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USING AN INTERDIGITAL MICROMIXER FOR SEPARATION OF In³⁺ FROM ZINC HYDROMETALLURGICAL PROCESS WITH D2EHPA AS AN EXTRACTANT

Experiments were performed in an interdigital micromixer with 30 microchannels (40 μm width of each channel) to separate In^{3+}, Fe^{3+} and Zn^{2+} from sulfate solutions using Di-(2-ethylhexyl)phosphoric acid (D2EHPA) as the extractant. The effects of pH, extractant concentration and flow rate on the extraction efficiency and flow rate on mass transfer coefficient of In^{3+}, Fe^{3+} and Zn^{2+} were investigated. At a phase flow rate of 7.0 mL/min and initial solution pH of 0.423, the extraction efficiency of In^{3+}, Fe^{3+} and Zn^{2+} was 99.29%, 3.43% and 2.54%, respectively and mass transfer coefficient of In^{3+}, Fe^{3+} and Zn^{2+} was 144.307 s⁻¹, 1.018 s⁻¹ and 0.750 s⁻¹. Then, the loaded organic phase was stripped in an interdigital micromixer. At a phase flow rate of 9.0 mL/min and HCl concentration of 160 g/L, stripping efficiency of In^{3+} was 98.92% and mass transfer coefficient of In^{3+} was 169.808 s⁻¹, while concentration of Fe^{3+} and Zn^{2+} was lower than 0.005 g/L with good separation of In^{3+} from Fe^{3+} and Zn^{2+}.

Keywords: Interdigital micromixer; Solvent extraction; Mass transfer coefficient; Indium; Stripping

1. Introduction

Indium, a rare and valuable metal [1-3], is an important element which is used in the field of electronics [4], energy-related industries [5] and making low melting alloy [6]. Indium has no its own minerals so it has to be recovered as a byproduct from other metallurgical processes [1], together with zinc, lead, copper and tin [6]. Solvent extraction is a commonly used method for the purification of indium from the zinc hydrometallurgical process [4,7,8]. Thus, the separation efficiency of indium from iron and zinc is of great importance for its purity.

As an emerging new technique, microfluidic technology enables the possibilities of operating and controlling the fluids in microscale [9].The technology has many merits such as larger interfacial area and concentration gradient, short diffusion length, facilitating a higher heat and mass rates [10-13].

Some researchers have studied the microfluidic solvent extraction. M. Darekar et al. [14] reported liquid-liquid extraction in microchannels with Zinc-D2EHPA system and K_La values was found to increase with reducing residence time. K.K. Singh et al. [15] compared the performance of microchannels and conventional stage-wise extractors for liquid-liquid extraction by using a standard phase system and the ratio of maximum overall volumetric mass transfer coefficient in microchannels and conventional stage-wise extractors is found to range from 1 to 8.1. Mayur Darekar et al. [16] studied single-stage solvent extraction of HNO_3 from 3 mol/L HNO_3 using 30% TBP in dodecane in microbore tubes and found that microbore tube contactor led to process intensification. These studies indicated that the micro fluid extraction could increase the mass transfer coefficient of extraction process.

In this paper, test solution from the zinc hydrometallurgical process was extracted to investigated the extraction behavior of In^{3+}, Fe^{3+} and Zn^{2+} in an interdigital micromixer. The effect of pH, extractant concentration and flow rate on extraction efficiency and mass transfer coefficient of In^{3+}, Fe^{3+} and Zn^{2+} was investigated. The loaded organic phase was stripped and the effect of HCl concentration and flow rate on stripping behavior of In^{3+} was also studied.

2. Experimental

2.1. Materials

The test aqueous solution from zinc hydrometallurgy consisting of 3.02 g•L⁻¹ of In^{3+}, 4.95 g•L⁻¹ of Fe^{3+} and 3.57 g•L⁻¹ of Zn^{2+}. The aqueous pH value was adjusted by adding a concentrate sulfuric acid solution (98%) and measured by a pH meter (CHN868, made in China).

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The extractant was prepared by dissolving 3 liters of D2EHPA solvent into 7 liters 260# solvent oil without saponification operation.

