RSC Advances

ROYAL SOCIETY OF CHEMISTRY

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Journal Name

RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Microfluidic Solvent Extraction and Separation of Cobalt and Nickel

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The extraction and separation of cobalt from sulphate solution containing Ni^{2+} and Co^{2+} by the process of microfluidic extraction was investigated on a counter-current flow interdigital micromixer with channels of 40 μm width, which has two opposite inlets and an upwards outlet. Meanwhile, the comparative batch extraction experiments were conducted in separatory funnels. The effects of pH and flow rates or contact time on the microfluidic and batch experiments were studied using an aqueous solution containing 73.09 $g \cdot L^{-1}$ of nickel and 2.44 $g \cdot L^{-1}$ of cobalt and 20 vol% PC88A diluted with $260^{\#}$ solvent naphtha. In addition, cobalt extraction isotherms (Mc-Cabe Thiele) were constructed to determine the number of stages. The results of percentage extraction and seperation factor of microfluidic extraction was better than that of batch extraction. The features of the microreactors, i.e. large specific surface area and short diffusion distance were effective for the efficient extraction and separation of cobalt from nickel.

1. Introduction

Cobalt and nickel are amongst the most important nonferrous metals. The extraction and separation of cobalt and nickel from sulphate, chloride, and ammoniacal solutions have been of interest to hydrometallurgists for a long time.[1-3] The very similar physical and chemical properties of these two metals have made their separation a challenging task. Many methods such as solvent extraction, liquid membrane, ion exchange, and precipitation have been conducted for the separation or preconcentration of cobalt and nickel.[4-7] Among these, solvent with organophosphorus acids has attracted much attention.

The organophosphorus reagents (D2EHPA, PC88A, and Cyanex272) were widely used to extract cobalt and nickel in sulphate solutions. Out of the three types of extractants, D2EHPA is the least selective and cyanex272, though most selective, is the most expensive. Therefore, the phosphonic acid based reagent PC88A was used in many Chinese companies for its relatively cheap price. However, there are some deficiencies by using the traditional technology, such as: (1) low extraction efficiency of a single stage and large extractant consumption; (2) complex operation for multistage of extraction and stripping; (3) prone to emulsification; and (4) significant footprint size and fire hidden trouble. Microfluidic extraction may be capable to overcome these disadvantages in extraction and separation of cobalt and nickel.

Microfluidic technology has attracted much attention in the fields of analytical chemistry, chemical synthesis, chemical engineering and biotechnology.[8-11] In microfluid systems, reagents and starting materials typically driven through microchannels on the order of 10-1000 μm, and mass/heat transfer is enhanced by promoting contact between very thin fluid reactant layers and realized rapid micromixing. Due to the small dimensions, chemical processes in microchannels can be different from those in macroscale processes. Secondary phenomena become significant in microreactors when the characteristic length decreases, i.e. mass diffusion, surface condition and heat conduction. Compared to conventional batch reactors, the unique operating characteristics of microreactors are as follows: (1) high reaction efficiency due to high surface area to volume ratio, rapid mass and heat transfer; (2) high degree of chemical selectivity due to precise control of the reaction temperature and time; (3) mini footprint size, save operation and friendly environment; and (4) fast and direct amplification via "numbering-up" parallel processing without scale-up effect.[12-14]

As the above unique advantages, microfluidic technology for the extraction process have emerged in the past few years. Shekhar et al.[15] mentioned a simple but effective micro-mixer-settler made of a rotated helical coil of 100 μm i.d. micro-tubing for nuclear solvent extraction. Nearly 100% efficiency was observed in extraction as well as stripping procedures. Syouhei et al.[16] investigated a micro solvent extraction system for the separation of lanthanides. The microchannel is fabricated on a PMMA plate with 100 μm width and 100 μm depth. The effective separation of lanthanides (Pr/Nd and Pr/Sm) can be achieved on the micro extraction chip. The phase separation of the aqueous and organic phases after extraction can be carried out by changing the cross section of the micro flow channel. Fukiko et al.[17] performed the extraction of three rare earth metals (yttrium, europium and lanthanum) with PC88A as the extractant dissolved in toluene on a microreactor fabricated on a silicon wafer (20 mm × 40 mm) by photolithography and wet etching methods. The aqueous and organic phases successfully kept an aqueous-organic interface in a microchannel, 92 μm in depth and 300- 434 μm in width, at volumetric flow rates from 5.6×10^{-10} to 2.8×10^{-9} $m^3\cdot s^{-1}$. The metals are satisfactorily extracted by the microreactor in the residence time of 0.7 sec. Osamu et al.[18] used slug flow channel microreactor for liquid-liquid extraction of cesium from cesium nitrate solution. The results indicated that the Cs^+ extraction rate was significantly increased with the slug flow microreactor, compared to conventional batch extraction, and extraction equilibrium was achieved within 40s. Craig et al.[19] invistigaed microfluidic extraction of copper from particle-laden solutions. Though in the presence of silica nanoparticles, the formation of particle-stabilised emulsions was prevented. Thus, microfluidic solvent extraction shows great promise for handling particle-laden solutions of industrial relevance.

