



Characteristic and mechanism of Cu(II) extraction with polymeric particle with interconnected spherical pores impregnating with LIX84-I

メタデータ	言語: jpn 出版者: 公開日: 2020-06-21 キーワード (Ja): キーワード (En): 作成者: 清山, 史朗, 塩盛, 弘一郎, Nov, Irmawati Inda, Fukumaru, Masaya, Sana, Takashi, Takei, Takayuki, Yoshida, Masahiro, Nakajima, Akira メールアドレス: 所属:
URL	<a href="http://hdl.handle.net/10458/6013">http://hdl.handle.net/10458/6013</a>

# Characteristics and Mechanism of Cu(II) Extraction with Polymeric Particles with Interconnected Spherical Pores Impregnated with LIX84-I

Nov Irmawati INDA<sup>1</sup>, Masaya FUKUMARU<sup>2</sup>, Takashi SANA<sup>2</sup>, Shiro KIYOYAMA<sup>3</sup>, Takayuki TAKEI<sup>4</sup>, Masahiro YOSHIDA<sup>4</sup>, Akira NAKAJIMA and Koichiro SHIOMORI<sup>2\*</sup>

<sup>1</sup>Department of Environment and Resource Sciences, Interdisciplinary Graduate School of Agriculture and Engineering, University of Miyazaki, 1-1 Gakuenkibanadai-nishi, Miyazaki-shi, Miyazaki 889-2192, Japan

<sup>2</sup>Department of Applied Chemistry, University of Miyazaki, 1-1 Gakuenkibanadai-nishi, Miyazaki-shi, Miyazaki 889-2192, Japan

<sup>3</sup>Department of Chemical Science and Engineering, National Institute of Technology, Miyakonojo College, 473-1 Yoshio-cho, Miyakonojo-shi, Miyazaki 885-8567, Japan

<sup>4</sup>Department of Chemical Engineering, Graduate School of Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima-shi, Kagoshima 890-0065, Japan

<sup>5</sup>Department of Biotechnology, Frontier Science Research Center, University of Miyazaki, 5200 Kihara, Kiyotake-cho, Miyazaki-shi, Miyazaki 889-1692, Japan

**Keywords:** Polymeric Particles, Cu(II) Extraction Behavior, LIX84-I-Cu(II) Complex

**LIX84-I was successfully immobilized and encapsulated in polymeric particle. Characterization of Cu(II) extracted into the polymeric particles impregnated with LIX84-I was also performed. Cu(II) ions were successfully extracted from an acidic solution and a constant value at a higher initial concentration of Cu(II) in the aqueous phase was achieved. Complex formation between Cu(II) and LIX84-I was identified via visual identification of a green cloudy powder. The extraction behavior of Cu(II) with the polymeric particles conformed well to Langmuir-type adsorption. However, when considering the purity of LIX84-I, it was suggested that two LIX84-I molecules reacted with one Cu(II) ion in the polymeric particles. Furthermore, the Fourier transform infrared spectrum showed an interaction between the polymeric particle wall and extractant. In addition, the electron paramagnetic resonance spectrum indicated that the structure of the LIX84-I-Cu(II) complex in the polymeric particles is a distorted octahedral structure composed of two LIX84-I, which consist of two nitrogen and two oxygen atoms, and two water molecules in axial positions of complex molecules, and its geometrical structure is similar to that in the solvent extraction system.**

## Introduction

Presently, copper is used in building construction, power generation and transmission, electronic product manufacturing and the production of industrial machinery and transportation vehicles (Ramachandra Reddy *et al.*, 2007; Baba *et al.*, 2015). This is because copper is easily stretched, molded and shaped, is resistant to corrosion and conducts heat and electricity efficiently. In addition, copper is essential for human metabolism, especially as an active center in enzymatic reactions (Gala *et al.*, 2014). As a result, copper is used as a supplement in order to help the human body produce red blood cells, keep nerve cells and the immune system healthy, and help form collagen as a key

of bones and connective tissue (Wu *et al.*, 2003; Macias *et al.*, 2003; Gala *et al.*, 2014).

The major source of copper is chalcopyrite, polymetallic manganese sea nodule, copper converter slag and now many e-wastes like printed circuit board (Sridhar and Verma, 2011). Many hydrometallurgical purification methods have been established for the extraction of copper from acidic solutions using organophosphorus, particularly solvent extraction (Sole and Hiskey, 1995). In fact, the solvent extraction method can be applied for the treatment of both concentrated and dilute solutions. However, the solvent extraction method has several problems: (1) use of large amounts of organic solvents that may affect the environment and the human body, (2) difficulty in phase separation between the organic and aqueous phases, (3) loss of extractants and/or

organic solvents via dissolution in the aqueous phase.

The immobilization (Nishihama *et al.*, 2004 and 2014; Ogata *et al.*, 2015a and 2015b; Kondo *et al.*, 2015a) and microencapsulation (Shiomori *et al.*, 2003; Minamihata *et al.*, 2007; Matsushita *et al.*, 2011; Kondo *et al.*, 2014 and 2015b) of the extractant is one of the methods used to solve these problems. Encapsulation of extractants used in solvent extraction systems within microcapsules is expected to be an effective method for separating various substances such as metal ions (Shiomori *et al.*, 2003; Minamihata *et al.*, 2007; Matsushita *et al.*, 2011), because of the good separation properties of the encapsulated extractants, which have been proven in solvent extraction systems, and because of the high capacity for the extracted chemicals in the interior of the polymeric particles. The extraction rate of metal ions for systems using polymeric particles containing extractants increases significantly when the diameter of polymeric particles containing tri-*n*-octylamine decreases to less than 20  $\mu\text{m}$  (Minamihata *et al.*, 2007).

Phenolic oximes are used extensively in the recovery of various transition metals, mostly the recovery of copper and their suitability arises from their coordination chemistry (Smith *et al.*, 2003). They are strong enough extractants to extract copper from acidic aqueous solutions because of the pseudo-macrocyclic structure of the complex. Furthermore, the strong interligand hydrogen bonds between oxime hydrogen and phenolic oxygen atoms compose a planar donor set, and the cavity fits Cu(II) particularly well (Wilson *et al.*, 2014). However, the hydrophobicity of the oximic extractants may cause the hydrolysis of the imine bond attached to the phenolic structure in two-phase systems to be difficult (Wilson *et al.*, 2014). Ketoximes appear to be more stable than aldoximes and the phenolic oximes are more stable than the aliphatic  $\alpha$ -hydroxyoximes such as LIX-63 (Wilson *et al.*, 2014). LIX84-I is a phenolic oximes derivative with the ability to extract copper from acidic aqueous solutions (Wilson *et al.*, 2014).

