Libo Zhang, Feng Xie, Shiwei Li, Shaohua Yin*, Jinhui Peng* and Shaohua Ju

Solvent extraction of Nd(III) in a Y type microchannel with 2-ethylhexyl phosphoric acid-2-ethylhexyl ester

Abstract: Conventional extraction equipment has many problems like a long mixing time, a large factory area occupation, a large amount of organic solvent consumption and so on. In this paper, a micro solvent extraction system for the extraction of Nd(III) was investigated to solve the above issues. The initial aqueous pH 4.0 and saponification rate 40% of 2-ethylhexyl phosphoric acid-2-ethylhexyl ester (P507) were selected as the optimal experimental conditions. The extraction equilibrium was quickly achieved within 1.5 s, without any mechanical mixing in a narrow channel (100 μm in width and 120 μm in depth) at a volumetric flow rate from 5.55×10^{-10} m^3/s to 1.53×10^{-9} m^3/s. The extraction behavior of Nd(III) in the microreactor is an interface chemical reaction or the diffusion rate of the Nd-complex in the organic phase at low pH and [P507], while the extraction rate is controlled by the rate of metal diffusion in the aqueous phase at high pH and [P507], and the apparent mass transfer rate is up to 3.29×10^{-5} $mol/m^2{\cdot}s$. The extracted complexes are determined by the infrared (IR) spectrum method, and confirm that the extraction is via a cation exchange mechanism in the microreactor.

Keywords: microreactor; Nd(III); P507 extractant; solvent extraction.

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1 Introduction

With the development of high-tech materials, rare earths and their compounds become more and more important owing to their unique properties. Especially, the element neodymium, which is one of the most abundant rare earths, is of current interest, because it is a basic material for the most common solid-state lasers, and also applied extensively as a catalyst, additive and permanent-magnet material [1–3]. Extraction of rare earths to achieve their pure products in suitable or various demands has gained increasing attention in the rare earth industry [4]. Currently, solvent extraction is one of the major techniques for extraction, separation, purification, and recovery of metal components, including rare earth metals, on an industrial scale [5]. Although solvent extraction has higher selectivity than ion change or adsorption techniques, it has one disadvantage – consuming a large amount of an organic solvent which is needed to dissolve both the extractant and the extracted species. Also, it has caused an environmental hazard due to the large quantities of organic solvents required [6]. More importantly, the common extraction equipment, such as the mixer-settler, centrifugal extractor and extraction column, have many problems with respect to a long mixing time, low processing capacity, large factory area occupation, high energy consumption and so on [7, 8]. Therefore, the next generation of processing devices will need to incorporate reductions in solvent use, and solve the abovementioned issues in the conventional extraction equipment.

Recently, microreactors, which are composed of microchannels fabricated on a microchip platform, have attracted much attention in the fields of analytical chemistry, extraction, and synthesis of chemicals [8–10]. Such microreactors, with regards to extracting metal ions, have advantages and disadvantages. In particular, they have the following advantages [11–15]: (1) an effective extraction in a short time due to high surface area to volume

ratio; (2) simple operation and an environment friendly system; and (3) fast and direct amplification via "numbering-up" parallel processing without scale-up effect. Many literatures indicate that solvent extraction can be carried out very efficiently in a microfluidic chip, due to the high surface-to-volume ratio [16–19].

The method is effective for reducing the path length for a chemical reaction and increasing the mass transfer rate through the interface of two phases, and the microreactor system has been expected to be applied in chemical engineering operations. Tamagawa and Muto [20] developed a slug flow microreactor to extract Cs^+, and the results showed that extraction equilibrium was achieved within 40 s when compared to conventional batch extraction. Tokeshi et al. [21] performed the extraction of metal ions such as Fe(III) in a microchannel and succeeded in monitoring the metal complex formation. Ciceri et al. [22, 23] used a microfluidic device to determine the extraction kinetics of Co(II) with DEHPA (di-(2-ethylhexyl) phosphoric acid) extractant, and study the kinetic rate constants using the finite volume numerical simulations. The extraction and separation of rare earths using a microchannel have been conducted using parallel streams of immiscible liquid–liquid phases, as reported by Kubota et al. [24], Nishihama et al. [25] and Hou et al. [8]. Thus it can be seen that microfluidic solvent extraction is a promising option for the hydrometallurgical extraction of metal ions.

