



Study on removal of cadmium by hybrid liquid membrane process

Hamid R. Mortaheb*, Alireza Zolfaghari, Babak Mokhtarani, Mohammad H. Amini, Valiollah Mandanipour

Chemistry and Chemical Engineering Research Center of Iran, Tehran, P.O. Box 14335-186, Iran

ARTICLE INFO

Article history:

Received 23 August 2009

Received in revised form

14 December 2009

Accepted 16 December 2009

Available online 24 December 2009

Keywords:

Hybrid liquid membrane

Complex

Supporting membrane

Mass transfer

Removal efficiency

Modeling

Effect of temperature

ABSTRACT

Removal of cadmium as a hazardous heavy metal is studied by applying a new design of hybrid cell for liquid membrane process. Tri-iso-octyl amine (TIOA) is used as the carrier in the organic phase. The concentration of cadmium in the samples is measured by atomic absorption spectroscopy. The effect of various parameters including type of supporting membrane, pH of feed and stripping phases, initial concentration of cadmium, carrier concentration, solvent nature, and also organic film resistance on mass transfer rate and removal efficiency are studied. The effect of temperature on mass transfer flux is studied by proposing a prediction model. The optimum carrier concentration is found to be about 0.05 M. The appropriate values of pH for feed and stripping phases are about 3 and 13, respectively.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Cadmium is a toxic heavy metal, which is found in industrial discharges of different industries such as manufacturing plants of cadmium–nickel batteries, phosphate fertilizers, pigments, stabilizers, alloys and electroplating industries [1,2]. Various treatment methods including precipitation [3,4], ion exchange by ionic resins [5], clays [6] or zeolites [7], adsorption of cadmium on the surface of materials such as carbon [8] or alumina [9] and biofiltration by microalgal [10] or bacteria [11] have been proposed for removal of cadmium from wastewaters. However, each of these processes has its own restrictions and disadvantages. Alternatively, a liquid membrane process can be applied for removal of cadmium from wastewater. The process induces high driving force and selectivity, where the separation performance is enhanced by combination of extraction and stripping processes in one step [12–14]. Besides bulk liquid membrane (BLM) as the simplest form of liquid membrane, two other processes of emulsion liquid membrane (ELM) and supported liquid membrane (SLM) are typically used. In the ELM process, which has been introduced by Li et al. in 1962 [15], and

studied more in recent years for removal of heavy metals [16–20], a dispersion of an emulsion included organic membrane and aqueous internal phase in a continuous external phase is incorporated. However, the process suffers from defects such as instability, i.e. breaking of the emulsion, and its swelling that renders the effectiveness of the process [21]. Supported liquid membrane (SLM) is more promising due to its advantages of high selectivity and that the further treatment of feed phase is not needed. However, several problems make it difficult to scale up the SLMs for industrial purposes. These difficulties are loss of liquid membrane solution from the support due to evaporation or dissolution into the aqueous phases. There are also problems due to the transmembrane pressure difference, rather low permeation rate because of difficulties in preparing of very thin membranes with high stability, and chemical degradation of carriers [22]. Some researchers have tried to minimize the loss of membrane liquid in SLMs by methods such as gelation of the membrane solution in the pores of supported membrane [23], coating of an SLM surface with a thin gel layer [23] and coating with a thin polymer layer by interfacial polymerization technique [24]. However, these treatments are technically difficult and may induce additional costs on the process while they may retard the transport flux due to higher mass transfer resistance of the membrane-side. On the other hand, re-impregnation of support membrane may regenerate the lost liquid membrane as applied in several designs by Teramoto and Tanimoto [25] and Nakao et al. [26] in hollow fiber SLMs. However, re-impregnating of the support membrane does

* Corresponding author at: Chemistry and Chemical Engineering Research Center of Iran, Pazhuhesh Blvd., Tehran-Karaj Highway, Tehran, P.O. Box 14335-186, Iran. Tel.: +98 21 44580751; fax: +98 21 44580781.

E-mail addresses: mortaheb@ccerci.ac.ir, mortahebfm@hotmail.com (H.R. Mortaheb).

Nomenclature

A	effective surface area of the membrane (m^2)
C_{carrier}	concentration of carrier in organic phase (M)
C_{Cd}^0	initial concentration of cadmium in feed phase (ppm)
C_{Cd}	concentration of cadmium in feed phase at time t (ppm)
C_{KI}^0	initial concentration of KI in feed phase (M)
D	distribution coefficient of cadmium, as defined by Eq. (8)
\bar{D}	diffusion coefficient (m^2/s)
J	removal mass flux ($mg/(m^2 s)$)
K_1, K_2, K_3, K_4	stepwise complex formation constants, as defined under Table 3
K_{eq}	complexation equilibrium constant
l	thickness of organic phase (mm)
m_{carrier}	mole of carrier (mmol)
pH_f^0	initial pH of feed phase
pH_s^0	initial pH of stripping phase
R	ideal gas constant ($J/(mol K)$)
RE	removal efficiency, as defined by Eq. (4)
t	experiment time (s)
T	temperature (K)
V	volume of feed solution (l)

Greek letters

ΔH_r	heat of reaction (J/mol)
ε	porosity of membrane
η	dynamic viscosity (cP)

Subscripts

0	reference conditions
f	feed–organic interface
feed	feed phase
org	organic membrane phase
s	stripping–organic interface
strip	stripping phase

not solve the problem of contamination of feed and stripping phases.

In recent years, some attempts have been made to construct new configurations of liquid membranes. In one of these researches, a combination of a SLM and a stripping liquid dispersion (SDHLM) was utilized to improve the extraction of heavy metals [27]. It is claimed that such a configuration could increase membrane stability and reduce processing costs. Similar systems were used by other researchers [28–32]. Because of diversity in operational conditions, the evaluation of performance in those systems would be difficult. Gu et al. [33] conducted some experiments to compare transport of cadmium through SLM and SDHLM systems, and concluded that applying the hybrid system could lead to 1.5–4 fold increase in transport rate of cadmium. However, such a system still may have problems with mixing and separation of the dispersed stripping solution as the solution saturates with the transported species and needs to be refreshed. Kislik and Eyal [34,35] introduced a hybrid liquid membrane system, in which a stream of extractant phase flows between two supporting membranes where the feed and stripping phases are located in the two sides of the membranes. They could represent their experimental data by a theoretical mass transfer model for transferring of titanium (IV) through the system and concluded that an efficient mass transfer may be obtained by increasing the stripping side membrane area and stripping flow via hollow fiber or spiral membrane types of

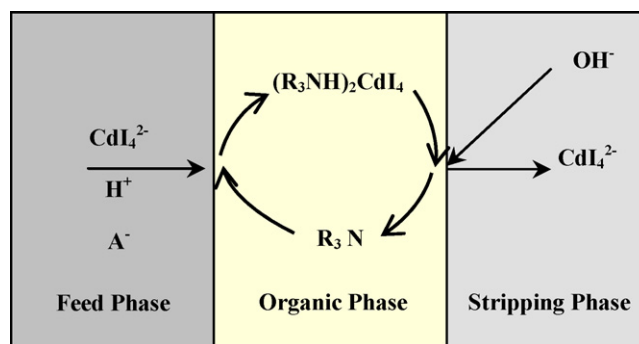


Fig. 1. Schematic of transportation mechanism.