Our previous work has shown the ability of LIX84-I impregnated with the polymeric particles extracted Ni(II) ion from aqueous phase in the range of pH 3–6 (Kitabayashi *et al.*, 2013). In this paper, we report on copper(II) metal extraction using polymeric particles containing LIX84-I, which has many large interconnected-spherical pores prepared from water-in-oil-in-water

(W/O/W) emulsions by *in situ* polymerization (Ijichi *et al.*, 1997; Kitabayashi *et al.*, 2013). The interconnected spherical pores are open to the outside of the polymeric particles and can be freely accessed by water from the exterior of the polymeric particles. The extraction of copper(II) using the polymeric particles containing LIX84-I from ammonium sulfate solutions has been investigated under various pH values and initial Cu(II) concentrations in the aqueous solution as well as the back-extraction of Cu(II) from polymeric particles to aqueous solutions. Further, the geometrical structure of the LIX-84-I-Cu(II) complex in the polymeric particles and in hexane was measured using Fourier transform infrared (FT-IR) spectroscopy and electron paramagnetic resonance (EPR) instrument analysis.

## 1. Experimental

### 1.1 Reagents

1-(2-hydroxy-5-nonylphenyl) ethanone oxime (LIX84-I, Cognis Co. Ltd.) was used as the extractant. Monomeric divinylbenzene (DVB) were purchased from Wako Pure Chemicals Co. and washed with a 10 wt% NaOH aqueous solution to remove the polymerization inhibitor. The monomers were stored in a refrigerator until use. Tri-*n*-octylamine (TOA), 2,2'-azobis (4-methoxy-2,4-dimethylvaleronitrile) (ADVN), polyvinyl alcohol (PVA, polymerization degree approximately 500), sodium dodecylsulphate (SDS), ammonium sulfate, copper sulfate hexahydrate were purchased from Wako Pure Chemical Co. Hexaglycerin ricinoleic acid (818SX) was purchased from Taiyo Kagaku Co.

### 1.2 Determination of LIX84-I purity

The extractant, LIX-84-I, is a mixture of the active extractant molecules that is, 1-(2-hydroxy-5-nonylphenyl) ethanone oxime and the diluent kerosene. The purity of the extractant molecule was determined based on the quantitative relationship between the extractant molecule and Cu(II) in the solvent extraction system (Sana *et al.*, 2000). An aqueous solution of  $\text{CuSO}_4/(\text{NH}_4)_2\text{SO}_4$  (10 mL) and the kerosene solution of LIX84-I (10 mL) were placed together in a 20 mL tube and shaken for 72 h at 303 K. The aqueous and organic phases were separated 30 min after shaking was stopped. The copper concentration was measured in either the aqueous or organic phase was measured using inductively coupled plasma atomic emission

spectroscopy (ICP-AES) (ICPS-8100, Shimadzu Corporation). The purity of LIX84-I was calculated from Eq. (1) as follows:

$$C_{\text{LIX84-I}} = 2Q_{\text{eq}} \quad [\text{mmol/L}] \quad (1)$$

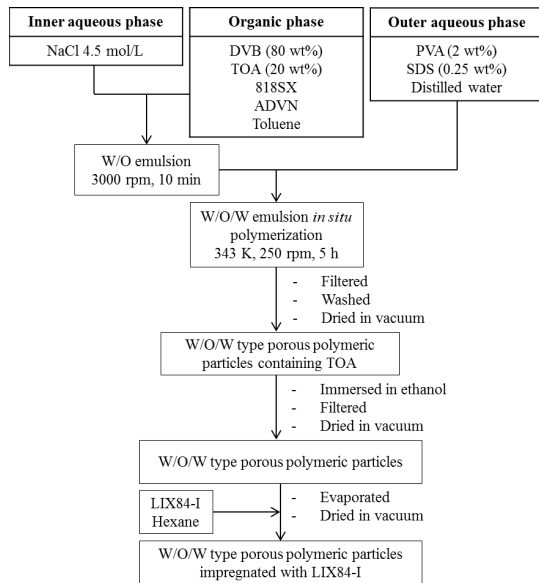
Purity  $\pi$  [wt%]

$$= \frac{C_{\text{LIX84-I}} \times M_{\text{LIX84-I}} \times V_{\text{kerosene}}}{W_{\text{LIX84-I}}} \times 100 \quad (2)$$

Where  $C_{\text{LIX84-I}}$ ,  $Q_{\text{eq}}$ ,  $M_{\text{LIX84-I}}$ ,  $V_{\text{kerosene}}$ ,  $W_{\text{LIX84-I}}$  are the molarity of LIX84-I in the solvent extraction system, equilibrium extraction amount of Cu(II), molecular mass of LIX84-I, volume of kerosene and weight of LIX84-I used, respectively.

### 1.3 Preparation of polymeric particles

The preparation scheme of the porous polymeric particles and the impregnation of LIX84-I into the particles is shown in **Figure 1**. An aqueous solution containing NaCl at 4.5 mol/L was used as the inner aqueous phase (8 mL). The organic phase (72 mL) was prepared by dissolving the extractant, TOA (20 wt%), the surfactant, 818SX (10 wt%), the initiator, ADVN (1 wt%), and the wall material DVB (80wt%) in toluene (10 wt%). The water-in-oil (W/O) emulsion was prepared by adding the inner aqueous phase to the organic phase and agitating at 3,000 rpm for 10 min. The (W/O) emulsion was added to the outer aqueous phase (720 mL), which was a mixture of the PVA (2 wt%) and SDS aqueous solutions (0.25 wt%), at 343 K with



**Fig. 1** Preparation scheme of polymeric particles with interconnected spherical pores impregnated with LIX84-I

stirring at 250 rpm to afford the (W/O/W) emulsion. The solution was agitated at 250 rpm and 343 K for 5 h. The polymeric particles obtained were washed with water, dried under vacuum overnight, and then immersed in ethanol to remove TOA. The polymeric particles were collected after filtration, dried under vacuum, and then immersed in a hexane solution of LIX84-I overnight. The hexane was removed from the polymeric particles with a rotary evaporator and the polymeric particles containing LIX84-I were obtained after drying under vacuum.

### 1.4 Measurement of degree of impregnation of the polymeric particles containing LIX84-I

In order to determine the amount of LIX84-I impregnated in the polymeric particles, the polymeric particles were added to ethanol to elute LIX84-I from the polymeric particles, and the amount of LIX84-I in the ethanol solution was measured using the weight measurement method. The molar content of LIX84-I,  $E'$ , the percentage content of LIX84-I in the polymeric particles,  $E$ , the impregnated yield of LIX84-I,  $E^*$ , and  $E''$  based on LIX84-I purity were calculated using Eqs. (3), (4), (5) and (6), respectively.

$$E' = \frac{W_{\text{pp+LIX84-I,ini}} - W_{\text{pp+LIX84-I}}}{W_{\text{pp+LIX84-I,ini}}} \left[ \frac{\text{mmol}}{\text{g}} \right] \quad (3)$$

$$E = E' \times M_{\text{LIX84-I}} \times 100 \quad [\%] \quad (4)$$

$$E^* = \frac{E \times Y_{\text{pp}}}{W_{\text{LIX84-I}}} [\%] \quad (5)$$

$$E'' = \frac{\text{purity} \times \pi \times E'}{100} \quad [\text{mmol/g}] \quad (6)$$

$W_{\text{pp+LIX84-I,ini}}$ ,  $W_{\text{pp+LIX84-I}}$ ,  $W_{\text{LIX84-I}}$ ,  $Y_{\text{pp}}$ , and  $M_{\text{LIX84-I}}$  are the initial weight of the polymeric particles and LIX84-I used in the elution, weight of the polymeric particles and LIX84-I after elution, weight of LIX84-I after impregnation, impregnation weight of polymeric particles, and molar mass of LIX84-I, respectively.

