Separation of Pb(II) Ion with Tetraacetic Acid Derivative of Calix[4]arene by Using Droplet-based Microreactor System

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Received: March 3, 2018
Accepted: May 15, 2018

DOI: 10.22146/ijc.34387

Abstract: *In this study, the microreactor system was investigated and compared with the batch-wise system as rapid and effective extractive Pb(II) separation over Fe(III), Cu(II) and Zn(II) with tetraacetic acid calix[4]arene. By using a microreactor system, the Pb(II) extraction percentages reached the maximum of 73, 89 and 100% in 8 sec residence time at equilibrium pH of 2.00, 2.25 and 2.50, respectively. The stripping percentage was 92% at 8 sec residence time by using a microreactor system with 2.0 M HNO_3 as a stripping reagent. Complete separation of Pb(II) over Fe(III), Cu(II) and Zn(II) ions with the tetraacetic acid calix[4]arene in a competitive metal system was achieved at pH 2.00. However, the batch system required 24 h to reach the equilibrium for both extraction and stripping processes. The results suggested that the microreactor system enhanced the Pb(II) extraction and stripping rate up to 10^4 times faster than the batch-wise system.*

Keywords: *microreactor; Pb(II) extraction; separation; calix[4]arene*

■ INTRODUCTION

Efforts concerning environmental research to reduce and prevent environmental pollution, such as green chemistry, renewable resource, efficient operation process and wastewater treatment, are increasing rapidly [1-6]. Amongst, wastewater treatment attracts worldwide attention for its serious effects on the ecosystem, especially in the developing countries. Once the toxic chemicals released into the environment, which reflects on human health damage. One of the main parameters of water pollution is the presence of heavy metals concentration, such as lead (Pb(II)), cadmium (Cd(II)), mercury (Hg(II)) and so on [7]. Pb(II) ion is commonly found in the environment from the mining and industrial activities. Even at the low concentration, Pb(II) pollution could damage the central nervous system and cause mortality [8]. Therefore, Pb(II) removal process has gained the highest interest over the past several years [9-13].

Solvent extraction is one of the widely applied separation methods, in which the extraction efficiency mainly determined by the extraction reagent properties. Several commercial extraction reagents evaluated for efficient Pb(II) separation, however, their separation ability and efficiency not good enough, especially to apply in wastewater treatment, the Pb(II) concentration is in traces while iron (Fe(III)), copper (Cu(II)) and zinc (Zn(II)) concentrations are very high. Calix[4]arene is one of the well-known host compounds due to its discriminatory ability. The size fitting effect and soft-hard nature of its coordination site are the main factors that contribute to calix[4]arene discrimination ability

[14]. By considering both factors as well as properties of the metal ions, some novel host calix[4]arene compounds have been designed for selective separation of Pb(II). It was reported earlier by our group that tetraacetic acid derivative (4Ac) of calix[4]arene showed a high Pb(II) selectivity over Fe(III), Cu(II) and Zn(II) in acidic media due to its suitable coordination site. Moreover, there are four carboxylic acid functional groups, two Pb(II) ions can be loaded for a single host molecule [15]. Therefore, 4Ac shows a very good selectivity and also extraction ability for Pb(II). However, the use of calix[4]arene as the extraction reagent has several drawbacks, such as high price and slow kinetics, as it needs 24 h to reach the equilibrium.

Microreactor is a micro-scale system that employs a reaction process with small amounts of the reactants inside the microchannel having ten to hundred micrometers dimension [16]. The microreactor system has some merits, such as the large surface area per unit volume [17], short diffusion distance for the heterogeneous reaction [18], a reduced amount of reagent [19] and portable analysis [20]. Because of these, the microreactor has been widely applied in protein crystallization [21], organic synthesis [22] and solvent extraction [23]. In our previous work, the precious metal recovery with calix[4]arene derivatives by using the microreactor system was investigated. It shows that high extraction and stripping percentages of Ag(I), Pd(II) and Pt(IV) were obtained just in few seconds reaction time. The stepwise recovery of these metal ions from the real metal waste was achieved, where calix[4]arene extraction reagent was regenerated after the stripping process [24].

In the present work, the microreactor system was investigated and compared with the batch-wise system as rapid and effective extractive Pb(II) separation from Zn(II), Cu(II) and Fe(III) with 4Ac extraction reagent. The separation process of Pb(II) from the model mixture containing the Pb(II), Zn(II), Cu(II) and Fe(III) was reported. Further, the stripping of Pb(II) from laden ligand was carried out with nitric acid as stripping reagent, and the regeneration of ligand after the stripping process was confirmed by FTIR study.