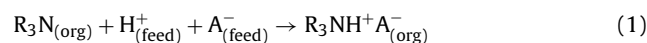
modules. They did not consider the effect of temperature on their results. In a later paper [36], Eyal and Kislik states the problems associated with the previous hybrid systems, such as losses of carrier through leakage and low diffusion rates due to high viscosity of the concentrated organic membrane phase. They presented then a more environment-friendly liquid membrane system, in which the liquid membrane phase is an aqueous solution such as water-soluble ionic or polyionic complexants. The carriers are blocked from leakage into the feed and strip solutions by charged or neutral hydrophilic membranes. The transport mechanisms in their system still need to be confirmed. The optimization of membrane and carrier selection is also required [36].

In the present research, a new configuration of hybrid liquid membrane (HLM) is proposed, in which the organic phase is placed between the two supporting membrane. The structure of the proposed system is simpler than those proposed in the previous researches by Kislik and Eyal [34]. In addition, the control of process temperature is provided in the proposed system. The effects of different parameters on removal of cadmium from wastewater are then studied by the proposed system.

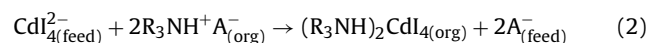
2. Transport mechanism

The transport mechanism can be explained by the following steps and schematic of transport mechanism is given in Fig. 1:

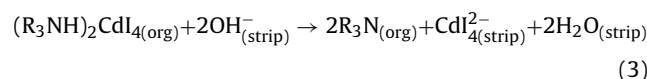
- (1) TIOA (shown as R_3N) in the organic phase reacts with H^+ of the feed phase at the feed–membrane interface to form $R_3NH^+A^-$, where A^- is a counter ion.



- (2) At the feed–membrane interface, CdI_4^{2-} is replaced by A^- of $R_3NH^+A^-$:



- (3) OH^- in the stripping solution reacts with the transferred $(R_3NH)_2CdI_4$ at the membrane–stripping interface to transfer cadmium into the stripping phase.



3. Experimental

3.1. Chemicals

The chemicals applied in the present study were analytical grade purchased from Merck and Aldrich with purity of more than 99% and were used without further purifications. The double-distilled

Table 1
The specifications of kerosene in organic membrane phase.

Property	Value
Sp. gr.	0.779
Flash point	43 °C
Aromatics	17%
Napthenics	26%
Iso-paraffin	27%
n-paraffin	30%

water was used for preparation of the solutions. In the present research, tri-iso-octyl amine (TIOA) is used as the carrier in the membrane phase. Kerosene with the specifications indicated in Table 1 was used as the organic solvent of the organic membrane phase unless otherwise noted.

3.2. Experimental setup and procedure

A schematic of the applied setup in the experiments is shown in Fig. 2. The setup consists of a cylindrical-shape cell with two separate compartments for feed and stripping phases with capacity of 50 ml each. Two membranes, which are impregnated in the organic phase for 24 h before the experiment, are placed between the flanged-shape wall of each container and a spacer. The set of support membranes and the spacer are fastened between the two glass flanges. By using the spacers with different thicknesses, a space with variable thickness is provided for injection of the organic phase. The setup is placed inside a coil-equipped water bath whose temperature is controlled by a circulator (Julabo FP-50). The aqueous phases are stirred by placing the whole setup on a magnet stirrer, where two magnets in circular wells at the bottom of each container stir the aqueous phases. Samples are taken from the feed phase at the specified time intervals and pHs of the aqueous phases are recorded periodically. The concentration of cadmium in the samples is measured by atomic absorption spectroscopy (PerkinElmer 1100B). Although the feed-phase samples are basically analyzed, however by measuring the concentration of cadmium in some of the stripping-phase samples, which are taken at the same time, it is confirmed that almost all of the cadmium is transferred to the stripping phase.

The removal efficiency and removal mass flux are then calculated by using the following equations, respectively:

$$RE = \frac{C_{Cd}^0 - C_{Cd}}{C_{Cd}^0} \quad (4)$$

$$J = -\frac{V}{A} \frac{dC_{Cd}}{dt} \quad (5)$$

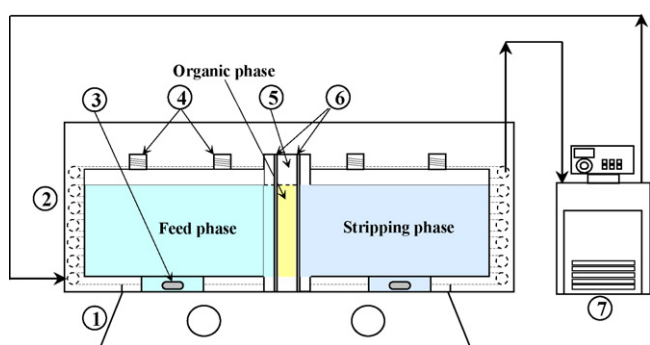


Fig. 2. Schematic diagram of applied setup: (1) magnet stirrer; (2) water bath; (3) magnet; (4) sampling and measurement openings; (5) spacer; (6) supporting membranes; (7) water circulator.

Table 2
The specifications of supporting membranes.