### 1.5 Observation and analysis of the polymeric particles

The morphologies of the polymeric particles containing LIX84-I were observed using scanning electron microscopy (SEM) (TM-1000, Hitachi, High Technology Corporation) and a digital microscope (VHX-600 system, KEYENCE Corporation). The diameter of the polymeric particles was measured from the digital microscope images (Kitabayashi *et al.*, 2013).

### 1.5.1 FTIR analysis procedure

A small amount of polymeric particles, polymeric particles impregnated with LIX84-I, and polymeric particles impregnated with LIX84-I-Cu(II) was placed on KBr plates and analysed using FT/IR-300 (JASCO Corporation).

### 1.5.2 EPR analysis procedure

Five milligrams of polymeric particles impregnated with LIX84-I-Cu(II) complex powder sample were placed in a quartz sample tube with diameter of 5 mm, and used for EPR analysis. One milliliter of LIX84-I-Cu(II) (prepared by using LIX84-I as the organic phase and Cu(II) solution as the aqueous phase) was also placed in a quartz tube. EPR spectra were measured using an X-band EPR spectrometer (JES TE-100, JEOL Ltd.) at a microwave frequency of 9.44 GHz, magnetic field of 335.8 mT, field amplitude of  $\pm 100$  mT, field modulation of 100 kHz, modulation width of 0.079 mT, microwave power of 5 mW, time constant of 0.3 s, and sweep time of 4 min. Mn(II) in MnO was used as the standard. A computer simulation of EPR spectra was conducted using a WIN-RAD EPR data analyzer. The software, being based on a well-known algorithm (Oehler and Janzen, 1982), provides an interactive least square fit with manual parameter optimization.

### 1.6 Extraction of Cu(II) from aqueous solutions

The extraction of Cu(II) into the polymeric particles was carried out batch-wise. The prepared polymeric particles impregnated with LIX84-I (0.1 g) were added to  $30 \times 10^{-3}$  L of the 0.5 mol/L  $(\text{NH}_4)_2\text{SO}_4$  aqueous solution containing Cu(II) and shaken for 12 h at 303 K. After extraction, the polymeric particles were removed from the raffinate via filtration. The concentrations of Cu(II) in the raffinate and the feed solutions were measured using ICP-AES (ICPS-8100, Shimadzu Corporation). The amount of Cu(II) extracted into the polymeric particles,  $q_{\text{eq}}$ , and the forward extraction ratio,  $E_{\text{e}}$ , were calculated using Eqs. (7) and (8):

$$q_{\text{eq}} = \frac{(C_{\text{Cu,aq,ini}} - C_{\text{Cu,aq}}) \times V_{\text{aq}}}{Mw_{\text{Cu}} \times W_{\text{pp}}} \quad [\text{mmol/g}] \quad (7)$$

$$E_{\text{e}} = \frac{C_{\text{Cu,aq,ini}} - C_{\text{Cu,aq}}}{C_{\text{Cu,aq,ini}}} \times 100 \quad [\%] \quad (8)$$

where  $C_{\text{Cu,aq,ini}}$ ,  $C_{\text{Cu,aq}}$ ,  $V_{\text{aq}}$ ,  $Mw_{\text{Cu}}$  and  $W_{\text{pp}}$  are the initial concentration of Cu(II) in the aqueous phase, equilibrium concentration of Cu(II) in the aqueous solution after extraction, volume of the aqueous phase, molar mass of Cu(II) and weight of the polymeric particles used for the extraction, respectively.

### 1.7 Back-extraction of Cu(II) extracted in the polymeric particles

The back-extraction of Cu(II) extracted into the polymeric particles to a new aqueous phase was carried out batch-wise. The polymeric particles impregnated with LIX84-I (0.10 g) were added to  $30 \times 10^{-3}$  L of the 0.5 mol/L  $(\text{NH}_4)_2\text{SO}_4$  aqueous solution containing excess Cu(II) and shaken for 12 h at 303 K. After extraction, the polymeric particles were recovered from the raffinate via filtration and dried. Then the impregnated polymeric particles loaded with Cu(II) were mixed with  $30 \times 10^{-3}$  L of an aqueous  $\text{H}_2\text{SO}_4$  solution adjusted to pH 1–9 for 24 h at 303 K. After back-extraction, the polymeric particles were recovered from the raffinate via filtration. The Cu(II) concentration in the raffinate solution was measured using ICP-AES (ICPS-8100, Shimadzu Corporation). The amount of Cu(II) eluted into the aqueous solution,  $q_{\text{b}}$ , and the back-extraction ratio of Cu(II) to the aqueous phase,  $E_{\text{b}}$ , were calculated using Eqs. (9) and (10);

$$q_{\text{b}} = \frac{C_{\text{Cu,aq,eluted}} \times V_{\text{aq}}}{W_{\text{pp}}} \quad [\text{mol/kg}] \quad (9)$$

$$E_{\text{b}} = \frac{q_{\text{b}}}{q_{\text{eq}}} \cdot 100 \quad [\%] \quad (10)$$

where  $C_{\text{Cu,aq,eluted}}$  is the concentration of Cu(II) in the aqueous solution after back-extraction.

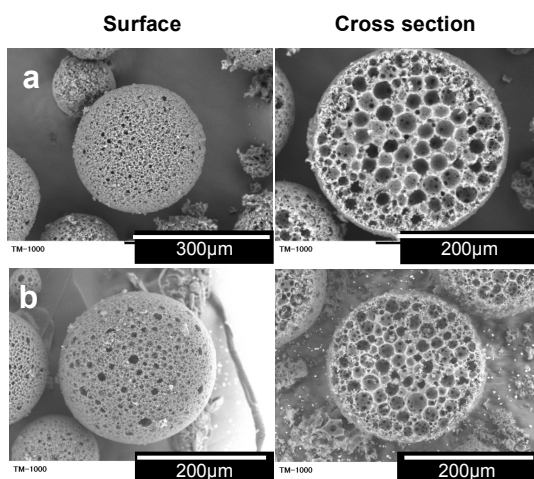
## 2. Results and Discussion

### 2.1 Observation of polymeric particles containing LIX84-I

The morphologies of the obtained (W/O/W) type polymeric particles impregnated with TOA and LIX84-I are shown in **Figure 2**.