■ EXPERIMENTAL SECTION

Materials

All metal salts in nitrate form, such as $Pb(NO_3)_2$, $Fe(NO_3)_3$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, nitric acid and chloroform are of analytical grade, were purchased from Wako Pure Chemicals (Osaka, Japan). The calix[4]arene derivative, 25,26,27,28-tetrakis(carboxymethoxy)-5,11,17,23-tetrakis (1,1,3,3-tetramethylbutyl)calix[4]arene, was prepared in a similar manner to the procedures previously described by our group [25].

Procedure

Pb(II) extraction and stripping in individual metal system

The aqueous phase prepared by mixing 0.1 mM (M = mol dm^{-3}) Pb(II) in 0.1 M HEPES and 0.1 mM Pb(II) in 0.1 M HNO_3 to adjust the pH solution. The organic phase prepared by dissolving 5.0 mM of 4Ac in chloroform. Batch-wise extraction carried out by mixing both the phases in equal volumes (3 cm^3: 3 cm^3) at 303 K with 150 rpm shaking speed. Extraction time was varied (0.25, 0.5, 1.0, 2.0, 4.0, 8.0, 12.0, 16.0, 20.0, 24.0 h) to find out the optimal time for Pb(II) extraction. The Pb(II) concentration before and after extraction was measured by inductively coupled plasma atomic emission spectroscopy (abbreviated as ICP-AES, Shimadzu ICPS-8100, Japan). The extraction percentage (%E) of Pb(II) calculated by equation (1),

$$\%E = \frac{[Pb(II)]_i - [Pb(II)]_t}{[Pb(II)]_i} \times 100 \quad (1)$$

where $[Pb(II)]_i$ and $[Pb(II)]_t$ are the Pb(II) concentration before and after the extraction process, respectively.

Extraction procedure by using droplet-based microreactor system was carried out in a similar manner to that described previously [14,24] and the experimental setup is shown in Fig. 1. Briefly, the micro-milling process was used to fabricate the glass-glass microreactor device with square microchannels having 200, 200 and 73,000 µm of width, depth, and lengths, respectively. Both phases were injected into the microreactor device through different inlets by using microsyringe pumps (BAS, Model 100, Japan) with an aid

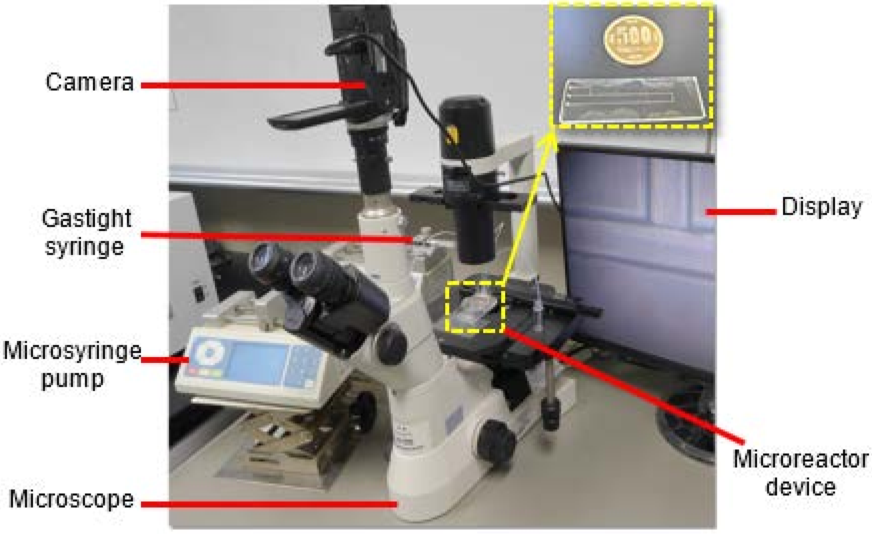

Fig 1. Experimental setup of the droplet-based microreactor system where the microreactor device is shown in the top right corner of the figure

of gastight syringe (Hamilton, Gastight 1001, USA) through PTFE tubes (i.d. 500 µm). The extraction and stripping percentages were investigated by changing the residence time. The volumetric flow rate of each phase was calculated from the ratio of the volume of the microchannel and residence time at room temperature. Both phases were collected in a glass vial and then separated immediately. The Pb(II) extraction percentage was calculated by the equation (1).