Property	Membrane type	
	F ₁	F ₂
Material	Hydrophilic PVDF	
Membrane code	VVLP	HVLP
Thickness (μm)	125	125
Membrane pore size (μm)	0.1	0.45
Porosity (%)	70	70
Membrane diameter (mm)	47	47
Water flow rate (ml/(min × cm ²))	2.5	29

4. Results

4.1. Effect of membrane type

In order to select the appropriate supporting membrane for the system, two Durapore® membranes from Millipore Inc. with different pore sizes, as indicated in Table 2, were used. As seen in Fig. 3, the removal efficiency is lower for the membrane with larger pore size. This might be related to the bulk diffusion of aqueous solution from the feed or stripping phases into the organic phase, which decreases the concentration driving force. Also, formation of an aqueous hindering film on the organic side of the supporting membrane may cause a resistance against the formation and transportation of the complex. Therefore, the membrane with lower pore size (F₁) was selected for the rest of experiments.

It is noticeable that the membranes applied in the present research are hydrophile. Applying a hydrophile membrane may cause a trouble in the case of SLM systems as the impregnated membrane may be washed out by the aqueous phase. However, this is not the case in our HLM system, in which there is a source of bulk organic membrane adjacent to the membrane and the organic phase is under the same hydrostatic pressure from both sides by the feed and stripping phases. However, since two different aqueous and organic phases are placed in the two sides of the membrane, either hydrophobe or hydrophile membranes may not be impregnated well by one of the phases, respectively. It may be more efficient to use a membrane with contrast interactions with water on both sides.

4.2. Effect of carrier concentration

Based on the transportation mechanism, cadmium is transferred faster as the concentration of carrier in the organic phase is increased. As shown in Fig. 4, this trend is observed in the experiments when the carrier is increased from 0.02 to 0.05 M. However,

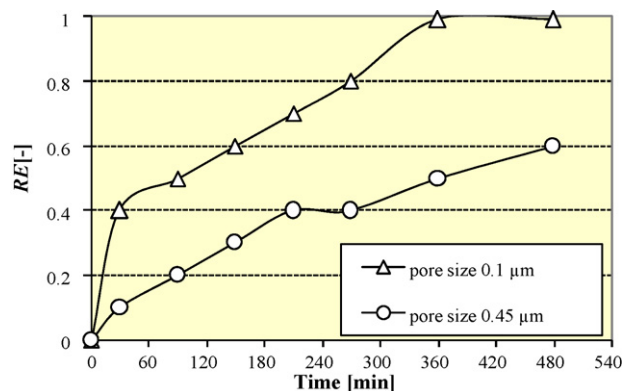


Fig. 3. Effect of supporting membrane type on removal efficiency: $C_{Cd}^0 = 50$ ppm; $pH_f^0 = 1.8$; $pH_s^0 = 13$; $C_{carrier} = 0.1$ M; $C_{KI}^0 = 0.01$ M; $l = 5$ mm.

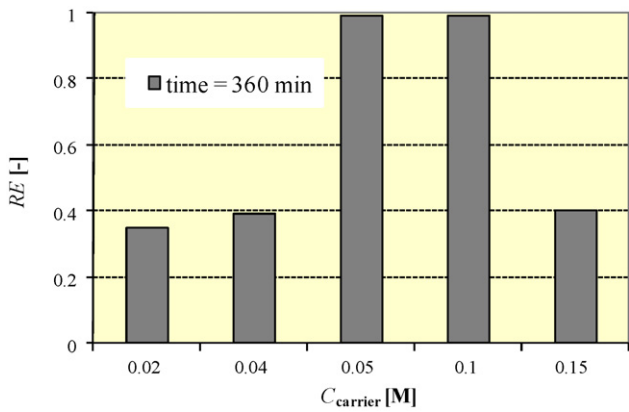


Fig. 4. Effect of carrier concentration on removal efficiency: $C_{\text{Cd}}^0 = 50 \text{ ppm}$; $\text{pH}_f^0 = 1.8$; $\text{pH}_s^0 = 13$; $C_{\text{KI}}^0 = 0.01 \text{ M}$; $l = 5 \text{ mm}$.

the removal efficiency remains to about the same level when the carrier concentration is increased from 0.05 to 0.1 M. The removal efficiency is then decreased significantly when the carrier concentration is increased to 0.15 M. This decrease in the removal efficiency can be attributed due to increase in viscosity of organic phase which decreases the transport. The optimum value is determined to be about 0.05 M.

4.3. Effect of temperature

Experiments were made to indicate the effect of temperature on mass transfer rate of cadmium through the membrane, where different temperatures were set for the setup in each experiment. Fig. 5 shows the observed fluxes of cadmium through the membrane as a function of temperature. As the figure shows, the flux of cadmium is increased by increasing of the temperature.

The effect of temperature can be modeled by considering its effects on the mass transfer rate of solute through the membrane in two different ways:

- (i) Increasing temperature will increase the diffusion coefficient and therefore mass transfer flux.
- (ii) Increasing temperature will also reduce the viscosity of liquid membrane. Since decreasing of viscosity inversely increases the diffusion coefficient, it will be a further enhancing factor that can increase the mass transfer rate.

These effects can be described by the following relationships [37].

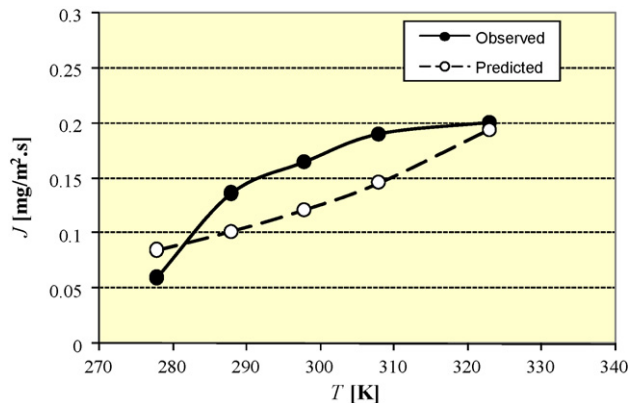
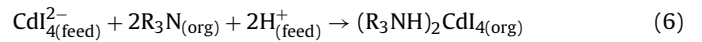


Fig. 5. Effect of temperature on observed and predicted removal fluxes of cadmium: $C_{\text{Cd}}^0 = 50 \text{ ppm}$; $C_{\text{carrier}} = 0.05 \text{ M}$; $\text{pH}_s^0 = 13$; $C_{\text{KI}}^0 = 0.01 \text{ M}$; $l = 5 \text{ mm}$.

