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Solvent extraction of In^{3+} with microreactor from leachant containing Fe^{2+} and Zn^{2+}

Abstract: The microreactor has been developed for a wide range of applications because of many advantages, such as high mass transfer efficiency, low energy consumption and the closed and safe system. The application of microreactors in the traditional hydrometallurgy extraction process is expected to overcome difficulties such as co-extraction of impurities, large consumption of extractant and hidden fire risks. In this study, the extraction and separation efficiency of In^{3+} from a complex sulfate solution containing impurities, such as Fe^{2+} and Zn^{2+}, were studied. The microreactor extraction was carried out in a Pyrex microchip, and the organic phase was prepared with the extractant di(2-ethylhexyl) phosphoric acid (D2EHPA) diluted in 260# kerosene. The results showed that with only 0.55 s contact between the organic and aqueous phases, the extraction ratio of In^{3+} can reach 90.80%, while only 0.16% of Fe^{2+} and 0.22% of Zn^{2+} were co-extracted; the average mass transfer speed of In^{3+} was calculated as high as 0.34 $g\cdot m^{-2}\cdot s^{-1}$. Compared with the traditional mixing settler process, microreactor extraction has advantages of higher extraction ratio of In^{3+}, lower trend of co-extraction of the impurities and emulsification.

Keywords: indium; mass transfer; microreactor; solvent extraction.

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1 Introduction

Various microreactors with micro-channel structures, the internal diameters of which are in the range of 10–500 μm, have been widely utilized in the field of chemical engineering and analysis fields for intensifying, due to their advantages over macro scale reactors, such as higher ratio of the contacting interface to the volume of the flows, shorter diffusion distance and the feasibilities of precisely controlling the temperature of the reaction. It is the rapid development of advanced micro scale manufacturing technology that pushed efficiently the application of microreactors in the above fields [1].

Thus, microreactor application usually embodies a much smaller chemical device, shorter reaction time, higher efficiency [2], lower consumption of materials and energy [3] and safer operation conditions. Another advantage of a microreactor is that it can easily scale up by simply “numbering up”. Different microreactor procedures have been applied to organic synthesis [4–6] and material preparation [7–9]. Microreactors can now generate tons of product per year [10].

Solvent extraction with a mixing settler is a traditional key process for separation and purification of some metal ions in a solution system [11, 12]. Although this device has some merits like a simple structure, low cost and is effective to some extent, there are still problems such as low efficiency [13], too many extraction stages, emulsifying easily [14–17] and occupation and fire risks [18].

For example, in a zinc plant in Yunnan Province, China, the extraction procedure of In^{3+} ion by di(2-ethylhexyl)

Table 1 Chemical composition and the pH value of the complex solution.

Elements	In^{3+}	Fe^{2+}	Zn^{2+}	pH
Unit	$g \cdot l^{-1}$	$g \cdot l^{-1}$	$g \cdot l^{-1}$	Value
Data	3.17	3.4	52.8	0.44

phosphoric acid (D2EHPA) contains 14 steps in total. They are a 2-step extraction process, a 3-step process of eluting impurities (mainly Fe^{2+} and Zn^{2+}), a 4-step process of stripping with hydrochloric acid, a 4-step process of stripping iron and a 1-step process of stripping chloride ion. Actually, the impurities co-extracted in the organic phase increase the complexity of the extraction process.

Very few researchers have explored the potential of using microreactors in the field of solvent extraction of metal ions. In Australia, the possibility of extraction Cu^{2+} from a particle-laden solution was investigated, with a positive result [19]. In Japan, it was shown that Cs^+ extraction from a complex solution in stable slug flow, by inserting a piece of glass bead into a microchannel, resulted in faster separation compared with conventional batch experiments [20].

In this paper, the extraction and separation efficiency of In^{3+} from a complex solution containing impurities, such as Fe^{2+}, Zn^{2+} and SO_4^{2-}, was studied in a laminar flow microreactor. The process of diffusion and mass transfer in the microreactor were also analyzed, and the extraction effects were compared with traditional extraction.