They have spherical structures, porous and rough surfaces with the large interconnected spherical pores inside the polymeric particles. The average diameters of (W/O) and (W/O/W) emulsion polymeric particles are approximately around 10 and 200  $\mu\text{m}$ , respectively. The

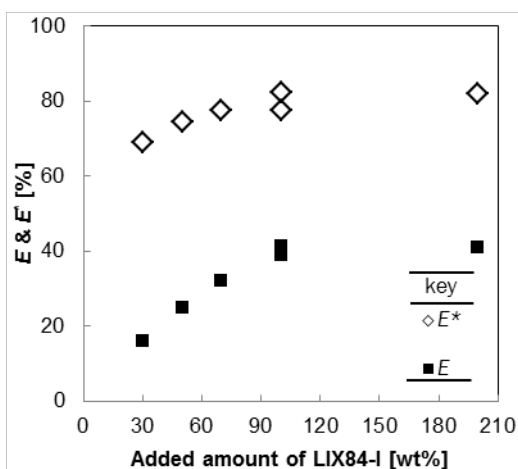
morphologies of polymeric particles containing TOA and those polymeric particles containing LIX84-I were nearly identical when considering that LIX84-I exists as a concentrated liquid in a small pore and in the surface of the polymer wall of the polymeric particles.



**Fig. 2** SEM images of polymeric particles containing (a) TOA and (b) LIX84-I

## 2.2 Impregnation efficiency of LIX84-I in the polymeric particles

The amount of LIX84-I impregnated in the polymeric particles was measured using the gravimetric method. The encapsulation efficiencies of LIX84-I shown as  $E$  and  $E^*$  were approximately 40% and 70–80%, respectively as shown in **Figure 3**. Visual identification of the color change from white to cloudy orange confirmed that LIX84-I was successfully impregnated in the polymeric particle and usable

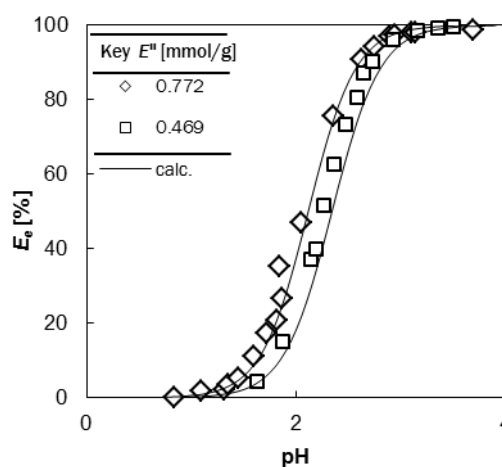


**Fig. 3** Effect of LIX84-I concentration on percentage content ( $E$ ) and impregnated yield ( $E^*$ ) of LIX84-I

for extraction of Cu(II).

## 2.3 Extraction and back-extraction behavior of Cu(II) using polymeric particles impregnated with LIX84-I

The extraction of Cu(II) was performed at initial pH of 1.4 using polymeric particles containing LIX84-I at 0.772 mmol/g, as shown in **Figure 4**. On the other hand, when the amount of LIX84-I encapsulated in the polymeric particles was 0.469 mmol/g, the initial pH of Cu(II) extracted into the polymeric particles was shifted to 1.6 and a constant value was reached at pH 3 for both. It can be postulated that at the higher amount of LIX84-I encapsulated in the polymeric particles, the starting pH of Cu(II) ion extraction was shifted to a lower pH by considering the susceptibility of LIX84-I to hydrolysis under acidic conditions (Wilson *et al.*, 2014). When there was a high concentration of LIX84-I in the polymeric particle, more LIX84-I would be hydrolyzed, increasing the hydrogen ion concentration in the polymeric particle. Hence, the extraction pH range decreased to an acidic range.



**Fig. 4** Effect of pH on Cu(II) extraction efficiency,  $E_e$  ( $C_{Cu,ini} = 10 \text{ mg/L}$ ,  $W_{pp} = 0.10 \text{ g}$ ,  $V_{aq} = 30 \times 10^{-3} \text{ L}$ )

The color of the polymeric particles after the extraction was dark green as the pH value increased. Since it is a liquid–solid extraction system, the liquid solution has a cloudy green color. The color change of the polymeric particles before and after the extraction proved that Cu(II) ions were extracted into the polymeric particles. The color of the polymeric particles at around pH 1 or lower was also observed. The polymeric particles remain white in color which meant that

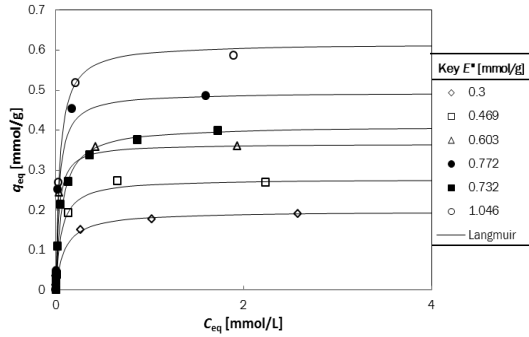
no Cu(II) was extracted into the polymeric particles at  $\text{pH} \leq 1$ .

The amount of Cu(II) extracted into the polymeric particles increased with increasing initial concentration of Cu(II) in the aqueous solution and amount of LIX84-I impregnated in the polymeric particles and reached a constant value at a high Cu(II) concentration as shown in **Figure 5**.

The extraction behavior of Cu(II) into the polymeric particles conformed well to Langmuir-type adsorption as shown in Eq. (11), where  $q_{\text{eq}}$ ,  $q_{\text{max}}$ ,  $K$ , and  $C_{\text{eq}}$  are the molar equilibrium amount of Cu(II) extracted into the polymeric particles, maximum molar amount of Cu(II) in the polymeric particles, equilibrium constant and equilibrium concentration of Cu(II) in the aqueous phase, respectively. The values of  $q_{\text{max}}$  and  $K$  were calculated from the results in Figure 5 using Eq. (12).

$$q_{\text{eq}} = \frac{q_{\text{max}} K C_{\text{eq}}}{1 + K C_{\text{eq}}} \quad (11)$$

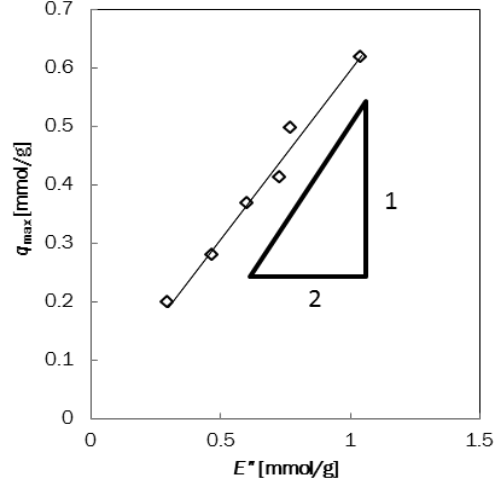
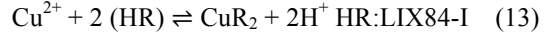
$$\frac{1}{q_{\text{eq}}} = \frac{1}{q_{\text{max}}} + \left( \frac{1}{K q_{\text{max}}} \right) \left( \frac{1}{C_{\text{eq}}} \right) \quad (12)$$



**Fig. 5** Effect of equilibrium concentration of Cu(II) on extraction of Cu(II) from the experimental results and by calculation ( $W_{\text{pp}}=0.1\text{g}$ ,  $V_{\text{aq}}=30 \times 10^{-3}\text{L}$ ,  $C_{\text{Cu,ini}}=0-9.442\text{mmol/L}$ ,  $\text{pH}_{\text{eq}}=3.0$ )

The relationship between the molar content of LIX84-I per gram of the polymeric particles,  $E^*$ , and the maximum molar amount of Cu(II) extracted into the polymeric particles,  $q_{\text{max}}$ , gave a straight line with a slope of 1/2 when considering that the purity of LIX84-I is 52.4wt% as shown in **Figure 6**. It is assumed that two molecules of LIX84-I react with each Cu(II) ion.