In the present work, we carried out the extraction of Nd(III) with 2-ethylhexyl phosphoric acid-2-ethylhexyl ester (P507) as an extractant dissolved in sulfonated kerosene by using a microreactor fabricated on a PMMA (polymethyl methacrylate) plate. The effects of process parameters such as pH value in the aqueous phase, flow rate, and channel width on the flow conditions in the microreactor were examined, together with extraction reaction time and extraction mechanism. The aim of the study was to apply the microreactor to solvent extraction for the development of an efficient extraction process for the rare earth metals.

2 Materials and methods

2.1 Reagents

The commercial extractant, P507, and sulphonated kerosene were kindly supplied by Luoyang Aoda Chemical Co., Ltd (China). The organic phase was prepared by mixing P507 dissolved in sulfonated kerosene with a certain volume of ammonia water (3 $mol \cdot l^{-1}$); this remained stationary until a single phase formed, and the concentration of the organic phase was titrated by HCl standard solution. Although these reagents, i.e., P507, sulfonated kerosene and ammonia water are toxic, the use of a microreactor for Nd(III) ions extraction limits the amount of dangerous reagents and also prevents evaporation. The aqueous $NdCl_3$ solution was prepared by dissolution of the oxides (purity >99.5%) in heated hydrochloric acid followed by removal of the excess acid by evaporation, and diluting with distilled water. The $NdCl_3$ solution was analyzed by titration with a standard solution of EDTA at pH 5.5, using xylenol orange as an indicator. All of the initial $NdCl_3$ concentration was maintained at 0.001 $mol \cdot l^{-1}$. NaCl (0.1 $mol \cdot l^{-1}$) was used in all extraction experiments to keep a constant ionic strength. All other reagents were of analytical reagent grade. The pH value in the aqueous phase was determined by a model pHs–3C pH meter (Leici, Shanghai, China).

2.2 Apparatus

The extraction apparatus employed is schematically illustrated in Figure 1A. Each aqueous and organic phase is fed into the microreactor at a constant flow rate using a programmable syringe pump (Harvard, PHD 2000-M). The two phases pass through the microreactor and are collected at the outlet of the chip, and then, are separated by a separatory funnel (10 ml). The Y type microreactor (supplied by Tsinghua University, Beijing) in Figure 1B is made on a PMMA plate which can provide good resistance to acids and alkali, and is composed of three sections: inlets, channel and outlets. The aqueous and organic phases are fed into inlets from the inflow plate, then joined at the Y-shaped confluence and continued through the channel, where the actual size of the channel is shown in Figure 1C.

2.3 Extraction procedure

Two plastic syringes containing, respectively, a solution of $NdCl_3$ (with density of ~998.2 $kg \cdot m^{-3}$ at 25°C) and a sulphonated kerosene solution of P507 (with density of ~888.4 $kg \cdot m^{-3}$ at 25°C) were placed in two independent syringe pumps, and then the liquids pumped into the microchannel via two inlets at equal volumetric flow rates (5.55×10^{-10}–1.52×10^{-9} m^3/s). The mixture was collected at the outlet of the chip and separated in a separatory funnel, and the flow patterns were monitored using optical microscopy. The Nd^{3+} concentration in the aqueous phase was measured by inductively coupled plasma atomic emission spectrometry, and the organic phase rare earth concentration was calculated from a mass balance. The extraction efficiency E (%) is defined by Eq. (1):

$$E = \frac{C_o - C_i}{C_o} \times 100\% \quad (1)$$

where C_o and C_i are the Nd(III) concentrations (mol/l) in the aqueous phase before and after extraction, respectively.

3 Results and discussion

3.1 Extraction equilibrium

The effects of initial aqueous pH value and saponification rate of P507 extractant on the extraction efficiency are