2 Experimental

2.1 Materials and devices

The experimental material, an aqueous solution in a sulfuric system with a pH value of 0.44, was obtained from a hydrometallurgy zinc plant in Yunnan Province, China. Its chemical composition was analyzed and is listed in Table 1. The organic phase for solvent extraction contained 30% of D2EHPA (mass fraction, w=0.99, DeZhong Chemical factory, ZhengZhou, HeNan province, China) and 70% of 260# kerosene (mass fraction, w=0.98, DeZhong Chemical factory, ZhengZhou, HeNan province, China). The main extraction equation is as follows [21]:

$$(In^{3+})_{AQ}+(3H\,R_2PO_4)_{ORG}=[In(\,R_2PO_4)_3]_{ORG}+(3H^+)_{AQ} \quad (1)$$

The microchip used in this study is shown in Figures 1 and 2. It was made of Pyrex glass (Institute of Microchemical Technology, Japan), produced with combined methods of photolithography, wet-etching and thermal bonding. The extraction reaction takes place in a 120 mm long microchannel (160 µm×40 µm), which is shown in Figure 1B,

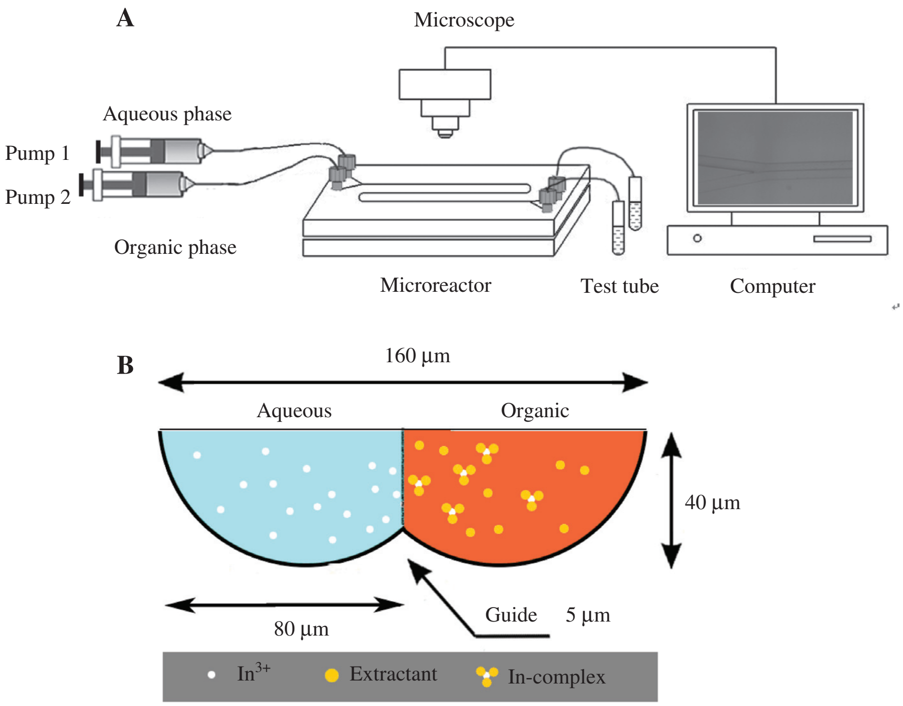

Figure 1 Schematic of microreactor system used in this study: (A) microreactor system; and (B) cross-section of the extraction channel.