Above literatures indicated that the microfluidic technology was applicable to be used in the solvent extraction process and was useful as a simple test plant for the construction of an efficient separation process. In this article, extraction and separation of cobalt and nickel in sulphate solution both in microfluidic and batch extraction were presented. The effects of equilibrium pH and the flow rates/contact time were investigated. In addition, the Mc-Cabe Thiele diagrames were constructed to determine the number of stages required at a chosen volume phase ratio.

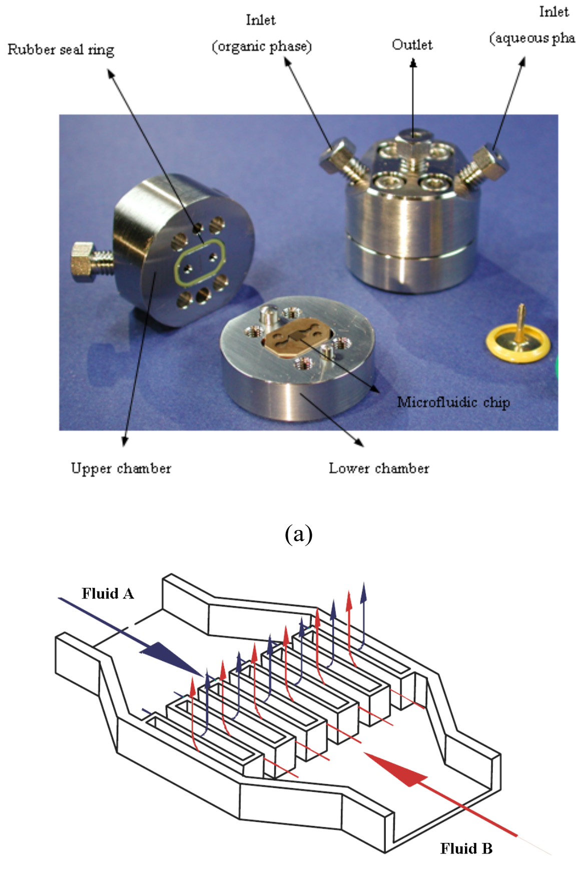
2. Experimental

2.1. Materials

The initial aqueous was a synthetic solution with 73.09 $g\cdot L^{-1}$ of nickel and 2.44 $g\cdot L^{-1}$ of cobalt, using AR grade $NiSO_4\cdot 6H_2O$ and $CoSO_{4}.7H_2O$ dissolved in pure water, concentrations similar to those of a real sulphate purification. The aqueous pH was adjusted by the addition of concentrated sodium hydroxide (5 $mol\cdot L^{-1}$) and sulfuric acid solutions (98%) to the appropriate value 5.0±0.1 measured by PHS-3D pH meter.

Industrial grade extractant, PC88A (C16H35O3P, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) and diluent, $260^{\#}$ solvent naphtha(C_{11}~C_{17} alkanes mixtures primarily, and containing 4wt% aromatic hydrocarbons) were simultaneously supplied by Aoda Chemical Co., LTD China. Both were used without further purification. The extractant PC88A was pre-neutralized by 10 $mol\cdot L^{-1}$ NaOH aqueous solution. Organic solution was prepared by dissolving 20% v/v Na-PC88A in 80% v/v $260^{\#}$ solvent naphtha to form a single phase.