The stoichiometry of the complex reaction of LIX84-I-Cu(II) in the polymeric particles is shown below:



**Fig. 6** Relationship between molar content of LIX84-I in the microcapsules and maximum extraction quantity of Cu(II) ( $W_{\text{pp}}=0.1\text{g}$ ,  $V_{\text{aq}}=30 \times 10^{-3}\text{L}$ )

## 2.4 Mechanism of Cu(II) extraction into the polymeric particles impregnated with LIX84-I

The extraction of Cu(II) with the polymeric particles impregnated with LIX84-I was analyzed according to Eq. (13), the equilibrium constant,  $K_{\text{eq}}$ , of the extraction can be represented as in Eq. (14). The distribution coefficient,  $D$ , of Cu(II) is written as in Eq. (15). The logarithm of Eq. (14) where  $D$  is substituted is shown in Eq. (16).

$$K_{\text{eq}} = \frac{[\text{CuR}_2][\text{H}^+]^2}{[\text{Cu}^{2+}][\text{HR}]^2} \quad [\text{kg/L}] \quad (14)$$

$$D = \frac{[\text{CuR}_2]}{[\text{Cu}^{2+}]} \quad [\text{L/kg}] \quad (15)$$

$$\log D = 2 \log \left( \frac{[\text{HR}]}{[\text{H}^+]} \right) + \log K_{\text{eq}} \quad (16)$$

The equilibrium constant,  $K_{\text{eq}}$ , of the complex reaction was obtained from Eq. (14) through the plot of  $\log D$  versus  $\log \frac{[\text{HR}]}{[\text{H}^+]}$ . All of the results lay on a straight line whose slope was 2, as shown in **Figure 7**, and the intercept obtained from the graph was  $K_{\text{eq}} = 1.65 \times 10^{-3}\text{kg/L}$  ( $\log K_{\text{eq}} = -2.78$ ).

The reaction mechanism shown in Eq. (13) is valid as the calculation result fits to the

experimental data well (see Figure 4) according to  $K_{eq} = 1.65 \times 10^{-3}$  kg/L and the stoichiometry of the reaction.

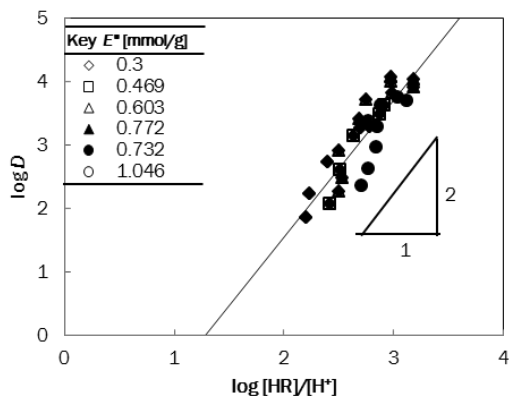


Fig. 7 Relationship between  $\log D$  and  $\log [HR]/[H^+]$

## 2.5 Back-extraction of Cu(II) from polymeric particles

Cu(II) trapped in the polymeric particles could be back-extracted using 20 mL of 0.5 M  $H_2SO_4$ ; the back extraction percentage of Cu(II) was over 100%. This shows that the Cu(II) ions trapped in the polymeric particles were completely back-extracted into the aqueous solution by 0.5 M  $H_2SO_4$ . This means the extraction of the metal ion using the polymeric particles impregnated with LIX84-I proceeds reversibly. The experimental data are listed in Table 1.

**Table 1** Results of back-extraction of Cu(II) from the polymeric particles

$pH_b$	$q_{eq}$ [mmol/g]	$q_b$ [mmol/g]	$E_b$ [%]
0.24	0.180	0.181	101
0.23	0.190	0.205	108
0.25	0.429	0.437	102
0.29	0.491	0.521	106

The protonation of the phenolic oxygen atom occurs under strong acidic conditions (0.5 M  $H_2SO_4$ ), so it could easily disrupt the formation of the bond in the LIX84I-Cu(II) and subsequently release the Cu(II) ion from LIX84-I trapped in the polymeric particles to the description medium (0.5 M  $H_2SO_4$ ).

## 2.6 FTIR analysis of the interaction between Cu(II) and LIX84-I in the polymeric particles

The Formation of the LIX84-I-Cu(II) complex in the polymeric particles was also investigated using FTIR spectroscopy (FT-IR/300, resolution of  $4\text{ cm}^{-1}$ ). IR spectra of each molecule shown in Figure 8 display the characteristic vibrations of PDVB, LIX84-I, PDVB-LIX84-I, and PDVB-LIX84-I-Cu(II). Absorption bands at 1579, 1593, 1438, 1456, and 1479  $\text{cm}^{-1}$  are the characteristic vibration bands of PDVB. The absorption bands at 1579 and 1593  $\text{cm}^{-1}$  are characteristic of carbon-carbon double bond in ring stretching vibrations and three absorption bands appears at 1438, 1456 and 1479  $\text{cm}^{-1}$  are assigned to conjugated carbon-carbon double bond stretching vibrations. The absorption band at 983  $\text{cm}^{-1}$  is assigned to  $=CH/=CH_2$  stretching vibrations (Goldmann *et al.*, 2009; Karagoz *et al.*, 2009; Chaiyasat *et al.*, 2011; Wang *et al.*, 2014).

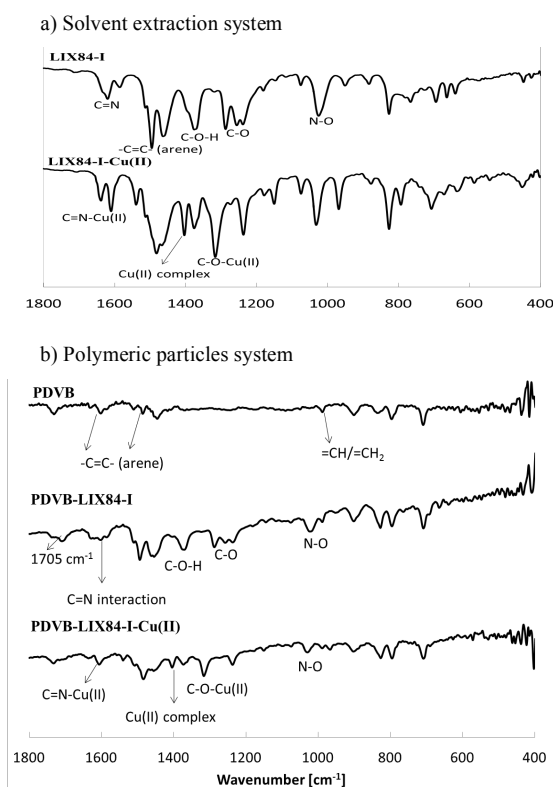


Fig. 8 FTIR spectrum of PDVB, LIX84-I, PDVB-LIX84-I, and copper(II) complex

The IR spectrum of pure LIX84-I is shown in Figure 8, and the absorption bands are attributed to the stretching vibrations characteristic of LIX84-I. The absorption bands at