Complexation reaction of cadmium can be represented by summation of Eqs. (1) and (2):



The complexation equilibrium constant, K_{eq} , is expressed as:

$$K_{\text{eq}} = \frac{[(\text{R}_3\text{NH})_2\text{CdI}_{4(\text{org})}]}{[\text{CdI}_{4(\text{feed})}^{2-}][\text{R}_3\text{N}_{(\text{org})}]^2[\text{H}_{(\text{feed})}^+]^2} \quad (7)$$

The distribution coefficient of cadmium, D , is defined as:

$$D = \frac{[(\text{R}_3\text{NH})_2\text{CdI}_{4(\text{org})}]}{[\text{CdI}_{4(\text{feed})}^{2-}]} \quad (8)$$

K_{eq} can then be rearranged:

$$K_{\text{eq}} = \frac{D}{[\text{R}_3\text{N}_{(\text{org})}]^2[\text{H}_{(\text{feed})}^+]^2} \quad (9)$$

The flux, J , of cadmium ions through the membrane, assuming that it follows the Fick's first law, is given by

$$J = \frac{\bar{D}\varepsilon(D_f[\text{Cd}^{2+}]_f - D_s[\text{Cd}^{2+}]_s)}{l} \quad (10)$$

where

$$D_f = \frac{[(\text{R}_3\text{NH})_2\text{CdI}_{4(\text{org})}]_f}{[\text{Cd}_{(\text{feed})}^{2+}]} \quad (11)$$

and

$$D_s = \frac{[(\text{R}_3\text{NH})_2\text{CdI}_{4(\text{org})}]_s}{[\text{Cd}_{(\text{strip})}^{2+}]} \quad (12)$$

If $D_s \rightarrow 0$, i.e. cadmium complex breaks on the stripping side of membrane immediately after reaching there by depleting the concentration inside the membrane, then Eq. (10) becomes:

$$J = \bar{D}\varepsilon \frac{D_f[\text{Cd}_{(\text{feed})}^{2+}]}{l} \quad (13)$$

In this case $D_f = D$, and putting its value from Eq. (9) into Eq. (13) gives:

$$J = \bar{D}\varepsilon \frac{K_{\text{eq}}[\text{R}_3\text{N}_{(\text{org})}]^2[\text{H}_{(\text{feed})}^+]^2[\text{Cd}_{(\text{feed})}^{2+}]}{l} \quad (14)$$

The diffusion coefficient, \bar{D} , based on the Wilkie–Chang equation is given by:

$$\bar{D} \propto \frac{T}{\eta} \quad \text{or} \quad \frac{\bar{D}\eta}{T} = K' \text{ (const.)} \quad (15)$$

Therefore, the flux of solute can be written as:

$$J = K_{\text{eq}}K'T\varepsilon \frac{[\text{R}_3\text{N}_{(\text{org})}]^2[\text{H}_{(\text{feed})}^+]^2[\text{Cd}_{(\text{feed})}^{2+}]}{\eta l} \quad (16)$$

It can be seen from the above equation that at constant concentration and with the same membrane type and thickness, the flux is a function of the following parameters:

$$J \propto K_{\text{eq}} \frac{T}{\eta} \quad (17)$$

in which, K_{eq} is a function of temperature as:

$$K_{\text{eq}} = K_{0\text{eq}} \exp\left(\frac{-\Delta H_f}{RT}\right) \quad (18)$$

Therefore, the flux of solute can be correlated as a function of temperature as follows:

$$J \equiv c_1 \left\{ \frac{T \exp[-c_2((1/T) - (1/T_0))]}{\alpha T + \beta} \right\} \quad (19)$$

Table 3
Complex formation constants^a of cadmium with some anions [40].

Anion	log K ₁	log K ₂	log K ₃	log K ₄
Cyanide (CN ⁻)	6.01	5.11	4.53	2.27
Iodide (I ⁻)	2.28	1.64	1.08	1.0
Chloride (Cl ⁻)	1.98	1.62	-0.2	-0.7
Thiocyanate (SCN ⁻)	1.89	0.89	0.02	-0.5
Nitriloacetate N(CH ₃ COO ⁻) ₃	9.83			

$$^a K_n = [\text{CdA}_n^{2-a(n)}] / ([\text{CdA}_{n-1}^{2-a(n-1)}][\text{A}^{-a}]) \text{ for } \text{CdA}_{n-1}^{2-a(n-1)} + \text{A}^{-a} \rightleftharpoons \text{CdA}_n^{2-a(n)}$$

in which, $(\alpha T + \beta)$ represents the viscosity of organic phase as a linear descending function of temperature, and c_1 and c_2 are constants. By adopting the assumption made to derive Eq. (13), the model can be applied in the temperature range of the experiments (5–50 °C).

The comparison between the trend of removal flux by increasing of temperature based on the above model and the observed values in Fig. 5 reveals that while the theoretical model predicts a steady increase in flux by increasing of temperature, the slope of increment in the observed fluxes levels off at higher temperatures. The slower increase at higher temperatures can be interpreted by considering the mechanism of mass transfer in the system. The mechanism comprises serial steps including mass transfer of solute in the feed phase toward the supporting membrane, diffusion through the supporting membrane, reaction with the carrier and diffusion through the organic phase, de-complexation at the stripping side of supporting membrane, and finally mass transfer of solute in the stripping phase. It is then predictable that while increasing of temperature will increase the reaction rate and diffusion through the organic phase, some parameters such as resistance of supporting membrane and limited concentration of carrier in the organic phase can retard the overall mass flux in the serial mass transfer mechanism.

4.4. Effect of complexing agent

Cadmium ion is transferred in the liquid membrane as an anion by reaction with the protonated carrier. Among the variety of complexing agents to form the anionic structure of cadmium, KI was selected in the present research. The reason is that the complex formation constant of CdI_4^{2-} is much higher than that with the other complexing anions except with cyanide, which cannot be used in acidic environments due to its high toxicity (see Table 3). Therefore, it is expected that it can act more efficient in removing cadmium. Furthermore, iodide can be easily recovered in ionic form [38,39].

An alternative of iodide as the complexing agent is chloride. In order to study the effect of presence of chloride on removal performance, some experiments in the presence of chloride has been performed. As seen in Fig. 6, the removal efficiencies of cadmium in the presence of 0.1 M chloride significantly decreases the removal efficiency. However, as the concentration of chloride is increased to 0.5 and 1 M, the removal efficiency slightly improves. The slight increase of removal efficiency in higher concentrations of chloride may be related to increase in contribution of CdCl_4^{2-} in transferring of cadmium at the feed–organic membrane interface. In general, it is observed that the presence of chloride may retard the transferring of cadmium in the process.