2.2. Apparatus and procedures

The microfluidic experiments were performed in an inter-digital micromixer with 40 μm width channels fabricated by IMM, Germany, as shown in Fig. 1a. It consists of a mixing element, two opposite inlets and one upwards outlet (shown in Fig. 2). The constant flow pumps (HLB-4015) provided by Yanshang Instrument Factory, China, were used to pump the two fluids into the microchannels and the flow rate was in the range of 0.1 mL·min^{-1}~40 mL·min^{-1}. The two fluids flowed through the interdigital channels and then flowed upwards into a slit, which is perpendicular to the interdigital structure (shown in Fig. 1b [17]) where the mixing and extraction reaction took place and then fluids were clarified and separated. The extraction efficiency was calculated by analyzing metal ion concentration change in aqueous phase.

The photograph of the micro-extraction system is shown in Figure 2.

The comparative batch extraction tests were carried out by contacting equal volumes of organic and aqueous phase, at a phase ratio of 1:1, in 125 mL pear shape separator funnels. Then the system was placed horizontally in the roundtrip thermostatic

(a) interdigital micromixer
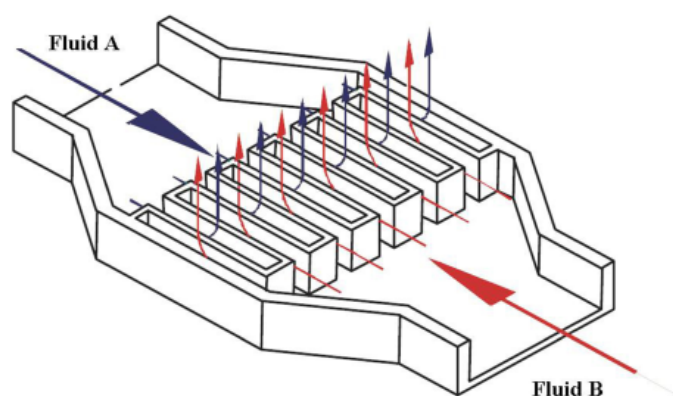
(b) Schematic of mixing and reaction

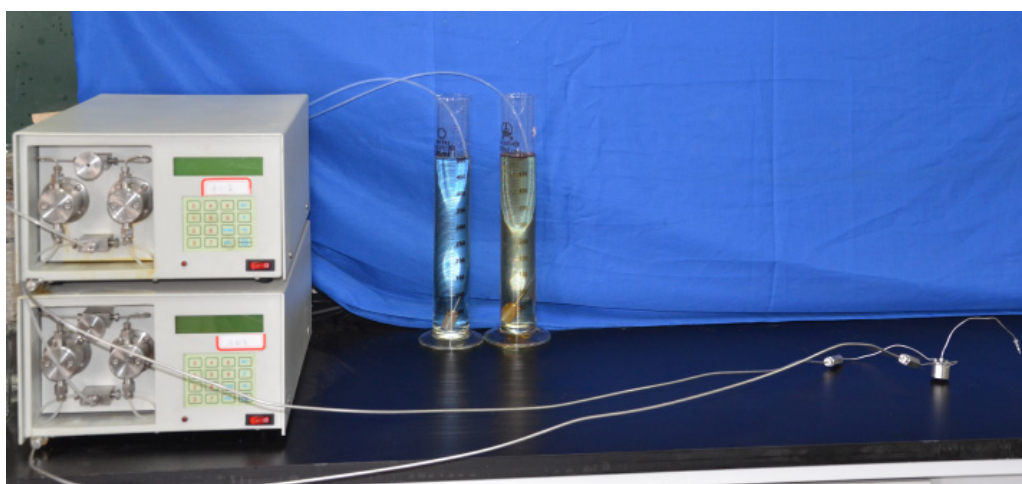Fig. 1. Schematic of interdigital micromixer

Fig. 2. The equipment photo of Micro-extraction system

water bath oscillator (WHY-2) to mix and react for certain duration, at an oscillation intensity of 200rpm. Subsequently, the mixture was separated after 30 min to form bottom aqueous phase containing Fe^{3+} and Zn^{2+} and upper organic phase loading In^{3+}. Each test was carried out twice to ensure the repeatability and to reduce the experimental error.
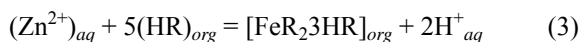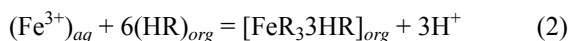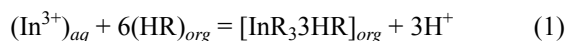
For all microfluidic and conventional experiments, the raffinate was analysed to estimate the concentrations of In^{3+} and Fe^{3+} using inductively coupled plasma-atomic emission spectroscopy (AA240FS ICP-AES spectrophotometer). The concentration of Zn^{2+} was detected using volumetric method. The concentration in the organic phase was estimated based on mass balance.