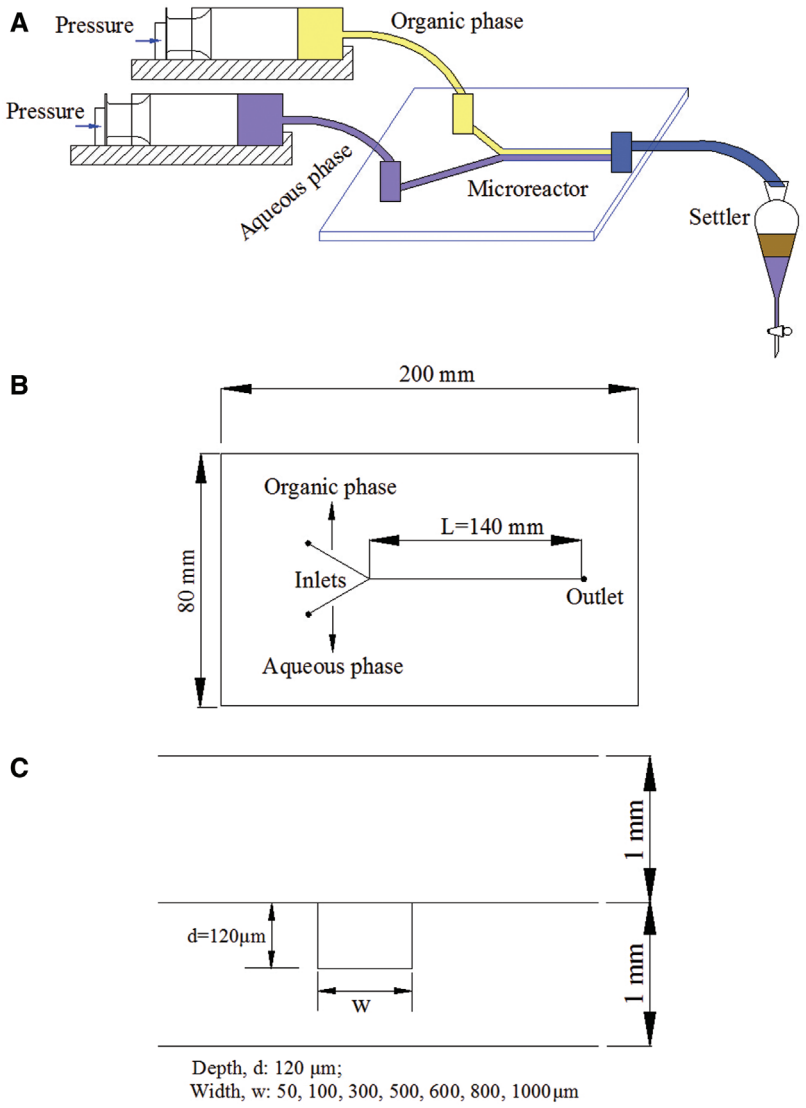

Figure 1 Sketch of microreactor set-up: (A) experimental apparatus, (B) microreactor, (C) specification of channel.

shown in Figure 2, to determine the optimal operational conditions in the microreactor. The extraction efficiency was observed to increase with increase in the initial aqueous pH value from 1.51 to 4.51, when the saponification rate of P507 was fixed at 20% and 40%, respectively, up to almost 100%. However, when the initial aqueous pH value was >3.0 at a saponification rate of 60%, the extraction efficiency started to decrease due to the strong basicity of the saponified extractant. Because the hydrolysis reaction Nd(III)→$Nd(OH)_3$ appeared under these conditions, the extraction efficiency was significantly reduced. In this regard, the initial aqueous pH 4.0 and saponification rate 40% of P507 were selected as the optimal experimental conditions for the microfluidic extraction.

3.2 Effect of channel width on the extraction efficiency

The effect of the channel width on the extraction efficiency was examined and the results are depicted in Figure 3 for a channel plate with L=140 mm and d=120 μm. The extraction efficiency had a decreasing trend with channel width increasing from 50 μm to 1000 μm at some fixed set of conditions; the extraction efficiency reached almost 100% when the channel width was 100 μm or 50 μm. That is because the narrower the microchannel, the larger was the ratio of the interface area (between aqueous and organic phases) to the volume of the aqueous and organic phases, which can provide better mass transfer performance due to the higher mass transfer coefficient and