The Pb(II) stripping process was evaluated from metal-loaded ligand in organic phase by varying nitric acid concentration in 1:1 ratio of volume. The stripping percentage (%S) was calculated by the following equation (2),

$$\%S = \frac{[Pb(II)]_{aq}}{[Pb(II)]_{org}} \times 100 \qquad (2)$$

where $[Pb(II)]_{aq}$ was the Pb(II) concentration in the aqueous phase after stripping process and $[Pb(II)]_{org}$ was the Pb(II) concentration extracted into the organic phase.

Pb(II) separation from competitive metal system

A mixture of Pb(II), Fe(III), Cu(II) and Zn(II) in 0.1 mM concentration of each metal ion was prepared in HEPES/HNO_3 buffer media as an aqueous phase, while the 5.0 mM 4Ac used as an organic phase. The Pb(II) separation from other metal ions was carried out in batch-wise and microreactor systems as described above. The %E calculated from the ICP-AES measurements and the separation factor for Pb(II) over Fe(III), $\beta_{Pb/Fe}$, described by equation (3),

$$\beta_{Pb/Fe} = \frac{D_{Pb(II)}}{D_{Fe(III)}} \qquad (3)$$

where the $D_{Pb(II)}$ and $D_{Fe(III)}$ is the distribution factor of Pb(II) and another metal ion.

Spectroscopic study of the ligand

The infrared spectra of the 4Ac ligand in the organic phase before and after the Pb(II) loading and also after stripping process were recorded by using a Fourier transform infrared spectrophotometer (abbreviated as FTIR, Shimadzu IR Affinity 1).

■ RESULTS AND DISCUSSION

Pb(II) Extraction and Stripping in the Individual Metal System

The time course dependency for Pb(II) extraction with 4Ac was investigated at pH 2.00 in batch and microreactor extraction systems, which are shown in Fig. 2. In a batch system, the extraction rate is slow, it required 24 h to reach equilibrium. On the other hand, by employing a droplet-based microreactor system, the extraction rate expected to be faster because each droplet works as an individual extraction compartment [24]. Since the microchannel material is made from glass, the

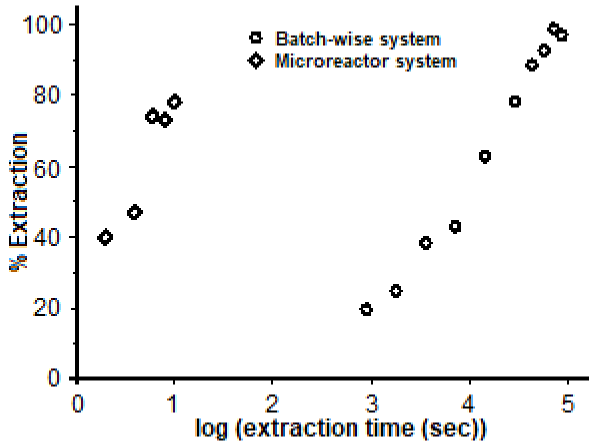

Fig 2. Time course profile of Pb(II) extraction in batch and microreactor systems

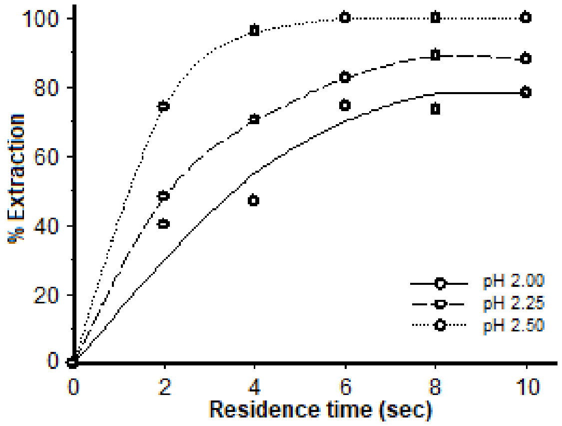

Fig 3. Pb(II) extraction profile at different pH of the aqueous phase in the individual metal system by using microreactor system