2.3. Extraction efficiency and mass transfer coefficient Estimation

According to Lee [18], in acidic sulfate media, the extraction of trivalent metals (In^{3+} and Fe^{3+}) by mixtures of acidic extractants (D2EHPA) can be presented by the following equi-

librium reaction,

$$(In^{3+})_{aq} + 6(HR)_{org} = [InR_3 3HR]_{org} + 3H^+ \qquad (1)$$

$$(Fe^{3+})_{aq} + 6(HR)_{org} = [FeR_3 3HR]_{org} + 3H^+ \qquad (2)$$

$$(Zn^{2+})_{aq} + 5(HR)_{org} = [FeR_2 3HR]_{org} + 2H^+_{aq} \qquad (3)$$

Extraction efficiency, E, is calculated based on the concentration of metal present as shown in the following equation:

$$E = \frac{C_{aO} - C_{al}}{C_{aO}} \times 100\% \qquad (4)$$

where C_{aO} and C_{al} represent metal ion concentration of aqueous phase before and after extraction respectively.

According to D. Doungdeethaveeratana [19], mass transfer coefficient, $k_L a$, is calculated as shown in the flowing equation:

$$\ln(\frac{C_{aq} - C^e_{aq}}{C^I_{aq} - C^e_{aq}}) = -k_L a(1 + \frac{C^e_{aq}}{C^e_{org}} \frac{V_{aq}}{V_{org}})t \qquad (5)$$

where C_{aq}, C^I_{aq} and C^e_{aq} represent metal ion concentration of aqueous phase, metal ion concentration of aqueous phase at the initial moment and metal ion concentration of aqueous phase at the moment of extraction equilibrium respectively. C^e_{org} represents metal ion concentration of organic phase at the moment of extraction equilibrium. V_{aq} and V_{org} represent volume of aqueous phase and volume of organic phase respectively.

3. Results and discussion

3.1. Extraction

3.1.1. Effect of pH on the extraction efficiency

Fig. 3 shows the effect of pH in the range of 0.1 to 0.9 with the other parameters held at flow rate of 7.0 mL/min, extractant concentration of 30%, phase ratio of 1:1 and temperature of 25°C.
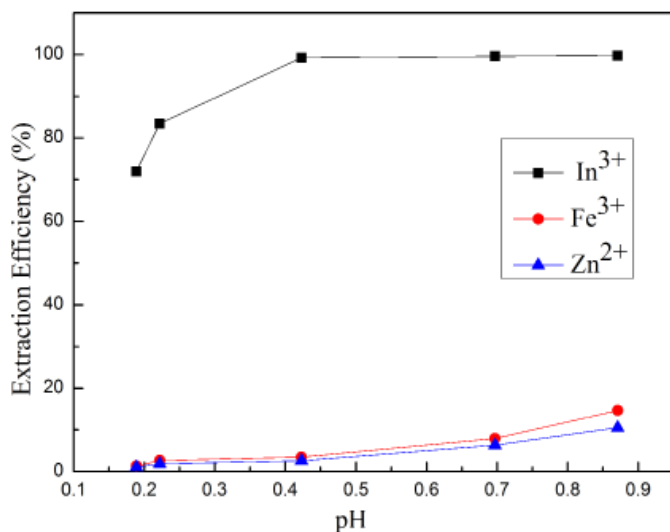

Fig. 3 Effect of pH on extraction efficiency of In^{3+}, Fe^{3+} and Zn^{2+}

Figure 3 shows an increase in the extraction efficiency with increase in the pH, with the maximum corresponding to a pH of 0.871. The increase in solution pH would facilitate better transfer of hydrogen ions in the D2EHPA to transfer to the aqueous phase which promote indium ion in aqueous phase to transport to the organic phase. At the flow rate of 7.0 mL/min, the droplets size of two phases formed in the channels was large and two-phase contact time was short so the extraction efficiency of In^{3+} improved significantly by reducing the acidity of aqueous phase. From these experimental results, it is believed that D2EHPA has good selectivity for indium over iron and zinc at pH of 0.423 so other extraction experiments were carried out in this condition.