4.5. Effect of pH of feed phase

Since H^+ is absorbed by carrier at the feed–organic interface to produce R_3NH^+ , the pH of feed phase, i.e. availability of H^+ at the interface, promotes the transported cadmium through the membrane. However, as shown in Fig. 7, among the experiments made by using hydrochloric acid 36% with pH_f^0 of 0.5, 1.8, and 3.0, the best removal efficiencies are obtained when $\text{pH}_f^0 = 3.0$ but very close to those when $\text{pH}_f^0 = 1.8$. The lower removal efficiencies of

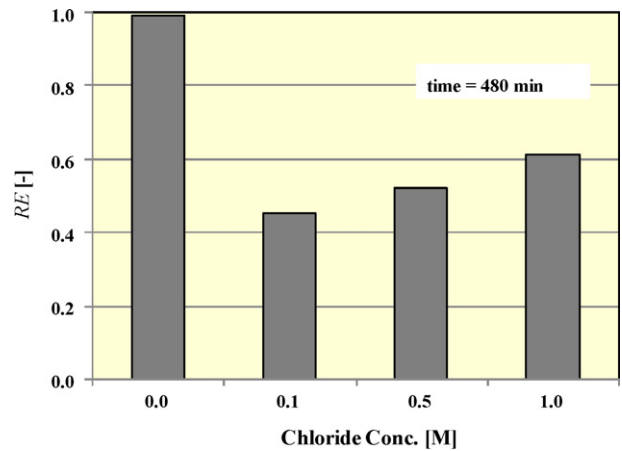


Fig. 6. Effect of presence of chloride in feed phase on removal efficiency: $C_{\text{Cd}}^0 = 50$ ppm; $C_{\text{carrier}} = 0.05$ M; $\text{pH}_f^0 = 1.8$; $\text{pH}_s^0 = 13$; $C_{\text{KI}}^0 = 0.01$ M; $l = 5$ mm.

the feed with $\text{pH}_f^0 = 0.5$ may be due to the oxidation of I^- , which presents in the feed phase, into I_2 indicated by its yellowish color. This will reduce the concentration of CdI_4^{2-} as the zwitterion of carrier (R_3NH^+) at the feed–organic interface.

4.6. Effect of acid nature in the feed phase

In order to examine the effect of nature of acid in the feed phase on removal efficiency, experiments were carried out using various acids such as acetic acid, nitric acid, and hydrochloric acid with the same pH_f^0 of 3.2. As seen in Fig. 8, the removal efficiencies show the following tendency: $\text{CH}_3\text{COOH} > \text{HCl} > \text{HNO}_3$. The trend can be explained by considering higher concentration of acetic acid, which was used to obtain the same pH for all of the experiments. The available H^+ , which is obtained by gradual dissociation of acetic acid, facilitates the transferring of cadmium. On the other hand, strong acidity of nitric acid oxidizes I^- into I_2 and decreases the concentration of iodide available for transferring of cadmium. It can be concluded that the removal efficiency is rather associated to the availability of H^+ in the feed phase than to the acidity of the applied acid.

4.7. Effect of pH of stripping phase

Fig. 9 shows the effect of pH of stripping phase on the removal efficiency using NaOH as the stripping agent. As seen in the figure, insignificant increase in removal efficiency is observed when the

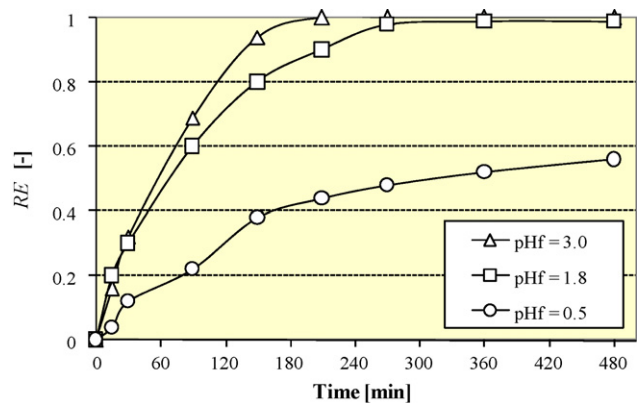


Fig. 7. Effect of pH of feed phase on removal efficiency: $C_{\text{Cd}}^0 = 50$ ppm; $C_{\text{carrier}} = 0.05$ M; $\text{pH}_s^0 = 13$; $C_{\text{KI}}^0 = 0.01$ M; $l = 5$ mm.

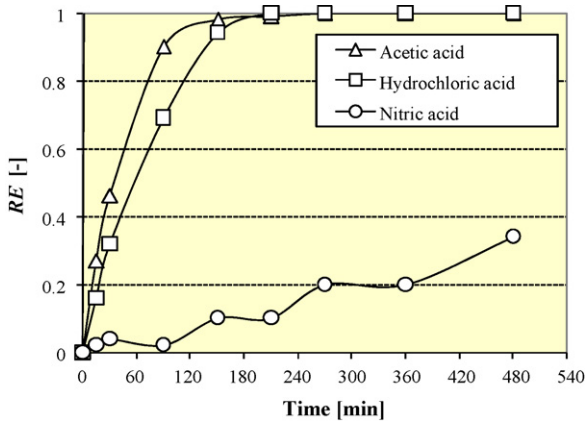


Fig. 8. Effect of nature of acid in feed phase on removal efficiency: $C_{Cd}^0 = 50$ ppm; $C_{carrier} = 0.05$ M; $pH_f^0 = 3.2$; $pH_s^0 = 13$; $C_{KI}^0 = 0.01$ M; $l = 5$ mm.

pH of stripping phase is increased from 9 to 11. However, as the pH_s^0 is set to 13, the removal efficiency increases considerably. This is because the concentration driving force between the feed and stripping phases remains almost constant when $pH_s^0 = 13$ while as observed in the experiments, pH of stripping phase and then the driving force is decreased by time when $pH_s^0 = 9-11$. Therefore, the pH of about 13 is selected as the desired pH for the stripping phase.

4.8. Effect of initial concentration of cadmium

Changing the solute concentration affects concentration driving force and possibly mass transfer rate. Fig. 10 shows the initial and average removal fluxes, and also removal efficiencies in the systems with four different solute concentrations of 10, 30, 70, and 100 ppm. As expected, by increasing solute concentration, which increases concentration driving force, both initial and average removal fluxes increase. However, removal efficiencies that first increase by increasing solute concentration are declined afterward due to approaching to an ultimate removal capacity.