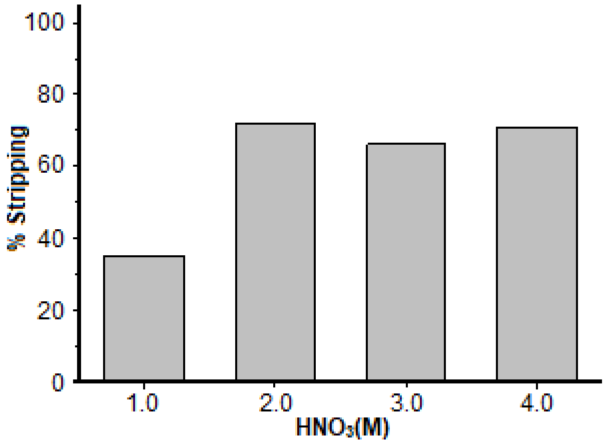

Fig 4. Stripping percentage profile of Pb(II) with varying concentration of nitric acid as stripping reagent

aqueous phase becomes the continuous phase, while the organic phase forms droplets inside the microchannel. The Pb(II) extraction percentage was 80% at 6 sec for microreactor system, while to reach the same extraction percentage, the batch system took 8 h (28,800 sec). In addition, although the temperature for extraction in a microreactor system is lower than the batch system, the microreactor system could enhance the Pb(II) extraction rate up to 10^4 times faster than batch-wise method due to the characteristics of the high specific surface area, short diffusion distance and rapid vortex mixing in each droplet. It was reported that the extraction rate of La(III) and Ce(III) was also enhanced by employing a microreactor system with EHEHPA as an extraction reagent compared with the batch system [26]. However, the enhancement was not so high probably due to using the monodentate EHEHPA ligand. Calix[4]arene as a multidentate ligand that might contribute to the stable complex formation, thus the extraction rate of Ag(I) ion was drastically enhanced from 72 h in a batch system to 2 sec in microreactor system [24].

The effect of aqueous phase pH on extraction percentage of Pb(II) was also investigated by varying the pH of the aqueous solution, i.e. 2.00, 2.25 and 2.50, which is shown in Fig. 3. The extraction percentages of Pb(II) were 73, 89 and 100% at 8 sec residence time for pH 2.00, 2.25 and 2.50, respectively. The results showed that the Pb(II) extraction percentage increased with increasing pH of the aqueous solution. The carboxylic acid functional groups of the 4Ac were easy to deprotonate at higher pH region and the ion exchange reaction took place. The extraction reaction was proposed as in equation (4) [15].

$$H_4L(org) + Pb^{2+}(aq) \rightleftarrows [Pb-H_2L](org) + 2H^+(aq) \qquad (4)$$

The stripping process of Pb(II) from the metal-laden 4Ac ligand at 4 sec residence time was evaluated using 1.0, 2.0, 3.0 and 4.0 M HNO_3 as stripping reagent by using a microreactor system. The result is shown in Fig 4. The stripping percentage was increased and reached a plateau after using 2.0 M HNO_3 as stripping reagent. By increasing residence time, the stripping percentages increased from 51, 72, 78 and 92% for 2, 4, 6 and 8 sec residence time, respectively. It showed that

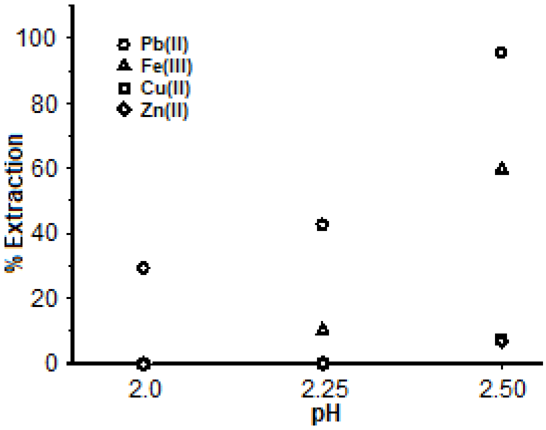

Fig 5. pH dependency on Pb(II) separation from the competitive metal system at 4 sec residence time

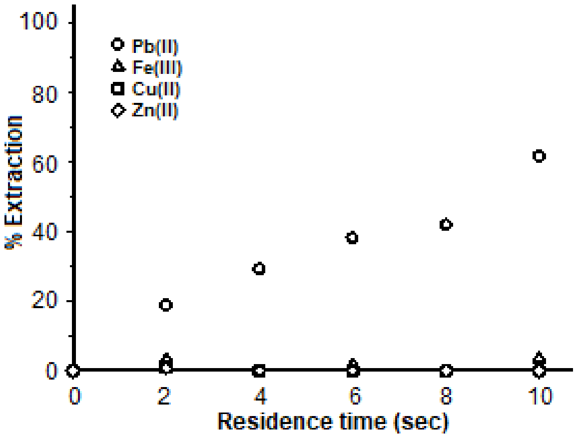

Fig 6. Time course dependency profile of Pb(II) separation from a competitive metal system at pH 2.00

the stripping rate also enhanced by employing the microreactor extraction method compared with the batch-wise system, although complete stripping was not achieved probably due to short residence time.