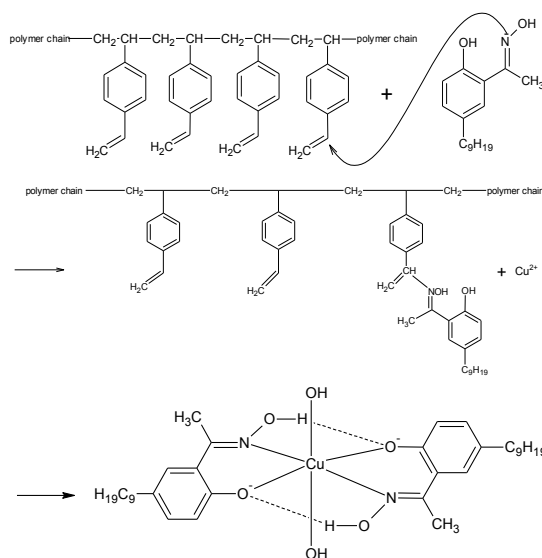
1577 and 1612  $\text{cm}^{-1}$  are assigned to C=N stretching vibrations. The absorption bands at 1506, 1493 and 1454  $\text{cm}^{-1}$  are assigned to -C=C- (arene) stretching vibrations. The absorption band of C-O-H attached to the phenolic structure appears at 1365  $\text{cm}^{-1}$ . Three absorption bands at 1258, 1233, and 1231  $\text{cm}^{-1}$  are assigned to stretching vibrations of carbon-oxygen bonds attached to the phenolic structure. Lastly, the absorption band at 1014  $\text{cm}^{-1}$  is assigned to nitrogen-oxygen stretching vibrations (Ramachandra Reddy and Priya, 2004; Park *et al.*, 2010).

On the other hand, further investigation of the LIX84-I-Cu(II) complex in the solvent extraction system was carried out and revealed a new absorption band, which indicates a coordination complex between Cu(II) and LIX84-I. The absorption band at 1600  $\text{cm}^{-1}$  is assigned to C=N-Cu(II) stretching vibrations; the higher wavenumber indicates coordination to Cu(II). The absorption band at 1402  $\text{cm}^{-1}$  is assigned to the Cu(II) complex. The shifted absorption band at 1363  $\text{cm}^{-1}$  indicates C-O-H stretching vibrations and a new absorption band at 1311  $\text{cm}^{-1}$  is assigned to the C-O-Cu(II) coordination bond. The absorption band at 1027  $\text{cm}^{-1}$  is assigned to N-O stretching vibrations (Ramachandra Reddy and Priya, 2004; Park *et al.*, 2010).

The IR spectrum of PDVB-LIX84-I displays a different small peak for C=N, and a new absorption band appears at 1705  $\text{cm}^{-1}$  near the absorption bands of C=N. The IR spectrum of LIX84-I shows two narrow absorption bands for C=N stretching vibrations; however the IR spectrum of PDVB-LIX84-I shows a broader absorption band for C=N. This indicates that there is an interaction between LIX84-I and the polymeric particle's wall. Furthermore, there are no differences in the IR spectrum of LIX84-I-Cu(II) complexes form in the solvent extraction and polymeric particle systems. They showed similar spectrum after complexation with Cu(II).

Polymeric particles have a vinyl chain attached to the wall which acts as an active group and can be modified, as the carbon-carbon double bond can be converted into a single bond (Goldman *et al.*, 2009; Karagoz *et al.*, 2009). The interaction between LIX84-I and the polymeric particle wall is caused by the attack of the free electron pair on the nitrogen atom on the vinyl chain. However, the copper in the aqueous

solution formed a stable complex with LIX84-I, as the oxygen and nitrogen atoms could act as donor atoms. A mechanism of the formation of a complex between LIX84-I and Cu(II) in the polymeric particles is suggested in **Figure 9**.



**Fig. 9** Schematic illustrations of interaction of LIX84-I with polymeric particle wall and formation of LIX84-I-Cu(II) complex

## 2.7 EPR analysis of LIX84-I-Cu(II) complex in the polymeric particles

To analyze the coordination structure of the LIX84-I-Cu(II) complex, the EPR spectra of LIX84-I-Cu(II) and PDVB-LIX84-I-Cu(II) were measured (**Figure 10**). Divalent copper ion, Cu(II), has a  $4s^2 3d^9$  electron configuration and an unpaired electron in the  $d$ -orbital that is naturally paramagnetic and suitable for analysis using EPR spectroscopy (Nakajima *et al.*, 2001, 2006). The paired and unpaired electrons in the orbital could determine the magnetic properties of metal ions. The EPR spectrum of the LIX84-I-Cu(II) complex shown in Figure 10 could be used to determine the geometrical structure of the LIX84-I-Cu(II) complex in the polymeric particles.

Copper with a  $3d^9$  electron configuration and nuclear spin,  $S = 1/2$  and  $I(\text{Cu}) = 3/2$ , could be coordinated by four ligands and form an octahedral geometrical structure (Nakajima *et al.*, 2001, 2006). The EPR spectrum given in Figure 10 could be used to determine the structure of the LIX84-I-Cu(II) complex in the polymeric particles, as the spectrum shows a peak similar to those of Cu(II) complexes with other ligands including

microbial cells. The spectra in Figure 10 indicate the octahedral geometrical structure (Nakajima *et al.*, 2001, 2006).

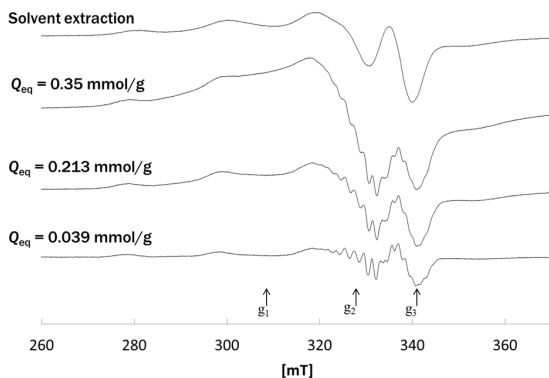


Fig. 10 EPR spectra of LIX84-I-Cu(II) complex formation in the polymeric particles

The EPR spectrum of the PDVB-LIX84-I-Cu(II) complex (Cu 0.35 mmol/g) indicates a typical axial type complex with hyperfine couplings caused by  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  ( $I = 3/2$ ) and  $^{14}\text{N}$  ( $I = 1$ ) nuclei. The EPR parameters  $g_{//}$ ,  $g_{\perp}$ ,  $A_{//}$ ,  $A_{\perp}$ , and  $A_N$  were estimated to be 2.198, 2.040, 216, 27, 15  $\text{mcm}^{-1}$ , respectively, by computer simulation. Similar EPR parameters were obtained for an LIX622-Cu(II) complex by Ocio and Elizalde (2006). Peisach and Blumberg showed a diagram (Peisach-Blumberg diagram) on the EPR parameters  $g_{//}$  and  $A_{//}$  for copper proteins, and found the separate areas for ligand atoms in the copper proteins as shown in Figure 11 (Peisach and Blumberg, 1974).