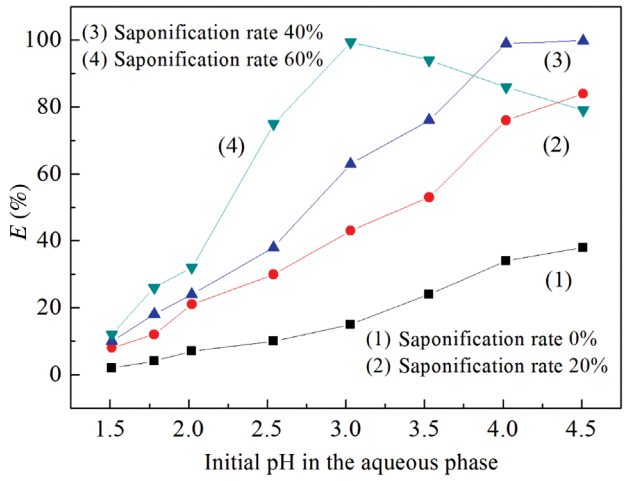

Figure 2 Effects of initial aqueous pH value and saponification rate on the extraction efficiency (conditions: [$NdCl_3$]=0.001 mol/l, [P507]=0.02 mol/l, flow rate=5.55×10^{-10} m^3/s, and channel width=100 μm).

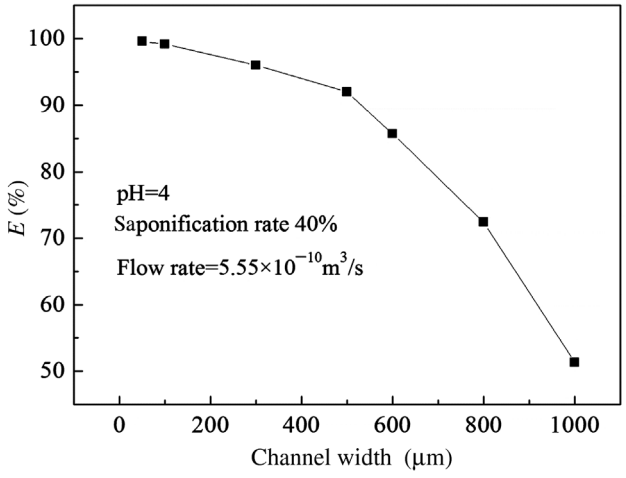

Figure 3 Effect of channel width on the extraction efficiency (conditions: [$NdCl_3$]=0.001 mol/l and [P507]=0.02 mol/l).

volumetric mass transfer coefficient [26]. In addition, the extraction equilibrium was hardly achieved even with a very slow flow rate in the case of w=800–1000 μm, while it was easily achieved in the narrow micro flow channel less than or equal to 100 μm (not shown).

3.3 Effect of flow rate on the extraction efficiency

The extraction behavior of single Nd^{3+} was carried out using the Y type micro solvent extraction chip, and the extraction properties in the micro flow channel were investigated. Figure 4 shows the effect of the linear velocity which is defined as the ratio of volumetric flow rate (m^3/s) to the cross area of the flow channel (S=1.2×10^{-8} m^2), on the extraction efficiency. The extraction efficiency decreased with an increase in linear velocity from 2.78 m/min to 7.65 m/min; this is because the lower flow rate can increase the longer contact time of both phases. Therefore, the volumetric flow rates of the aqueous and organic phases were both set at 5.55×10^{-10} m^3/s. Also, the two phases run through the microchannel without changing shape. At all values of linear velocities, two phases successfully flowed without mixing, and there were also no slugs or droplets in the microchannel (shown in Figure 5).

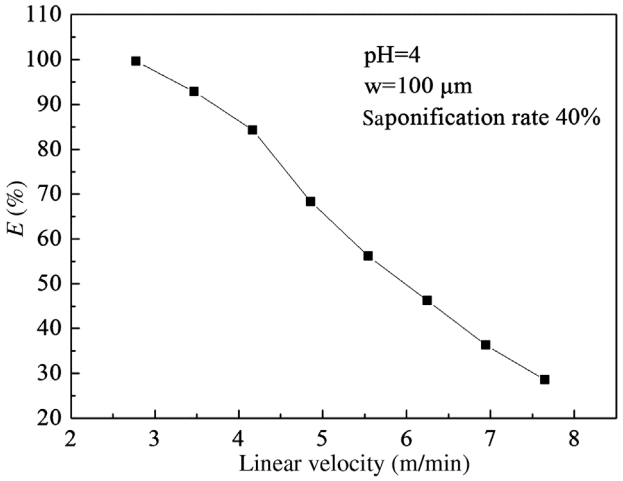

Figure 4 Effect of linear velocity on the Nd^{3+} extraction efficiency on the micro solvent extraction chip (conditions: [$NdCl_3$]=0.001 mol/l and [P507]=0.02 mol/l).