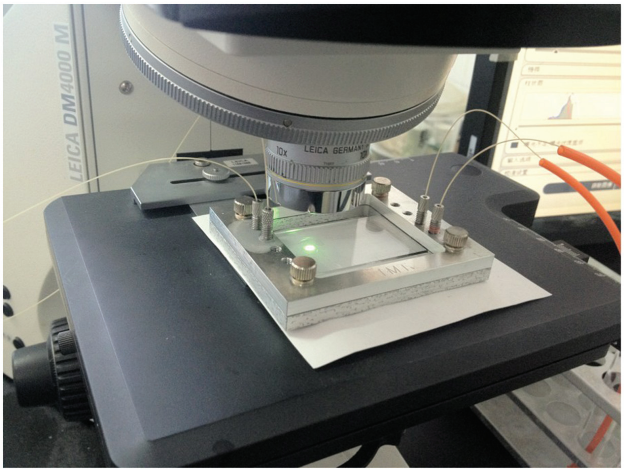

Figure 2 Microreactor channel conditions monitored by optical microscopy.

with a guide structure for obtaining a stable flow interface of the two immiscible liquid-liquid phases.

2.2 Procedures

During the experiments of microreactor extraction, the aqueous and oil phases were, respectively, pumped into the Pyrex glass microchip by two constant flow pumps (HLB-4015, Yansan). The flow stability of the contacting interface of the aqueous and oil phases in the microchip was monitored with an optical microscope (Leica DM 4000 M). The flow rate of the aqueous phase ranged from 1 to 6 ml·h^{-1} at a fixed organic/aqueous flow rate ratio of 0.8. Along the contacting channel, there is an arched guide lug in its middle for producing a stable aqueous-oil interface. The extraction channel terminates at a second Y-junction, where the two phases are separated and flow out of the microchip for samples collection and analysis.

The experiments of conventional extraction were carried out in a 250 ml separating funnel. The phase ratio was set as O:A=2:1, 1:1, 1:2 and 1:4, respectively. Each time, 40 ml solution was added to the organic phase (30% D2EHPA in 260$^{\#}$ kerosene) in a 250 ml separating funnel. Then, the funnel was stirred on a shaking machine for 5 min at a speed of 200 rpm. After separation, the aqueous phase was diluted and analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES).

2.3 Analysis method

The concentrations of In^{3+}, Fe^{2+} and Zn^{2+} in the aqueous phase before and after the extraction were determined by an ICP-AES (Leeman ICP-AES PS1000). The acidity of the aqueous solution was determined by an acidity meter. Equation (2) is an expression of extraction rate, where C_{ao} and C_{al} signify the elements contained before and after extraction, respectively:

$$E=\frac{C_{ao}-C_{al}}{C_{ao}}\times 100\%. \tag{2}$$

3 Results and discussion

3.1 Stability of liquid-liquid interface

Figure 3 contains two photos of aqueous and oil flows taken by an optical microscope. A stable liquid-liquid interface was observed during this experiment under the condition of optimal flow rate ratio (oil/aqueous), R=0.80, and flow was laminar in all cases. Compared with the emulsions which easily appeared in conventional