3.1.2. Effect of extractant concentration on the extraction efficiency

Fig. 4 shows the effect of extractant concentration in the range of 10% to 40% with the other parameters held at flow rate of 7.0 mL/min, pH of 0.423, phase ratio of 1:1 and temperature of 25°C.
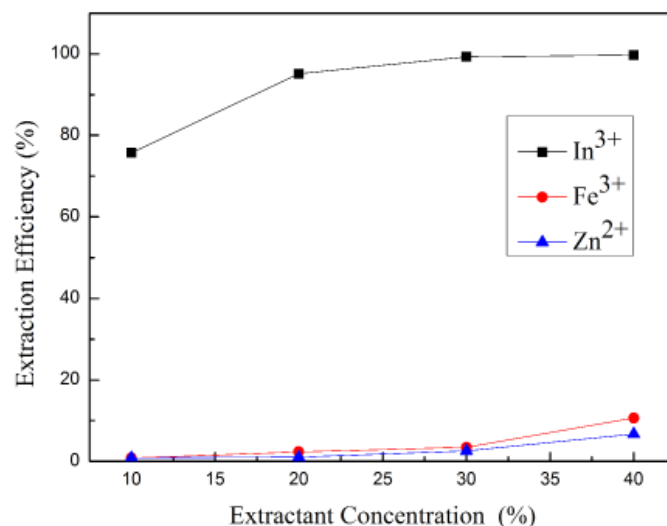

Fig. 4. Effect of extractant concentration on extraction efficiency of In^{3+}, Fe^{3+} and Zn^{2+}

Figure 4 shows the effect of extractant concentration on extraction efficiency of In^{3+}. With an increase in extractant concentration, an increase in the extraction efficiency was observed, however with the maximum indium extraction efficiency of only ca. 75.71% at low concentration of 10%. However, at concentrations in excess of 30% a near 99% extraction efficiency of In^{3+} could be achieved. At high extractant concentration (40%) it should be noted that the extraction efficiency of Fe^{3+} and Zn^{2+} also enhanced up 10.62% and 6.68%, respectively, indicating the negative effect. Furthermore, the increase in viscosity with increase in the extractant concentration leads to a higher pressure drop, demanding higher pumping pressure, indicates another negative effect on the process. From these experimental results, it is suitable to separate indium over iron and zinc at extractant

concentration of 30% so other extraction experiments were carried out in this condition.

3.1.3. Effect of flow rate on the extraction efficiency and mass transfer coefficient

The experiments were performed in an interdigital micro-mixer with the pH held at 0.423, an extractant concentration of 30 vol%, phase ratio of 1:1 and temperature of 25°C.
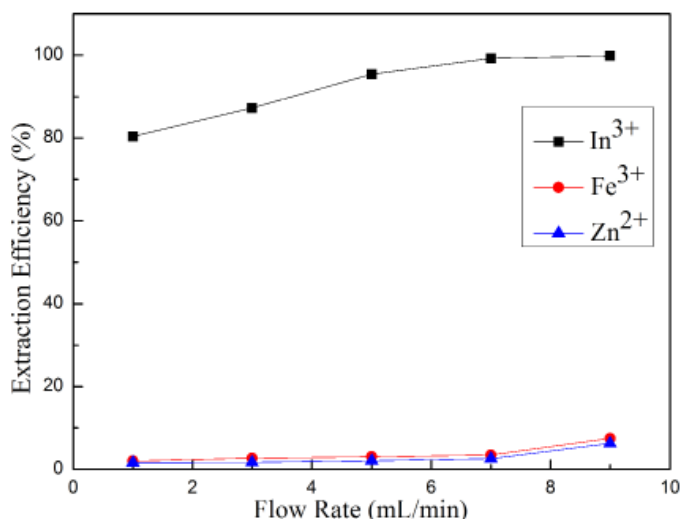