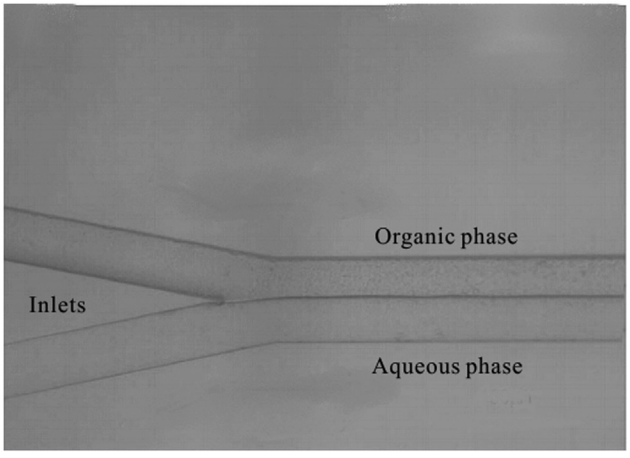

Figure 5 Microscopic image magnified 100 μm of two phase flows from inlet to outlet (conditions: [$NdCl_3$]=0.001 mol/l, [P507]=0.02 mol/l, saponification rate 40%, pH=4.0, flow rate=5.55×10^{-10} m^3/s, and channel width=100 μm).

3.4 Extraction of Nd(III) in the microreactor

The change in extraction efficiency over reaction time is shown in Figure 6. The definition of reaction time in the batch extraction is the time from the start of mixing of the two phases until phase separation and collection of the aqueous phase [20]. The reaction time in a microreactor is the time from the Y junction of the two phases until exhaustion at the outlet of the two phases. The residence time t is calculated by Eq. (2):

$$t=\frac{V}{\nu_{aq}+\nu_{org}} \tag{2}$$

The reaction time was variable, according to the flow rate of the phases; as the flow rate increased, the reaction time decreased. Emulsification appeared if the flow rate was too high. The t value was about 1.5 s at $\nu_{aq}=\nu_{org}$ of 5.55×10^{-10} m^3/s, where the volume of the microreactor channel, V is calculated as 1.68×10^{-9} m^3 by the actual size in Figure 1C. The reaction time of 1.5 s indicates that the maximum extractability could be obtained for a short contact time of both phases in the microreactor, while the extraction equilibrium was achieved in at least 60 s in the batch reactor, as seen in Figure 6. The extraction rate of the microreactor was higher than that of the batch reactor. The results suggest that the features of microreactor, i.e., large specific surface area and short diffusion distance, are effective for the efficient extraction of Nd(III).

The apparent mass transfer rate of Nd(III), J (mol/m^2·s) for the extraction is expressed as Eq. (3), which is based on the variation in the concentration of the Nd^{3+} in the aqueous phase:

$$J=\frac{\nu_{aq}(C_o-C_i)}{A} \tag{3}$$

where the aqueous-organic interfacial area in the microchannel, A (m^2), is calculated as 1.68×10^{-5} m^2 in the case of L=140 mm and d=120 μm. Figure 7 shows the relationship between J and pH in the aqueous phase, together with P507 concentration in the organic phase ([P507]). The mass transfer rate J increased with increasing pH and [P507], and then converged to an almost constant of 3.29×10^{-5} mol/m^2·s at high pH and [P507]. In this manuscript, we quantitatively illustrate the mass transfer mechanism. In general, an extraction process is divided into three steps when ignoring the intermiscibility: (1) the metal ion and extractant diffuse from the bulk to the aqueous-organic phase interface; (2) the metal ion reacts with extractant at the interface to form the metal complex; and (3) the complex diffuses to the bulk organic phase according to the "similarity-intermiscibility theory". Therefore, as can be seen from Figure 7, the extraction rate is controlled by the rate of metal diffusion in the aqueous phase, because the mass transfer rate J is independent of the concentration of chemical species at high pH and [P507]. However, mass transfer rate is considered to be controlled by an interface chemical reaction or the diffusion rate of the Nd-complex in the organic phase at low pH and [P507], because the reactivity of the complex formation is affected by the pH and [P507].