Present results depicted in the Peisach-Blumberg diagram include in the 2N2O area (Figure 11), which confirmed the proposed structure of the LIX84-I-Cu(II) complex in Figure

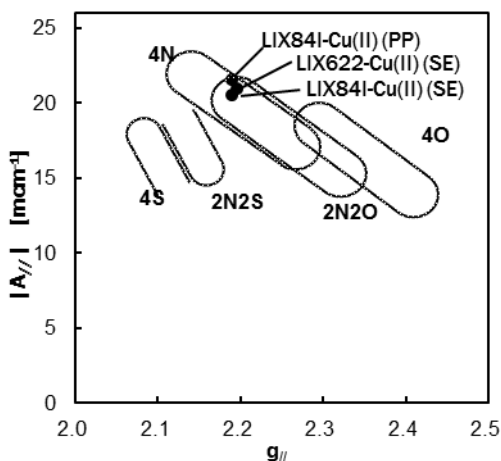


Fig. 11 Relationship between spin Hamiltonian parameters  $g_{//}$  and  $A_{//}$

9. The EPR spectrum of LIX84-I-Cu(II) in the solvent extraction system, prepared by using LIX84-I as the organic phase and a Cu (II) solution as the aqueous phase, also indicated axial type, though the hyperfine structure at  $g_{\perp}$  was not observed owing to the restricted molecular motion of the LIX84-I chain in the solvent extraction system.

## Conclusion

Polymeric particles impregnated with LIX84-I successfully extracted Cu(II) ions from aqueous solution in the pH range of 1–3 and plateau was reached at a high initial concentration; they gave an equilibrium constant of  $K_{\text{eq}} = 1.65 \times 10^{-3} \text{ kg/L}$ . The FTIR spectra of polymeric particles without and with trapped ligand, indicated an interaction between the polymeric particle wall and the ligand, as a new absorption band appeared at  $1705 \text{ cm}^{-1}$ . Furthermore, the EPR spectrum and parameters of the LIX84-I-Cu(II) complex in polymeric particles indicated an octahedral geometrical structure.

## Nomenclature

$A_{//}, A_{\perp}$	= hyperfine term	[ $\text{mcm}^{-1}$ ]
$C$	= concentration	[ $\text{mol/L}$ ]
$D$	= distribution coefficient	[ $\text{L/kg}$ ]
$E$	= percentage content of LIX84-I	[%]
$E_e$	= extraction efficiency of Cu(II)	[%]
$E_b$	= back-extraction efficiency of Cu(II)	[%]
$E'$	= molar content of LIX84-I	[ $\text{mmol/g}$ ]
$E^*$	= impregnated yield of LIX84-I	[%]
$E''$	= $E'$ based on LIX84-I purity	[ $\text{mmol/g}$ ]
$g_{//}, g_{\perp}$	= Zeeman term	
$K_{\text{eq}}$	= equilibrium constant of eq. (12)	[ $\text{kg/L}$ ]
$M_w$	= molar mass	[ $\text{g/mol}$ ]
$Q_{\text{eq}}$	= extracted amount	[ $\text{mmol/g}$ ]
$q_b$	= amount of Cu(II) back-extracted from the particles	[ $\text{mmol/g}$ ]
$q_{\text{eq}}$	= equilibrium extracted amount of Cu(II) in the particles	[ $\text{mmol/g}$ ]
$q_{\text{max}}$	= maximum amount of Cu(II) in the particles	[ $\text{mmol/g}$ ]
$V$	= volume	[ $\text{L}$ ]
$W$	= weight	[ $\text{g}$ ]

<Subscript>

aq	= aqueous solution
b	= back-extraction
Cu	= copper

eluted = eluted  
e = extraction  
eq = equilibrium  
ini = initial  
LIX84-I = 1-(2-hydroxy-5-nonylphenyl)  
ethanone oxime  
pp = polymeric particle