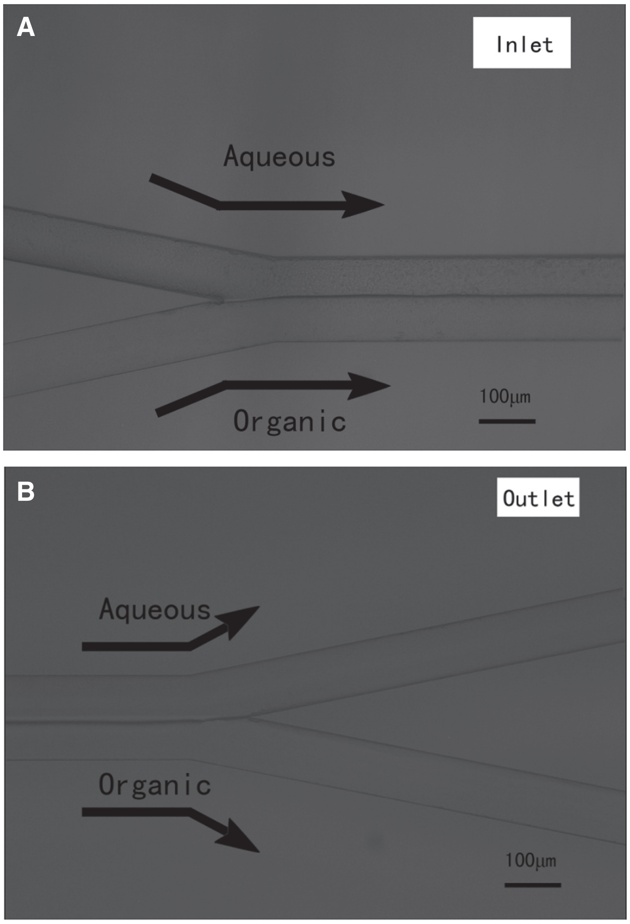

Figure 3 Photos of the merging and diverging of aqueous and oil flows.

extractions, this type of microreactor extraction radically abandoned the formation of emulsions of oil-in-water [22].

3.2 Calculation of contact time in the microchannel

The changes of geometry structure of a microreactor have a great influence on the flow pattern and the shape of the interface between L-L phases [23]. According to the microchannel geometry in Figure 4, the cross-section area of the aqueous channel, S_a, was estimated by Eq. (3). The volume of aqueous channel, V_a, was calculated by Eq. (4):

$$S_a=\int_0^{80}\left[\sqrt{59.4^2-(x-23.9)^2}-19.4\right]dx \tag{3}$$

$$V_a=S_a\times L. \tag{4}$$

In Eq. (3), L is the total length of the channel, which is equal to 12 cm. It is calculated that V_a=3.08×10^{-10} m^3. When the flow rate of the aqueous phase was 2 ml·h^{-1}, which means volumetric flow rate of the aqueous phase v=(5.56×10^{-10} m^3/s), the phase ratio R=0.8. The residence time, t, of the aqueous phase in the microchannel can be expressed as Eq. (5):

$$t=V_a\,/\,v. \tag{5}$$

The value of t is calculated as 0.55 s, which indicated that the extractability could be measured for a short contact time of both phases in the microreactor. In traditional solvent extraction plants with a mixing settler system, the extraction time is usually about 4 min (1 min of mixing and 3 min of phase separating).

3.3 Microreactor extraction of In^{3+} in a complex solution

A complex solution with a composition in Table 1 was used in the experiment of microreactor extraction. When the flow rate of the aqueous phase was set as 2 ml·h^{-1} and that of the organic phase was set as 1.6 ml·h^{-1}, the raffinate was collected and analyzed by ICP-AES. The results are shown in Table 2.

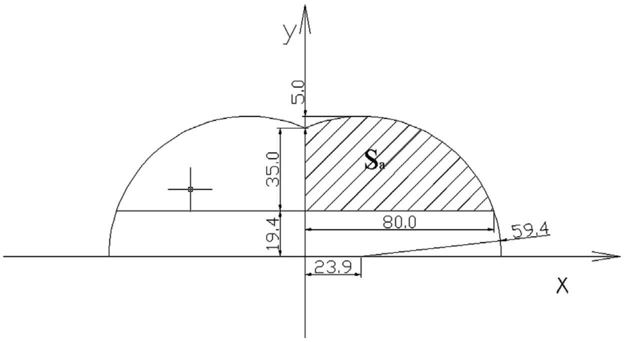

Figure 4 The actual size of cross-section/μm.

Table 2 The chemical composition of the original solution and the raffinate after microreactor extraction.

Composition	In^{3+}	Fe^{2+}	Zn^{2+}
Original solution (g/l)	3.17	3.46	52.82
Raffinate (g/l)	0.29	3.41	51.65
Extraction rate (%)	90.8	0.16	0.22

It is shown in Table 2 that the extraction percentage of In^{3+} is much higher than that of Fe^{2+} and Zn^{2+}.

In an industry plant, after 2-step extraction of In^{3+} ion by D2EHPA, Fe^{2+} and Zn^{2+} concentration in the organic phase is much higher. Thus a 3-step eluting process was needed to remove the above impurities.