2.2. Apparatus and procedures



(a)

(b)

Fig. 1 Schematic diagram of microreactor
(a) microreactor, (b) mixing and reacting principle

The microfluidic experiments characterizing the extraction efficiency were performed in a counter-current flow interdigital micromixer (stainless steel) with 40 μm width channels fabricated by IMM, Germany, as shown in Fig. 1(a). It consists of a mixing element, two opposite inlets and one upwards outlet. The feed flows including aqueous and organic solution were introduced to a mixing element inside the micromixer via the two inlets, from opposite directions. As shown in Fig. 2, constant flow pumps were used to feed the two fluids into the microchannels, which were provided by Yanshang Instrument Factory, China, and the flow velocity was in the range of 0.1 ~40 mL·min^{-1}. The two fluids flow through the interdigital channels and then flow upwards into a slit, which is perpendicular to the interdigital structure, as shown in Fig. 1(b),[20] where, the mixing and extraction reaction took place, the most of Co in the aqueous was extracted to the organic phase by Na-PC88A, and most of Ni was still remained in the aqueous phase. The mixed fluid was separated and clarified to form two clear phases in the settler, the upper dark blue Co loaded organic phase and the bottom green Ni raffinate. The microreactor was immersed in a water bath to keep the constant temperature at 25±0.2℃.

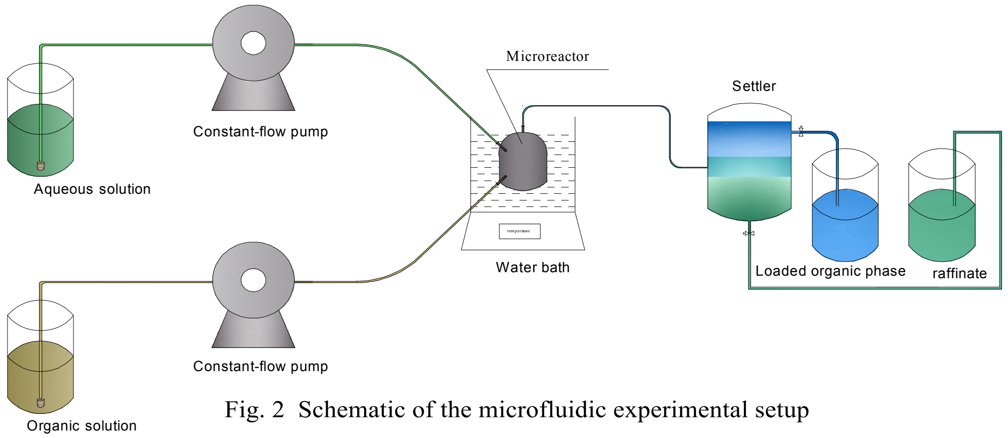


Fig. 2 Schematic of the microfluidic experimental setup

The comparative batch extraction tests were carried out by contacting equal volumes of the organic and aqueous phases, i.e. phase ratio O:A=1:1, in 125 mL pear shape separatory funnels. Then the system was placed horizontally in the roundtrip thermostatic water bath oscillator (WHY-2) to mix and react at a certain time, and the oscillation intensity was 200rpm. Subsequently, the mixture was separated after 30min to form bottom aqueous phase containing Ni and upper organic phase loading Co.

For all microfluidic and batch experiments, the raffinate was taken to determine the concentrations of the metals Ni and Co by inductively coupled plasma-atomic emission spectroscopy (AA240FS ICP-AES spectrophotometer). Those in the top loaded organic phase were calculated in accordance with mass balance.

3. Results and discussion

The extractant PC88A was converted to the sodium salt by the addition of sodium hydroxide. The neutralization reaction can be written as :

$$\mathrm{Na}^+_{aq} + 1/2(\mathrm{HR})_{2org} \rightarrow \mathrm{NaR}_{org} + \mathrm{H}^+_{aq} \quad (1)$$

According to Sarangi et al.,[21] the neutral form of the extractant exists as monomer, whereas the acidic form as a dimmer, both forms take part in the extraction. In acidic sulfate media, the extraction of divalent metals by mixtures of acidic extractants can be presented by the following equilibrium:[22]

$$\mathrm{M}^{2+}_{aq} + R^-_{org} + 2(HR)_{2,org} \Leftrightarrow MR_2 \cdot 3HR_{org} + H^+_{aq} \quad (2)$$

where the distribution ratio, D, was calculated as the concentraion of metal present in the organic phase to that in the aqueous phase at equilibrium, as shown in the flowing equation:

$$\mathrm{D} = \frac{[\mathrm{M}]_{org}}{[M]_{aq}} \quad (3)$$

From the D values, the percentage extraction E and separation factor of cobalt and nickel $\beta_{\mathrm{Co/Ni}}$ were calculated using the flowing equations:

