated by an organic extractant embedded in the supported liquid membrane. The schematic representation of the chemical reaction of mercury(II) ions with Calix[4]arene nitrile (L) to form complex species is shown in Fig. 1. The reactions involved are as follows in Eqs. (1) and (2). The extraction of Hg^{2+} from the feed phase is as described in Eq. (1) [29]:

$$Hg^{2+}_{(aq)} + 2C_6H_2(NO_2)_3O^-_{(aq)} + L_{(org)} \rightleftharpoons Hg(C_6H_2(NO_2)_3O)_2 \times L_{(org)} \quad (1)$$

The stripping reaction is shown below in Eq. (2) [29]:

$$Hg(C_6H_2(NO_2)_3O)_2 \times L_{(org)} + 2H^+OH^- \rightleftharpoons Hg^{2+}_{(aq)} + 2C_6H_2(NO_2)_3OH_{(aq)} + L_{(org)} + 2OH^-_{(aq)} \quad (2)$$

where the subscript (aq) designate aqueous species and the subscript (org) is the organic species in the liquid membrane phase.

3. Experimental

3.1. Feed solution and reagents

Feed solution was petroleum produced water from one of the oil and gas operators in the Gulf of Thailand. The composition of the petroleum produced water, as shown in Table 2, was analysed by an inductively coupled plasma optical emission spectrometer (ICP-OES). The liquid membrane was composed of Calix[4]arene nitrile (5,11,17,23–Tetra–*tert*–butyl–25,27–dicyano–methoxy–26,28–dihydroxycalix[4]arene) and NOPE (2-nitrophenyl octyl ether). The stripping solution was de-ionized water (H_2O). The source and mass fraction purity of materials are listed in Table 3. All materials were used without further purification. All the chemicals were of GR grade.

3.2. Apparatus

The HFSLM (Liqui–Cel Extra–Flow membrane contactor) was manufactured by Hoechst Celanese, USA. The module was Celgard micro-porous polypropylene fibers that were woven into a fabric. The properties of the hollow fiber module are shown in Table 4. An inductively coupled plasma optical emission spectrometer (ICP-OES) (model JY-2000; HORIBA Jobin Yvon, Edison NJ, USA) was used to determine the concentration of metal ions whereby the minimum detection limit for Hg^{2+} is 5 ppb [30].

3.3. Procedure

A single module HFSLM operation is shown in Fig. 2. At first, the liquid membrane was prepared by dissolving the extractant Calix [4]arene nitrile in NPOE. Then, the extractant was simultaneously pumped into the tube and shell sides of the hollow fiber module for 40 min. To ensure that the liquid membrane was entirely embedded in the micro-pores of the hollow fibers. Subsequently, both feed and stripping solution was fed counter-currently into the tube and shell sides of the hollow fiber. The pattern flow is single-pass of feed solution and circulating of stripping solution. Mercury (II) ions moved across the liquid membrane to the stripping phase and were collected in the stripping reservoir. Operating time for one cycle for each operation was 40 min. The concentration of Hg^{2+} in the sample from the feed and stripping solution was analyzed by ICP-OES in order to determine the percentages of extraction and stripping. In this research, the extractability of Hg^{2+} can be determined by the extraction percentage as shown in Eq. (3):

Table 1
Summary of previous research on mercury(II) ions separation.

Authors	Feed solutions	Extractants	Diluents	Stripping	Flow pattern	Methods	% Ex	Ref.
Fontàs et al.	Synthetic water	*N*-benzoyl-*N*′,N′-diheptadecyl thiourea	Cumene	Thiourea	CFS	HFSLM	100	[16]
Gubbuk et al.	Synthetic water	Calix[4]arene nitrile	Chloroform	DI-water	NF	BLM	N/A	[17]
Korkmaz Alpoguz et al.	Synthetic water	Calix[4]arene dinitrile	CH_2Cl_2	DI-water	NF	FBLM	N/A	[18]
Alpoguz et al.	Synthetic water	Calix[4]arene ketone derivative	CH_2Cl_2	DI-water	NF	FSLM	N/A	[19]
Jabbari et al.	Synthetic water	DC18C6	Chlorofrom	DI-water	NF	BLM	95	[20]
Shaik et al.	Synthetic water	TOA	Dichloro ethane	NaOH	NF	BLM	95	[21]
Chakabarty et al.	Synthetic water	TOA	Dichloro ethane	NaOH	NF	FSLM	95	[22]
Sangtumrong et al.	Synthetic water	TOA	Toluene	NaOH	SFS	HFSLM	100	[23]
Pancharoen et al.	Produced water	TOA	Toluene	NaOH	SFS	HFSLM	100	[24]
Lothongkum et al.	Produced water	Aliquat 336 + Cyanex471	Toluene	Thiourea	SFS	HFSLM	100	[25]
This work	Produced water	Calix[4]arene nitrile	NPOE	DI-water	SFCS	HFSLM	99.5	

Note: BLM: bulk liquid membrane; CFS: circulating of feed and stripping solutions; FSLM: flat sheet supported liquid membrane; HFSLM: hollow fiber supported liquid membrane; L–L: liquid–liquid extraction; NF: non-flow; SFCS: single-pass of feed solution and circulating of stripping solution and SFS: single-pass of feed and stripping solutions.