The microreactor provides a good separation effect of In^{3+} and impurities. The main reason lies in the fact that the mass transfer speed of In^{3+} is much higher than Fe^{2+} and Zn^{2+} [24].

During the microchannel extraction, the flow pattern is much different with the mixing settler system. The mass transfer of the former is by diffusion through a stable interface, which may lead to better selection of metal ions.

For checking the co-extraction effects of Fe^{2+} and Zn^{2+} during the traditional mixing settler system, the extraction experiment was carried out in separating funnels. The relationship between the extraction rate and phase ratio of this experiment is shown in Figure 5.

From Figure 5, we can see that the co-extraction ratio of Fe^{2+} and Zn^{2+} is about one magnitude higher than that of microreactor extraction.

3.4 Surface-to-volume ratio of the microchannel and its mass transfer character

The aqueous-organic interfacial area A (m^2) can be calculated with follow equation:

$$A=(d-h_g)\times L, \tag{6}$$

where d is the height of the microchannel and h_g is height of the guide structure. Thus, A is calculated to be 4.2×10^{-6} m^2. In a contact time of 0.55 s, 3.08×10^{-10} m^3 of solution involved in the reaction and 0.98×10^{-6} g of In^{3+} transferred into the

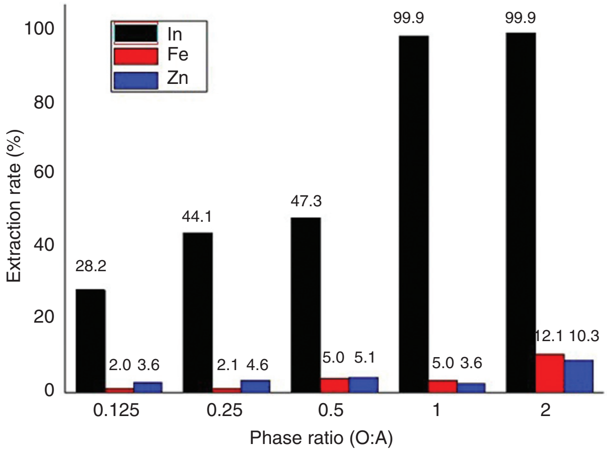

Figure 5 Extraction in different phase ratios during separating funnel experiments.

organic phase calculated by the data shown in Table 2. The mass transfer speed can be as high as 0.34 g·m^{-2}·s^{-1}.

The surface-to-volume ratio was about 6.8×10^{3} m^{2}/m^{3} for this channel, which is much higher than that of the traditional mixing settler process. The surface-to-volume ratio of conventional scale laboratory or industrial reactors are usually in the range of 100~1000 m^{2}/m^{3} [25].

4 Conclusions

The extraction of In^{3+} from a complex solution with D2EHPA was conducted in a glass laminar flow microreactor. According to the results, the following conclusions are drawn:

1. In the traditional mixing settler process, the operation time of a single stage is about 4 min, while in the microreactor, the time can be as short as 0.55 s.
2. In the microreactor process, the extraction rate of In^{3+} is very high and the average mass transfer speed can be as high as 0.34 g·m^{-2}·s^{-1}.
3. In the mixing settler process, the co-extractions of Fe^{2+} and Zn^{2+} into the organic phase can be as high as 5.0% and 3.6%, respectively, while in the microreactor, their co-extractions are only 0.16% and 0.22%, respectively, which shows a great benefit of reduction of the eluting stages after the extraction.

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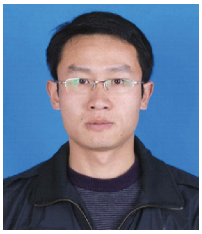

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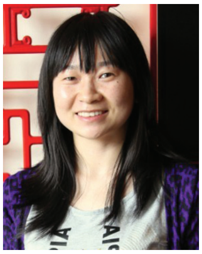

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