4.9. Effect of different organic solvents

As seen in Fig. 11, by selecting 3 different solvents of toluene, kerosene, and n-hexane, the removal efficiencies show the following trend; kerosene > toluene > n-hexane. The difference is attributed mainly to the difference of wettability of supporting membrane by the solvent. The interaction between the transported cadmium and the organic solvent also may affect the mass trans-

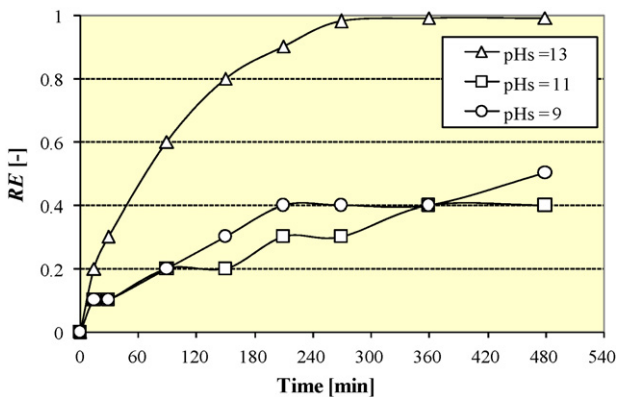


Fig. 9. Effect of pH of stripping phase on removal efficiency: $C_{Cd}^0 = 50$ ppm; $C_{carrier} = 0.05$ M; $pH_f^0 = 1.8$; $pH_s^0 = 13$; $C_{KI}^0 = 0.01$ M; $l = 5$ mm.

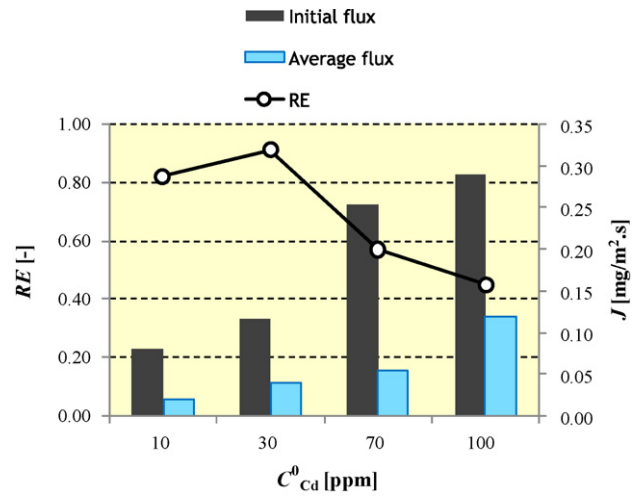


Fig. 10. Effect of solute concentration on removal efficiency and removal fluxes: $C_{carrier} = 0.05$ M; $pH_f^0 = 1.8$; $C_{KI}^0 = 0.01$ M; $l = 5$ mm.

fer rate through the organic phase. Since kerosene, which shows the best wettability, has the highest removal efficiency, it may be concluded that the former parameter is more significant than the latter one.

4.10. Effect of organic phase thickness

Changing the thickness of organic phase may alter the resistance against diffusion through this phase. The effect was examined by three different thicknesses of 3, 4, and 5 mm, provided by replacing of spacers in the experiments. The weight of carrier was fixed in these experiments. As it can be seen in Fig. 12, the initial removal fluxes of cadmium for the thicker organic phases (4 and 5 mm) are relatively higher than that in the thinner one (3 mm). This is possibly due to less hindrance caused by large molecules of the carrier against transferring of the complex molecules in the thicker organic phases, i.e. lower carrier concentrations, at initial times when enough concentration driving force exists. However, as the concentration driving force is decreased afterward, the removal fluxes of cadmium in the systems with thicker organic phases fall below flux in the system with thinner organic phase due to the higher resistance against diffusion in the organic phase.

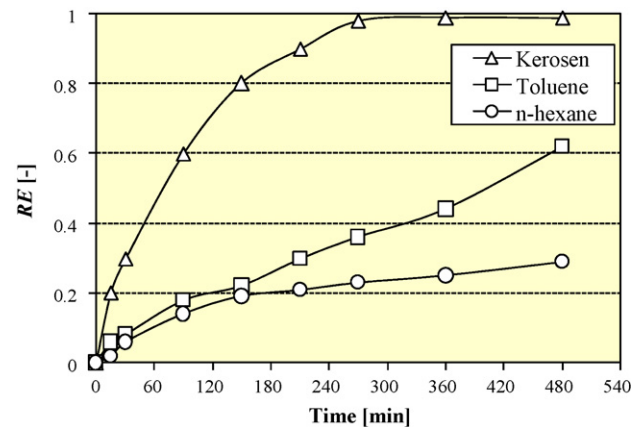


Fig. 11. Effect of solvent on removal efficiency: $C_{Cd}^0 = 50$ ppm; $C_{carrier} = 0.05$ M; $pH_f^0 = 1.8$; $pH_s^0 = 13$; $C_{KI}^0 = 0.01$ M; $l = 5$ mm.

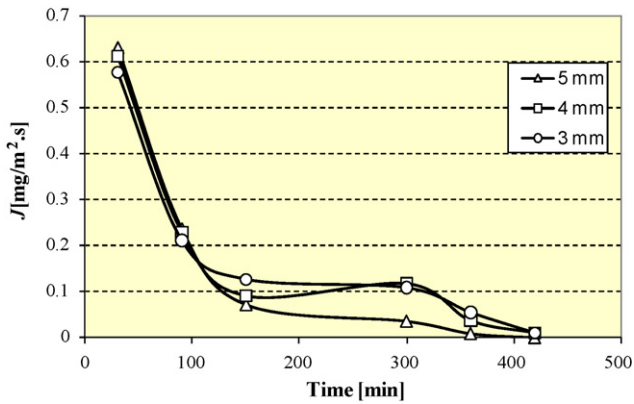


Fig. 12. Effect of organic phase thickness on removal flux: $C_{Cd}^0 = 50$ ppm; $m_{carrier} = 0.2$ mmol; $pH_f^0 = 1.8$; $pH_s^0 = 13$; $T = 50$ °C; $C_{KI}^0 = 0.01$ M.