#### Literature Cited

- Baba, A. A., K. I. Ayinla, F. A. Adekola, M. K. Ghosh, P. C. Rout and A. I. Ambo; "Extraction and Purification of Copper from a Nigerian Chalcopyrite Ore Leach Liquor by Dithizone in Kerosene," *Solvent Extr. Res. Dev. Jpn.*, **22**, 135–146 (2015)
- Chaiyasat, P., A. Chaiyasat, W. Boontung, S. Promdsorn and S. Thipsit; "Preparation and Characterization of Poly(divinylbenzene) Microcapsules Containing Octadecane," *Mater. Sci. Appl.*, **2**, 1007–1013 (2011)
- Gala, L., M. Lawson, K. Jomova, L. Zelenicky, A. Congradyova, M. Mazur and M. Valko; "EPR Spectroscopy of a Clinically Active (1:2) Copper(II)-histidine Complex Used in the Treatment of a Menkes Disease: a Fourier Transform Analysis of a Fluid CW-EPR Spectrum," *Molecules*, **19**, 980–991 (2014)
- Goldmann, A. S., A. Walther, L. Nebhani, R. Joso, D. Ernst, K. Loos, C. Barner-Kowollik, L. Barner and A. H. E. Muller; "Surface Modification of Poly(divinylbenzene) Microspheres via Thiol-ene Chemistry and Alkyne-azide Click Reaction," *Macromolecules*, **42**, 3707–3714 (2009)
- Ijichi, K., Y. Hatate, S. Kiyoyama, K. Shiomori, Y. Baba and Y. Kawano; "Preparation of Cross-linked Microcapsules with Spherical Pores by in Situ Polymerization in (W/O/W) Emulsion System," *Kagaku Kagaku Ronbunshu*, **23**, 303–306 (1997)
- Karagoz, B., Y. Y. Durmaz, B. N. Gacal, N. Bicak and Y. Yagci; "Functionalization of Poly(divinylbenzene) Microspheres by Combination of Hydrobromination and Click Chemistry Processes: a Model Study," *Des. Monomers Polym.*, **12**, 511–522 (2009)
- Kitabayashi, T., T. Sana, S. Kiyoyama, T. Takei, M. Yoshida and K. Shiomori; "Extraction Properties of Nickel (II) with Polymeric Particles with Interconnected Spherical Pores Impregnating with LIX84-I," *Solv. Extr. Res. Dev. Japan*, **20**, 137–147 (2013)
- Kondo, K., S. Hirao and M. Matsumoto; "Column Separation of Nickel and Cobalt Using a Microencapsulated Extractant," *Hydrometallurgy*, **149**, 87–96 (2014)
- Kondo, K., M. Takeda and M. Matsumoto; "Separation of Rare Metals Using Silica Gel Modified with a Surfactant Micelle Containing an Extractant," *Hydrometallurgy*, **158**, 107–113 (2015a)
- Kondo, K., T. Matsuo and M. Matsumoto; "Adsorptive Separation of La, Ce and Pr Using Microcapsules Containing 2-ethylhexylphosphonic Acid Mono-ethylhexylester," *Hydrometallurgy*, **152**, 204–213 (2015b)
- Macias, B., M. V. Villa, I. Garcia, A. Castineiras, J. Borrás, C. Rocio and M. Rocio; "Copper Complexes with Sulfonamides: Crystal Structure and Interaction with pUC18 Plasmid and Hydrogen Peroxide," *Inorg. Chim. Acta*, **342**, 241–246 (2003)
- Matsushita, A., T. Sana, S. Kiyoyama, M. Yoshida and K. Shiomori; "Preparation of Microcapsules Containing PC-88A with Interconnected Spherical Pores and their Extraction Properties of Zn(II)," *Solvent Extr. Res. Dev., Jpn.*, **18**, 123–135 (2011)
- Minamihata, K., S. Kiyoyama, K. Shiomori, M. Yoshida and Y. Hatate; "Preparation of Effective and Fast Extraction Media for Palladium (II) Using Microcapsules," *Ars Separatoria Acta*, **5**, 55–67 (2007)
- Nakajima, A., M. Yasuda, H. Yokoyama, H. Ohya-Nishiguchi and H. Kamada; "Copper Biosorption by Chemically Treated *Micrococcus luteus* Cells," *World J. Microbiol. Biotechnol.*, **17**, 343–347 (2001)
- Nakajima, A., N. Sakai and J. Yamauchi; "Mechanism of Copper(II) Adsorption by Polyvinyl Polyacrylate," *J. Appl. Polym. Sci.*, **102**, 5372–5377 (2006)
- Nishihama, S., A. Kawasaki and K. Yoshizuka; "Separation and Recovery of Eu(III) and Y(III) with Solvent Impregnated Resin Coated by Crosslinked Chitosan," *J. Ion Exch.*, **25**, 93–98 (2014)
- Nishihama, S., G. Nishimura, T. Hirai and I. Komasa; "Separation and Recovery of Cr(VI) from Simulated Plating Waste Using Microcapsules Containing Quaternary Ammonium Salt Extractant and Phosphoric Acid Extractant," *Ind. Eng. Chem. Res.*, **43**, 751–757 (2004)
- Ocio, A. and M. P. Elizalde; "Copper(II) Extraction from Phosphoric Acid Media by

- 5-Dodecylsalicylaldoxime (LIX-622),” *Solvent Extr. Ion Exch.*, **24**, 861–875 (2006)
- Oehler, U. M. and E. G. Janzen; “Simulation of Isotropic Electron Spin Resonance Spectra: a Transportable Basic Program,” *Can. J. Chem.*, **60**, 1542–1548 (1982)
- Ogata, T., H. Narita and M. Tanaka; “Adsorption Behavior of Rare Earth Elements on Silica Gel Modified with Diglycol Amic Acid,” *Hydrometallurgy*, **152**, 178–182 (2015a)
- Ogata, T., H. Narita and M. Tanaka; “Rapid and Selective Recovery of Heavy Rare Earths by Using an Adsorbent with Diglycol Amic Acid Group,” *Hydrometallurgy*, **155**, 105–109 (2015b)
- Park, K. H., H. I. Kim and P. K. Parhi, “Recovery of Molybdenum from Spent Catalyst Leach Solutions by Solvent Extraction with LIX 84-I,” *Sep. Purif. Technol.*, **74**, 294–299 (2010)
- Peisach, J. and W. E. Blumberg; “Structural Implications Derived from the Analysis of Electron Paramagnetic Resonance Spectra of Natural and Artificial Copper Proteins,” *Arch. Biochem. Biophys.*, **165**, 691–708 (1974)
- Ramachandra Reddy, B. and D. N. Priya; “Solvent Extraction of Ni(II) from Sulfate Solutions with LIX 84I: Flow-sheet for the Separation of Cu(II), Ni(II) and Zn(II),” *Anal. Sci.*, **20**, 1737–1740 (2004)
- Ramachandra Reddy, B., K. H. Park and D. Mohapatra; “Process Development for the Separation and Recovery of Copper from Sulfate Leach Liquors of Synthetic Cu-Ni-Co-Fe Matte Using LIX 84 and LIX 973N,” *Hydrometallurgy*, **87**, 51–57 (2007)
- Sana, T., K. Shiomori, Y. Kawano and K. Nagayoshi; “Extraction Equilibrium of Nickel from Aqueous Ammonium Sulfate Solution with 5-dodecylsalicylaldoxime in Kerosene,” *Solvent Extr. Res. Dev., Jpn*, **7**, 206–211 (2000)
- Shiomori, K., H. Yoshizawa, K. Fujikubo, Y. Kawano, Y. Hatate and Y. Kitamura; “Extraction Equilibrium of Precious Metals from Aqueous Acidic Solutions Using Divinylbenzene Homopolymeric Microcapsules Encapsulating Ternary Amine as a Core Material,” *Sep. Sci. Technol.*, **38**, 4057–4077 (2003)
- Smith, A. G., P. A. Tasker and D. J. White; “The Structure of Phenolic Oxime and their Complexes,” *Coord. Chem. Rev.*, **241**, 61–85 (2003)
- Sole, K. C. and J. B. Hiskey; “Solvent Extraction of Copper by Cyanex 272, Cyanex 302 and Cyanex 301,” *Hydrometallurgy*, **37**, 129–147 (1995)
- Sridhar, V. and J. K. Verma; “Recovery of Copper, Nickel, and Zinc from Sulfate Solutions by Solvent Extraction Using LIX 94N,” *E-J. Chem.*, **8(S1)**, S434–S438 (2011)
- Wang, X., L. Chen, Y.-N. Liu and J. Huang; “Macroporous Crosslinked Polydivinylbenzene/polyacryldiethylenetriamine (PDVB/PADETA) Interpenetrating Polymer Networks (IPNs) and their Efficient Adsorption to *o*-aminobenzoic Acid from Aqueous Solutions,” *J. Colloid Interface Sci.*, **429**, 83–87 (2014)
- Wilson, A. M., P. J. Bailey, P. A. Tasker, J. R. Turkington, R. A. Grant and J. B. Love; “Solvent Extraction: the Coordination Chemistry Behind Extractive Metallurgy,” *Chem. Soc. Rev.*, **43**, 123–134 (2014)
- Wu, G., G. Wang, X. Fu and L. Zhu; “Synthesis, Crystal Structure, Stacking Effect and Antibacterial Studies of a Novel Quaternary Copper(II) Complex with Quinolone,” *Molecules*, **8**, 287–296 (2003)