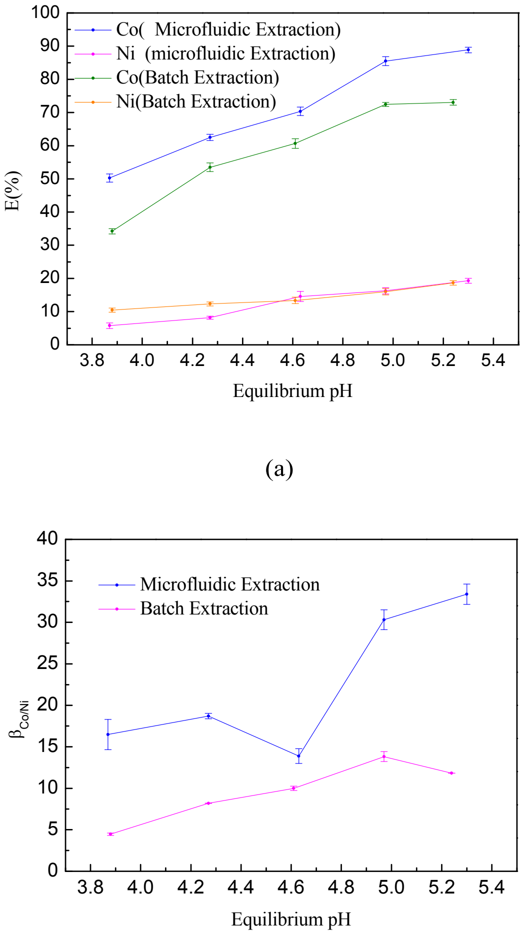
$$\mathrm{E} = \frac{[\mathrm{M}]_{org} \cdot V_{org}}{[M]_{org} \cdot V_{org} + [M]_{aq} \cdot V_{aq}} \times 100\% \quad (4)$$

$$\beta_{Co/Ni} = \frac{D_{Co}}{D_{Ni}} = \frac{[Co]_{org} \cdot [Ni]_{aq}}{[Co]_{aq} \cdot [Ni]_{org}} \quad (5)$$

where M represented the corresponding metal cobalt and nickel respectively, and V represented the volume. The subscript aq and org denoted the aqueous and organic phases respectively.

3.1. Effect of equilibrium pH

The extraction of Co with a cation exchange type of extractant, PC88A, was pH dependent and involved the release of protons from the extractant during metal transfer from the aqueous phase to the organic phase. As a result, the pH of the aqueous phase decreased. pH values would be raised by the addition of alkali solution or by using a partially saponified PC88A for effective metal extraction. We followed the later methodology of partial saponification of PC88A for Co separation studies.



(a)

(b)

Fig. 3 Effect of equilibrium pH on the extraction of Co and Ni

As in the microfluidic and batch experiments, the extraction of cobalt and nickel from aqueous sulphate medium with pH 5.0 was studied using the sodium salt of PC88A (20%v/v) which was neutralised with concentrated NaOH to 25-85%, correspongding to the equilibrium pH changing in the range 3.80-5.30, respectively. The flow rates of organic and aqueous phase were the same as 25 mL·min^{-1} in microfluidic extraction. The time of mixing and reaction in batch extraction was 10 min which was enough to ensure complete cobalt extraction reaction. By analyzing the raffinate, data shown in Fig. 3 were obtained.

The percentage extraction of cobalt and nickel increased with increasing neutralisation of the solvent obviously due to a change in the equilibrium pH value in both microfluidic and batch extraction (Fig. 3(a)). The optimum equilibrium pH of the aqueous phase appears to be in the range 4.9-5.3 with about more than 72% Co extraction in the batch extraction and more than 85% Co extraction in the microfluidic extraction. The separation factor, β (Fig. 3(b)) was low due to high co-extraction of nickel. Highest separation factor of 33 in microfluidic extraction at an equilibrium pH of ~5.3 were obtained, whereas in case of batch extraction it was 13 at an equilibrium pH of ~5.0.