Fig. 5. Effect of flow rate on extraction efficiency of In^{3+}, Fe^{3+} and Zn^{2+}

Figure 5 shows a near linear increase in extraction efficiency of In^{3+} with increase of flow rate without excess of 7 mL/min. At a phase flow rate of 7 mL/min, extraction efficiency higher than 99 % In^{3+} could be achieved and the extraction efficiency of Fe^{3+} and Zn^{2+} was 3.43% and 2.54%, respectively. At a phase flow rate of 9 mL/min, the extraction efficiency of Fe^{3+} and Zn^{2+} was up to 7.43 % and 6.27%, respectively. At a phase flow rate
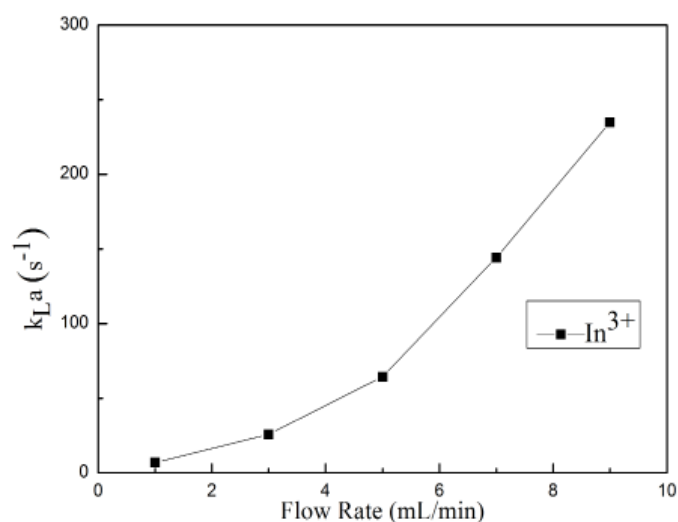
in excess of 9 mL/min or more, the emulsification of the two phases occurred and hence each phase flow rate was limited to less than 9 mL/min. In conclusion, flow rate of 7 mL/min was suitable for extracting In^{3+}. Furthermore, the effect of flow rate on mass transfer coefficient, k_La, of In^{3+}, Fe^{3+} and Zn^{2+} was also investigated that is shown in Figure 6.

Figure 6 shows a significant increase in mass transfer coefficient of In^{3+}, Fe^{3+} and Zn^{2+} with increase of flow rate. At the extraction equilibrium of In^{3+}, mass transfer coefficient of In^{3+} was up to 144.307 s^{-1}, which was 142 times of Fe^{3+}, 192 times of Zn^{2+} with good separation of In^{3+} from Fe^{3+} and Zn^{2+} through extraction. In the interdigital micromixer the droplet size is less than that generated in conventional solvent extraction, offering a high specific surface area between the two phases and hence a larger effective mass transfer area. In addition, the internal circulation flow within the droplets reduce the boundary layer thickness of the droplets and increase the contact surface renewal rate which further enhances the mass transfer performance between the two phases [20-21].

3.2. Stripping

The load of In^{3+} is very high but that of Fe^{3+} and Zn^{2+} is very low under the optimal extraction conditions. Therefore, the effect of HCl concentration and flow rate on stripping behavior of In^{3+} was mainly studied.

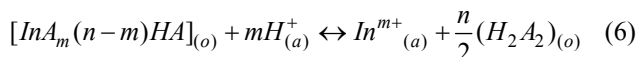### 3.2.1. Effect of HCl concentration on the stripping behavior of In^{3+}