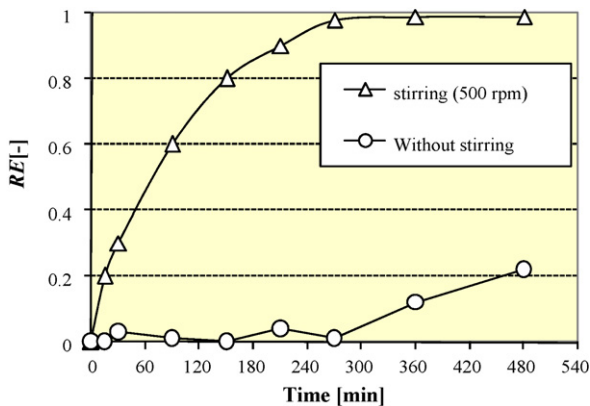


Fig. 13. Effect of stirring on removal efficiency: $C_{Cd}^0 = 50$ ppm; $C_{carrier} = 0.05$ M; $pH_f^0 = 1.8$; $pH_s^0 = 13$; $C_{KI}^0 = 0.01$ M; $l = 5$ mm.

4.11. Effect of stirring of aqueous phases

As the stirring of feed and stripping phases reduces the thickness of boundary layers at the interfaces of these phases and the organic phase, it reduces the resistance against mass transfer. This effect is shown in Fig. 13, in which removal efficiencies with and without stirring is compared. As seen in the figure, the removal efficiency

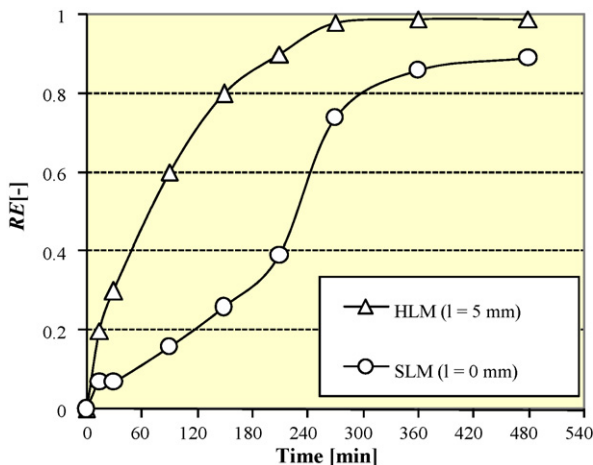


Fig. 14. Effect of organic phase on removal efficiency: $C_{Cd}^0 = 50$ ppm; $C_{carrier} = 0.05$ M; $pH_f^0 = 1.8$; $pH_s^0 = 13$; $C_{KI}^0 = 0.01$ M.

in the experiment without stirring is significantly lower than that in the experiment with stirring.

4.12. Comparison of HLM with SLM

In order to investigate the effect of bulk organic phase, i.e. comparison of HLM and SLM processes, the results obtained by the current system are compared with those obtained when instead of two membranes and a specified thickness of bulk organic phase, only one impregnated supporting membrane is applied between the feed and stripping phases. As seen in Fig. 14, removal efficiency in the HLM process is higher than that in the SLM process. Although the mass transfer resistance for diffusing through the bulk liquid is less in the SLM system, this advantage may be nullified by washing out of the organic phase from the pores of the membrane in that process. In addition, the solute in the HLM process is transferred more efficiently possibly because of the larger amount of available carrier.

5. Conclusion

Separation of cadmium from wastewater was investigated using a hybrid liquid membrane process. Effect of different parameters on separation of cadmium can be summarized as follows:

- Increasing carrier up to 0.05 M increases the removal efficiency. However, the efficiency declines when a higher concentration is used possibly due to interference caused by the carrier.
- The optimum pH of external phase is about 3 while lower pHs reduce efficiency due to oxidation of iodide in the feed phase. Also, acetic acid shows the best removal efficiency due to availability of H^+ by gradual dissociation of the acid.
- The optimum pH of the stripping phase is found to be about 13 because of constant concentration driving force between the two aqueous phases.
- Higher solute concentration increases mass transfer flux due to the higher concentration driving force.
- Kerosene, which induced the best wettability for the supporting membrane shows highest removal efficiencies among the applied organic solvents.
- When the same amount of carrier is used, the higher thickness of organic phase shows higher initial removal fluxes possibly due to less hindrance caused by the carrier. The removal fluxes of the systems with thicker organic phase are then decreased due to resistance against diffusion.
- Stirring of aqueous phases enhances the mass transfer efficiency due to decreasing of film resistance at the interfaces.
- It is shown that the removal efficiency enhances significantly when SLM process is replaced by the HLM process while the same other conditions are used.

References

- [1] L.J.J. Janssen, L. Koene, The role of electrochemistry and electrochemical technology in environmental protection, *Chem. Eng. J.* 85 (2002) 137–146.
- [2] K. Jüttner, U. Galla, H. Schmieder, Electrochemical approaches to environmental problems in the process industry, *Electrochim. Acta* 45 (2000) 2575–2594.
- [3] H.A. Aziz, N. Otham, M.S. Yusuff, D.R.H. Basri, F.A.H. Ashaari, M.N. Adlan, F. Otham, M. Johari, M. Perwira, Removal of copper from water using limestone filtration technique—determination of mechanism of removal, *Environ. Int.* 26 (2001) 395–399.
- [4] C. Kim, Q.H. Zhou, B.L. Deng, E.C. Thornton, H.F. Xu, Cr^{6+} reduction by hydrogen sulfide in aqueous media: stoichiometry and kinetics, *Environ. Sci. Technol.* 35 (2001) 2219–2225.
- [5] S. Yalcin, R. Apak, J. Hizal, H. Afsar, Recovery of Cu^{2+} and $Cr^{3+/6+}$ from electroplating industry wastewater by ion exchange, *Sep. Sci. Technol.* 36 (2001) 2181–2196.
- [6] K.R. Reddy, S. Chinthamreddy, Sequentially enhanced electrokinetic remediation of heavy metals in low buffering clayey soils, *J. Geotech. Geoenviron. Eng.* 129 (2003) 263–277.