Pb(II) Separation from the Competitive Metal System

Since 4Ac showed a good extraction ability as well as easy stripping process, the Pb(II) separation over Fe(III), Cu(II) and Zn(II) metal ions in the competitive metal system was carried out. At first, the extraction process of these metal ions was evaluated by varying the pH of the aqueous solution at 4 sec residence time as shown in Fig. 5. The increasing pH of the aqueous solutions also increases the extraction percentages of other metal ions.

Complete separation of Pb(II) from Fe(III), Cu(II) and Zn(II) were achieved at pH 2.00 however the Pb(II) extraction percentage was 29%. On the other hand, 96% extraction of Pb(II) was achieved at pH 2.50 but Fe(III), Cu(II) and Zn(II) found to be 60, 6.9 and 7.5%, respectively. Although the Pb(II) extraction percentage was very high at pH 2.50, the Pb(II) separation was not achieved well. Application of microreactor system for metal ion separation was also reported by other groups, but complete separation was not achieved even just for two ions model mixture [26-27]. Separation factor for La(III) over Ce(III) with EHEHPA extraction reagent was less than 7.0 and the separation factor was found to decrease by increasing pH of the aqueous phase and residence time [26]. On the other hand, separation for Co(II) over Ni(II) with PC88A extraction reagent was less than 32.0 [27]. Poor separation of those ions was mainly caused by the deficient selectivity of the extraction reagent. It was reported earlier by our group [15] that 4Ac extraction reagent has high selectivity for Pb(II) over Fe(III), Cu(II) and Zn(II) in acidic media. Amazingly, in this study, it was found that by using 4Ac, the separation factor of Pb(II) over Fe(III) reached 973.16 at pH 2.00 employing microreactor system. The separation factor of Pb over Fe, $\beta_{Pb/Fe}$ was decreased by increasing the pH of the aqueous solution as listed in Table 1 because the extraction reaction of Fe(III) was different from that of Pb(II) due to a different charge. While the separation factor of Pb over Cu and Zn were established well at pH 2.00 to 2.50. However, in the environment, Fe(III) was also found together with Cu(II) and Zn(II) therefore the time course dependency for Pb(II) separation over Fe(III), Cu(II) and Zn(II) were further investigated at pH 2.00. The results are shown in Fig. 6. As mentioned earlier, complete separation of Pb(II) was achieved and the Pb(II) extraction percentage was increased with increasing the residence time. It clearly shows that complete separation of Pb(II) from the competitive metal

Table 1. The separation factor of Pb(II) over Fe(III) at pH 2.00 to 2.50

pH	$\beta_{Pb/Fe}$
2.00	973.16
2.25	23.27
2.50	14.21

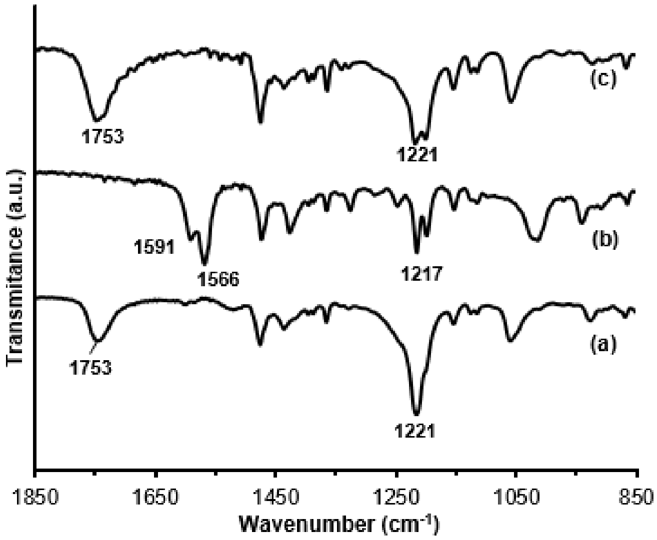

Fig 7. FTIR spectra of 4Ac ligand (a) before and (b) after loading with Pb(II) ion and (c) after stripping with 2.0 M HNO_3 by using microreactor system