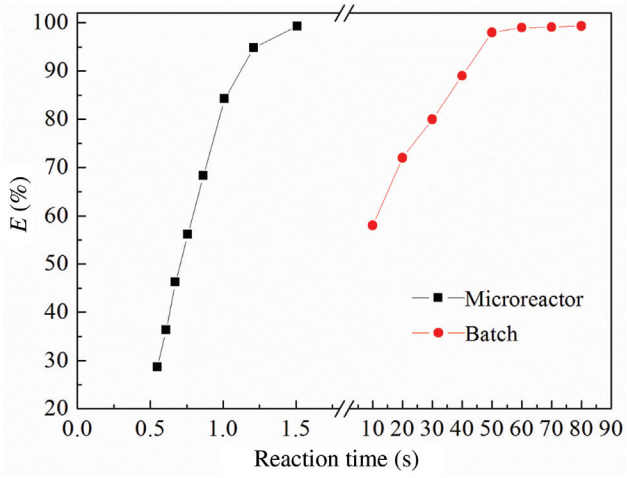

Figure 6 Comparison of extraction efficiency between the microreactor and a conventional batch reactor (conditions: [$NdCl_3$]=0.001 mol/l, [P507]=0.02 mol/l, saponification rate 40%, pH=4.0, flow rate=5.55×10^{-10}–1.52×10^{-9} m^3/s, and channel width=100 μm).

3.5 Infrared spectrum

In order to further confirm the composition of the extracted complexes, infrared (IR) spectrum measurements were conducted and are shown in Figure 8. As shown in Figure 8, the characteristic absorption of P507 at 981 cm^{-1} is attributed to O–H, 1195 cm^{-1} is assigned to p=O stretch, and 1030 cm^{-1} is due to the bending vibration of P–O–C. For the Na-P507 (H_2A_2), the extraction mechanism is written as Eq. (4):

$$Na^+ + H_2A_2 = NaA{\cdot}HA + H^+ \tag{4}$$

For the complex of Nd-P507, the IR spectrum has similar characteristics to the saponified P507. The adsorption peak at 981 cm^{-1} shifts to a lower wavenumber 976 cm^{-1}, and the intensity of absorption peak declines significantly, suggesting a cation exchange mechanism. At the same time, the p=O stretching at 1195 cm^{-1} shifts to lower wavenumber

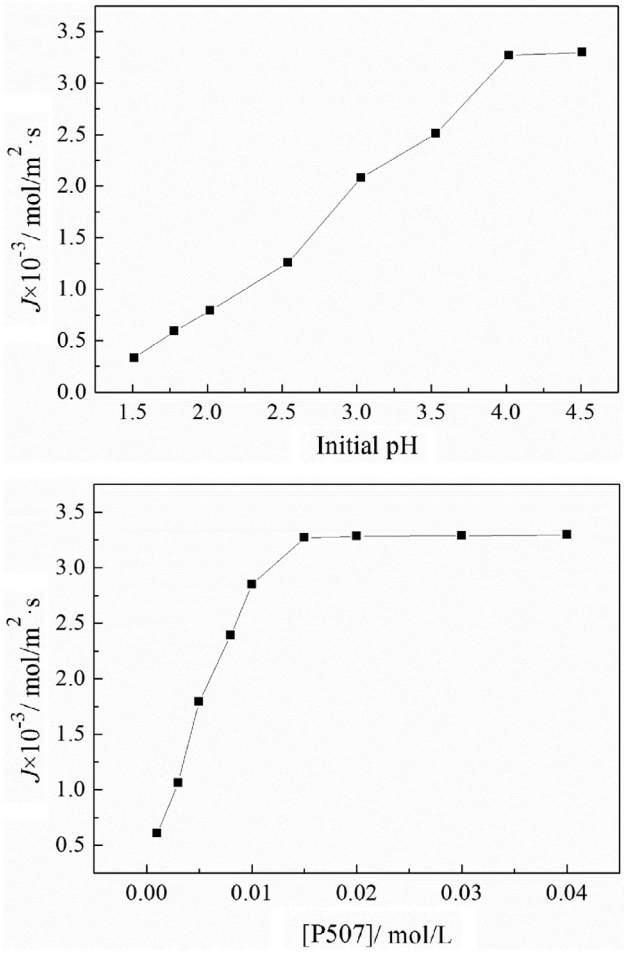

Figure 7 The relationship between mass transfer rate *J* and pH in the aqueous phase, together with P507 concentration in the organic phase [P507] (conditions: [$NdCl_3$]=0.001 mol/l, saponification rate 40%, flow rate=5.55×10^{-10} m^3/s, and channel width=100 μm).