The stripping of In^{3+} is reverse reaction of In^{3+} extraction and chemical equation can be presented by Eq. 6. According to the chemical equation, the high concentration of H^+ which has a significant effect on stripping efficiency of In^{3+} could cause
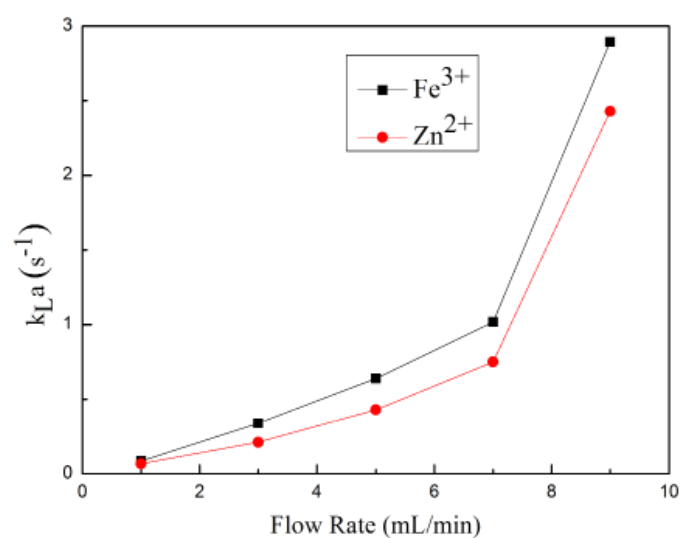
(a) k_La of In^{3+}

(b) k_La of Fe^{3+} and Zn^{2+}

Fig. 6. Effect of flow rate on mass transfer coefficient of In^{3+}, Fe^{3+} and Zn^{2+} (pH = 0.423; T = 298K; O/A = 1:1)

corrosive working environment and corrosion of extraction equipment and it is very important to choose the appropriate concentration of HCl solution.

$$[InA_m(n-m)HA]_{(o)} + mH^+_{(a)} \leftrightarrow In^{m+}_{(a)} + \frac{n}{2}(H_2A_2)_{(o)} \quad (6)$$

The effect of HCl concentration on stripping behavior of In^{3+} at the phase ratio of 1:1 and flow rate of 7.0 mL/min in an interdigital micromixer was investigated, and the results are shown in Fig. 7.
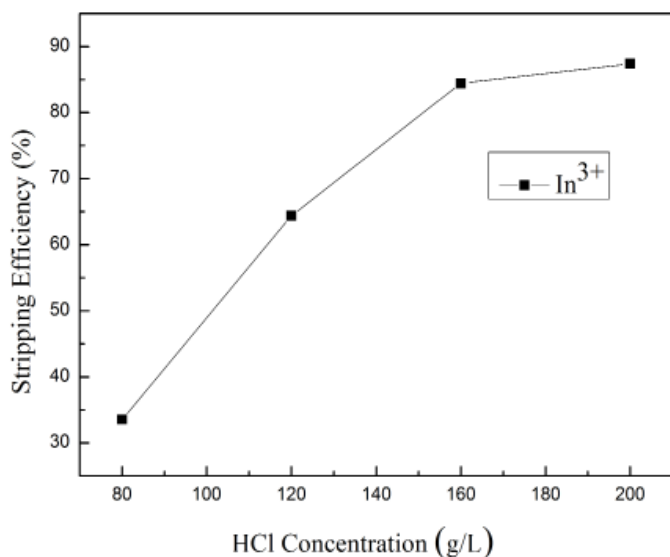

Fig. 7. Effect of HCl concentration on the stripping behavior of In^{3+}

The Fig. 7 shows that the stripping efficiency of In^{3+} increased with the increase of HCl concentration in the range from 80 g/L to 200 g/L. Higher hydrochloric acid concentration would corrode the equipment then 160 g/L hydrochloric acid was chosen to strip In^{3+}.

3.2.2. Effect of flow rate on the stripping behavior of In^{3+}

The effect of flow rate on stripping behavior of In^{3+} at the phase ratio of 1:1 and 160 g/L hydrochloric acid was investigated, and the results are shown in Fig. 8.