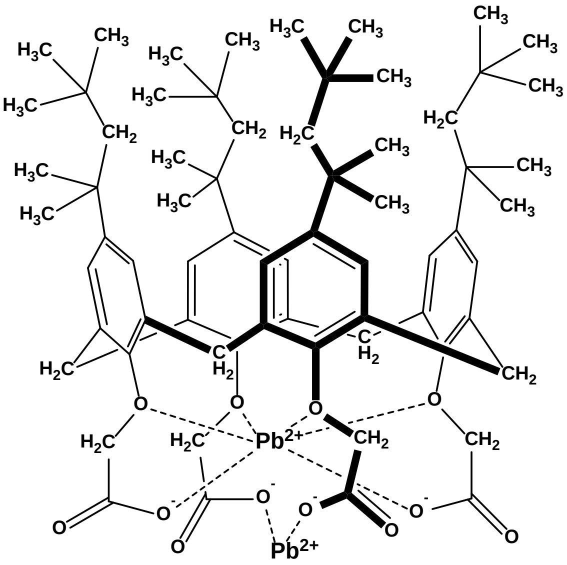

Fig 8. The proposed structure of the $[Pb_2\text{-}L]$ complex

system was achieved by using microreactor. In our recent study, a success separation of Pb(II) over Fe(III), Zn(II), Ni(II), Co(II), and Cu(II) ions in 1.0 M HNO_3 media was also achieved with an amide derivative of calix[4]arene by using microreactor system [28].

Spectroscopic Study of the Ligand

To understand the coordination site of Pb(II) on the 4Ac ligand, the spectroscopic study of the ligand was investigated by FTIR spectra. The FTIR spectra of 4Ac before and after Pb(II) loading as well as after stripping with 2.0 M HNO_3 are shown in Fig. 7. The C=O carbonyl peak was shifted and split from 1753 to 1591 and 1566 cm^{-1} due to the coordination of two Pb(II) ions. While C-O phenoxy peak was slightly shifted from 1221 to 1217 cm^{-1} indicating that the coordination site for Pb(II) was located between phenoxy oxygen atoms and carbonyl oxygen atoms. It was found that a single molecule of 4Ac was able to load two Pb(II) ions through the ion exchange mechanism. The loading reaction was proposed in equation (5) [15].

$$H_4L(org) + 2Pb^{2+}(aq) \rightleftarrows [Pb_2 - L](org) + 4H^{+}(aq) \qquad (5)$$

Splitting of C=O carbonyl peak was found due to the stepwise loading of two Pb(II) ions on the single 4Ac molecule. The $[Pb_2\text{-}L]$ complex structure was proposed in Fig. 8. The similar spectra with the spectra of a free ligand were obtained after the stripping process. This confirms that the recycling of the extraction reagent was achieved with 2.0 M HNO_3 as stripping reagent.

■ CONCLUSION

Pb(II) extraction and separation over Fe(III), Cu(II) and Zn(II) ions with 4Ac calix[4]arene derivative was reported by using batch-wise and microreactor extraction methods. Although the batch method required 24 h to reach the equilibrium for both extraction and stripping process, the microreactor extraction method enhanced the extraction and stripping rate up to 10^4 times faster than batch-wise method. The highest extraction percentage of Pb(II) was 100% at 8 sec residence time at pH 2.50, while, the stripping percentage of Pb(II) was 92% at 8 sec residence time with 2.0 M HNO_3 as stripping reagent by employing microreactor method. Complete separation of Pb(II) over Fe(III), Cu(II) and Zn(II) ions in a competitive metal system was achieved at pH 2.00 by a microreactor extraction method in a very short residence time compared with batch method. The FTIR spectra confirm that the extraction reagent was regenerated and repeatedly employed. Therefore, a rapid and efficient separation of Pb(II) ion, including extraction and stripping with microreactor extraction method has been established.

■ ACKNOWLEDGMENTS

We thank to Ms. Kazuma Matsuura for her assistance in the microreactor fabrication. This work was partially supported by “Collaborative research expense of partner graduate school between Graduate School of Science and Engineering, Saga University, and AIST Kyushu”.

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