- [7] M.J. Zamow, J.E. Murphy, Removal of metal-cations from water using zeolites, *Sep. Sci. Technol.* 27 (1992) 1969–1984.
- [8] K. Kadirvelu, C. Faur-Brasquet, P. Le Cloirec, Removal of Cu^{2+} , Pb^{2+} , and Ni^{2+} by adsorption onto activated carbon cloths, *Langmuir* 16 (2000) 8404–8409.
- [9] M.L. Cervera, M.C. Arnal, M. Guardia, Removal of heavy metals by using adsorption on alumina or chitosan, *Anal. Bioanal. Chem.* 375 (2003) 820–825.
- [10] A.M.Y. Chong, Y.S. Wong, N.F.Y. Tam, Performance of different microalgal species in removing nickel and zinc from industrial wastewater, *Chemosphere* 41 (2000) 251–257.
- [11] M. Vainshtein, P. Kusch, J. Mattusch, A. Vatsourina, A. Wiessner, Model experiments on the microbial removal of chromium from contaminated groundwater, *Water Res.* 37 (2003) 1401–1405.
- [12] R.P. Cahn, N.N. Li, Separation of phenol from wastewater by liquid membrane technique, *Sep. Sci. Technol.* 9 (1974) 505–519.
- [13] M. Ruppert, J. Draxler, R. Marr, Liquid-membrane permeation and its experiences in pilot-plant and industrial scale, *Sep. Sci. Technol.* 23 (1988) 1659–1666.
- [14] A. Nemeš, A.P. Van Peteghem, Extraction of multicomponent system metals from simulated and industrial effluents by liquid surfactant membranes, *Hydrometallurgy* 31 (1992) 149–159.
- [15] N.N. Li, Separation hydrocarbons with liquid membrane, U.S. Patent 3,410,794 (1968).
- [16] J. Draxler, W. Furst, R. Marr, Separation of metal species by emulsion liquid membranes, *J. Membr. Sci.* 38 (1988) 281–293.
- [17] G. Szejner, A. Marmur, Cadmium removal from aqueous solutions by an emulsion liquid membrane—the effect of resistance to mass transfer at the outer oil–water interface, *Colloid Surf. A* 151 (1999) 77–83.
- [18] J. Fang, B. Tang, M. Li, Z. Xu, Recovery of cadmium from a zinc hydrometallurgical leachate using reactive emulsion liquid membrane technology, *J. Chem. Technol. Biotechnol.* 79 (2004) 313–320.
- [19] X. Liu, D. He, M. Ma, Transfer and separation of Cd(II) chloride species from Fe(III) by a hybrid liquid membrane containing tri-*n*-octylamine–secondary octylalcohol–kerosene, *Chem. Eng. J.* 133 (2007) 265–272.
- [20] H.R. Mortaheb, H. Kosuge, B. Mokhtarani, M.H. Amini, H.R. Banihashemi, Study on removal of cadmium from wastewater by emulsion liquid membrane, *J. Hazard. Mater.* 165 (2009) 630–636.
- [21] H.R. Mortaheb, M.H. Amini, F. Sadeghian, B. Mokhtarani, H. Daneshyar, Study on a new surfactant for removal of phenol from wastewater by emulsion liquid membrane, *J. Hazard. Mater.* 160 (2008) 582–588.
- [22] M. Teramoto, N. Takeuchi, T. Maki, H. Matsuyama, Gas separation by liquid membrane accompanied by permeation of membrane liquid through membrane physical transport, *Sep. Purif. Technol.* 24 (2001) 101–112.
- [23] A.M. Neplenbroek, D. Bargeman, C.A. Smolder, Supported liquid membranes: stabilization by gelation, *J. Membr. Sci.* 67 (1992) 149–165.
- [24] A.J.B. Kemperman, H.H.M. Rolevink, T. van den Boomgaard, H. Strathmann, Hollow-fiber supported liquid membranes with improved stability for nitrate removal, *Sep. Purif. Technol.* 12 (1997) 119–134.
- [25] M. Teramoto, H. Tanimoto, Mechanism of copper permeation through hollow fiber liquid membranes, *Sep. Sci. Technol.* 18 (1983) 871–892.
- [26] M. Nakao, K. Takahashi, H. Takeuchi, A method for continuous regeneration of supported liquid membranes, *J. Chem. Eng. Jpn.* 20 (1987) 326–328.
- [27] W.S. Winston Ho, Combined supported liquid membrane/strip dispersion process for the removal and recovery of metals, U.S. Patent 6,350,419 (2002).
- [28] R. Basu, K.K. Sirkar, Citric acid extraction with microporous hollow fibers, *Solv. Extr. Ion Exch.* 10 (1992) 119–143.
- [29] M. Teramoto, N. Tohno, N. Ohnishi, H. Matsuyama, Development of a spiral-type flowing liquid membrane module with high stability and its application to the recovery of chromium and zinc, *Sep. Sci. Technol.* 24 (1989) 981–999.
- [30] O. Kedem, L. Bromberg, Ion-exchange membranes in extraction processes, *J. Membr. Sci.* 78 (1993) 255–264.
- [31] A. Eyal, E. Bressler, Industrial separation of carboxylic and amino acids by liquid membranes; applicability, process considerations and potential advantages, *Biotechnol. Bioeng.* 41 (1993) 287–295.
- [32] M. Teramoto, Y. Sakaida, S.S. Fu, N. Ohnishi, H. Matsuyama, T. Maki, T. Fukui, K. Arai, An attempt for the stabilization of supported liquid membrane, *Sep. Purif. Technol.* 21 (2000) 137–144.
- [33] S. Gu, Y. Yu, D. He, M. Ma, Comparison of transport and separation of Cd(II) between strip dispersion hybrid liquid membrane (SDHLM) and supported liquid membrane (SLM) using tri-*n*-octylamine as carrier, *Sep. Purif. Technol.* 51 (2006) 277–284.
- [34] V.S. Kislik, A.M. Eyal, Hybrid liquid membrane (HLM) system in separation technologies, *J. Membr. Sci.* 111 (1996) 259–272.
- [35] V.S. Kislik, A.M. Eyal, Hybrid liquid membrane (HLM) and supported liquid membrane (SLM) based transport of titanium(IV), *J. Membr. Sci.* 111 (1996) 273–281.
- [36] A. Eyal, V. Kislik, Aqueous hybrid liquid membrane—a novel system for separation of solutes using water-soluble polymers as carriers, *J. Membr. Sci.* 161 (1999) 207–221.
- [37] A.O. Adebayo, K. Sarangi, Separation of copper from chalcopyrite leach liquor containing copper, iron, zinc and magnesium by supported liquid membrane, *Sep. Purif. Technol.* 63 (2008) 392–399.
- [38] E. Venkat, R.J. Magliette, D. McKinney, A.S. Michaels, Recovery of iodide from chemical process wastewater, U.S. Patent 6,379,556 (2002).
- [39] H.W. Tsao, Method of iodide removal, U.S. Patent 7,588,690 B1 (2009).
- [40] D. Harvey, *Modern Analytical Chemistry*, first ed., McGraw Hill, USA, 2000.