Figure 8 also shows the effect of flow rate on stripping efficiency of In^{3+}. It was observed that increasing the flow velocity an increase of the stripping efficiency was observed. At flow rate of 9 mL/min, 98.92% In^{3+} could be stripped and Fe^{3+} and Zn^{2+} were hardly stripped. However, at flow rate in excess of 9 mL/min an increase in the stripping efficiency of In^{3+} was not significant. A slight emulsion observed at flow rate of 11 mL/min gives to negative effect on the process. Finally, at a flow rate of 9.0 mL/min and HCl concentration of 160 g/L, the concentration of In^{3+} was about 2.97 g/L, while concentration of Fe^{3+} and Zn^{2+} was lower than 0.005 g/L with good separation of In^{3+} from Fe^{3+} and Zn^{2+}. Furthermore, the effect of flow rate on mass transfer coefficient of In^{3+} is shown in Figure 9 in stripping process.
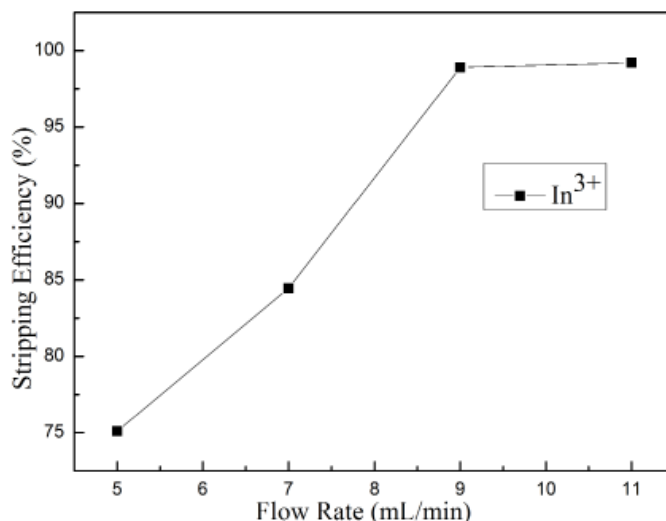

Fig. 8. Effect of flow rate on the stripping behavior of In^{3+}

Tendency of Fig. 9 is similar to that of Fig. 6 that mass transfer coefficient of In^{3+} increase significantly with increase of flow rate. An interdigital micromixer, with high flow rate could offer intensive mixing of two phases and finer droplet size. At a phase flow velocities in excess of 10 mL/min or more, the emulsification of the two phases occurred and hence each phase flow rate was limited to less than 10 mL/min.
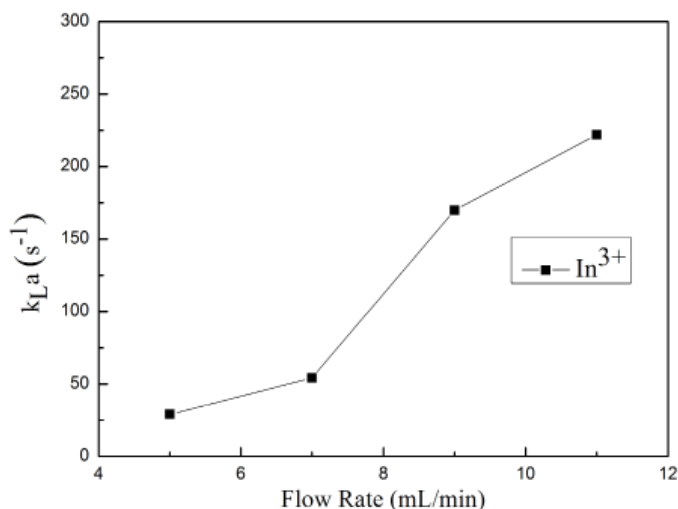

Fig. 9. Effect of flow rate on t mass transfer coefficient of In^{3+}

4. Conclusion

The effect of pH, extractant concentration and flow rate on the extraction behavior and flow rate on mass transfer coefficient of In^{3+}, Fe^{3+} and Zn^{2+} were investigated and the effect of stripping agent concentration and flow rate on stripping behavior of In^{3+} was also studied in an interdigital micromixer. At a phase flow rate of 7.0 mL/min, the extraction efficiency of In^{3+} was more than 99% but that of Fe^{3+} and Zn^{2+} was low

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without emulsification. At the extraction equilibrium of In^{3+}, mass transfer coefficient of In^{3+}, Fe^{3+} and Zn^{2+} is 144.307 s^{-1}, 1.018 s^{-1} and 0.750 s^{-1}, respectively. The stripping of In^{3+} was affected by stripping agent (HCl) concentration and 160g/L was suitable for stripping. At a phase flow rate of 9.0 mL/min, stripping efficiency of In^{3+} was 98.92% and mass transfer coefficient of In^{3+} was as high as 169.808 s^{-1}.

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