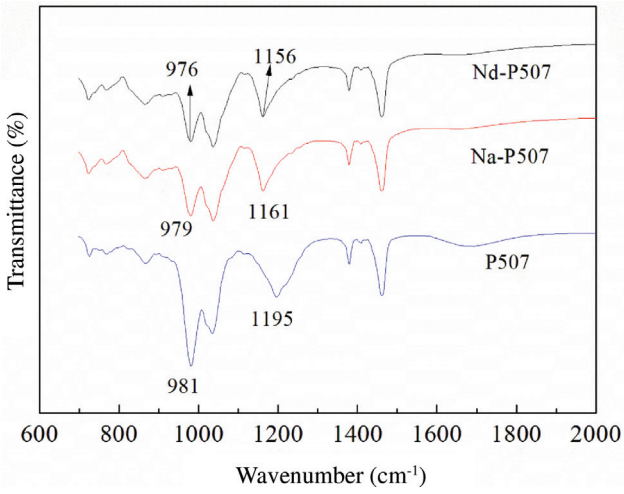

Figure 8 Infrared spectrum of P507 and Nd-P507 extracted compound (conditions: [$NdCl_3$]=0.001 mol/l, [P507]=0.02 mol/l, saponification rate 40%, pH=4.0, flow rate=5.55×10^{-10} m^3/s, and channel width=100 μm).

1156 cm^{-1}, which means the oxygen of p=O participates the complex formation through coordination. Compared with the IR spectrum of Na-P507 and Nd-P507, the displacement amplitudes of p=O stretching for Nd-P507 are larger than that for Na-P507, because the ionic potential of Nd^{3+} is larger than that of Na^+. Conclusively, IR spectrum changes of the organic systems in the microreactor again confirm a cation exchange mechanism proposed previously in the conventional extraction.

4 Conclusions

The extraction behavior of Nd(III) with saponified P507 was investigated using a Y type microreactor, and the results demonstrate the applicability of the microreactor to liquid-liquid extraction of rare earths. The following conclusions can be obtained:

- Extraction equilibrium experiences show that extraction efficiency increases with increasing initial aqueous pH and saponification rate of P507, and initial aqueous pH value 4.0 and saponification rate 40% are the optimal operation conditions.
- The extraction efficiency decreases with increasing channel width and flow rate under fixed conditions, and the two phases successfully flow while keeping an aqueous-organic interface in a microchannel (100 μm width and 120 μm depth) at volumetric flow rates of the aqueous phase from 5.55×10^{-10} m^3/s to 1.53×10^{-9} m^3/s.
- The Nd(III) extraction rate is significantly increased with the Y type microreactor, compared to conventional batch extraction, and extraction equilibrium is achieved within 1.5 s.
- The extraction behavior of Nd(III) in the microreactor is an interface chemical reaction or the diffusion rate of the Nd-complex in the organic phase at low pH and [P507], while the extraction rate is controlled by the rate of metal diffusion in the aqueous phase at high pH and [P507].
- IR spectrum analysis shows that the extraction mechanism in the microreactor is a cation exchange process.

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Bionotes

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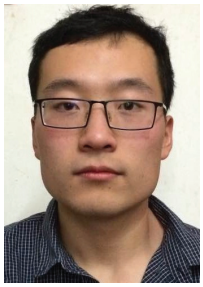
Libo Zhang is a PhD supervisor in Kunming University of Science and Technology, and is mainly engaged in microwave heating in the application of metallurgy, chemical engineering, materials and so on.



Feng Xie

Feng Xie has started his MSc at the Kunming University of Science and Technology, China, where he is currently carrying out research on microwave energy application, metallurgy and chemical engineering under the supervision of Professor Libo Zhang. His main research subject is the extraction and separation of rare earths by the microfluidics technique.

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and Technology. Her primary research interests include microwave metallurgy, solvent extraction of rare earth and the efficient use of rare earth resources.

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Jinhui Peng is a PhD supervisor in Kunming University of Science and Technology, and is mainly engaged in microwave heating in the application of metallurgy, chemical engineering, and materials science. He has received many awards, among which are the State Technological Invention Award, and the Natural Science Award of Kunming province.

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