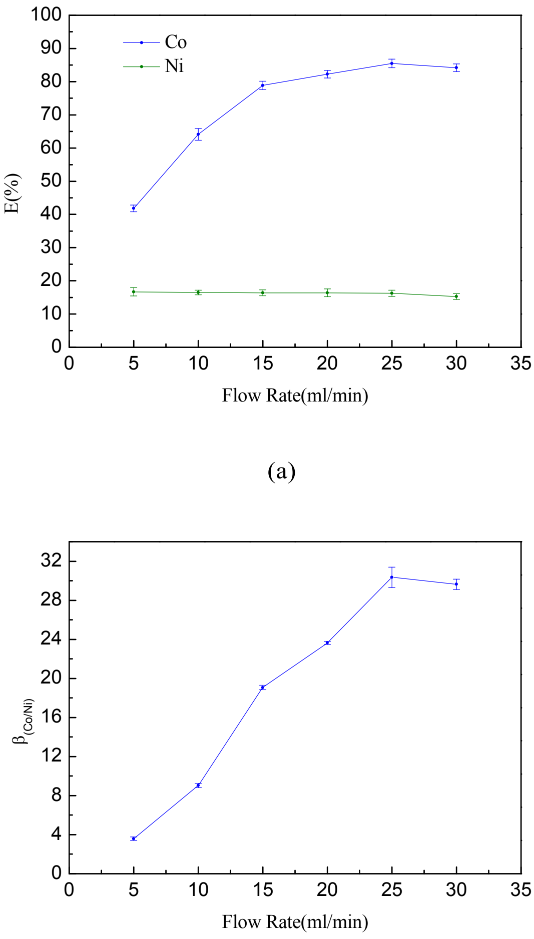
The cobalt extraction ratio in microfluidic extraction was much greater than that in batch extraction under the same conditions. The reason was that components were mixed through intensive oscillation in batch extraction, while in microstructures this process was mainly realized through diffusion. Multilamination phenomenon happened in the interdigital micromixer of IMM. The micromixer produced thin liquid lamellae and guided them to contact and flow through chambers. Splitting the inlet streams into substreams and recombining them increases the contact surface between the two fluids causing diffusion to occur faster.[23] Despite laminar flows in microstructures, molecules had short paths to exceed the surface of organic-aqueous interface so that a nearly complete mixture was achieved within a few seconds, and often as little as a few milliseconds.[24] The features of the micromixer, e.g., large specific surface area and short diffusion distance were effective for the efficient extraction and separation of Co from Ni.

During the course of microfluidic extraction, cobalt was preferentially extracted and the co-extraction of nickel was not negligible resulting in 5.78-19.30% extraction with increase equilibrium pH from 3.8-5.3, that was not very different from batch extraction results.

3.2. Effect of flow rate

For study the influence of flow rate on the extraction of cobalt and nickel, the aqueous solution and the organic phase were contacted at a 1:1 phase ratio in microfluidic extraction, and the other reaction conditions were shown in section 2.1. The volumetric flow rate of the aqueous phase, V_{aq} , was equal to that of the organic phase, V_{org} , the flow rate of 5, 10, 15, 20, 25 and 30 mL·min^{-1} was adapted to investigate the influence on the extraction and separation of Co and Ni.

The relationship between the extraction degree of cobalt and nickel, E, and the flow rate was shown in Fig. 4(a). As the flow rate increased, the extraction ratio of the cobalt increased as well, but the extraction ratio of the nickel almost kept constant. This suggested that exchange reaction between Co in the organic phase and Ni in the aqueous phase reached the extraction equilibrium state. When the flow rate decreased less than 15 mL·min^{-1}, the percentage extraction of cobalt was almost linear growth with the flow rate increased. However, when the flow rate was greater than 15 mL·min^{-1}, the percentage extraction of cobalt was slowdown in growth trend. The percentage extraction had a maximum at intermediate to high flow rates and decreased at very high flow rates (＞25 mL·min^{-1}). Fig. 4(b) showed the results of the seperation factor of cobalt and nickel. The $\beta_{Co/Ni}$ was also increased with the increase of flow rate ＜25 mL·min^{-1}. But with the further increase of flow rate, $\beta_{Co/Ni}$ was reduced in contrast. The highly effective seperation can be achieved at high flow rate of 25 mL·min^{-1} and the extraction rate of cobalt was 85.49%. If the flow rate was too high, it was difficult to seperate of the aqueous and organic phases in the settler.

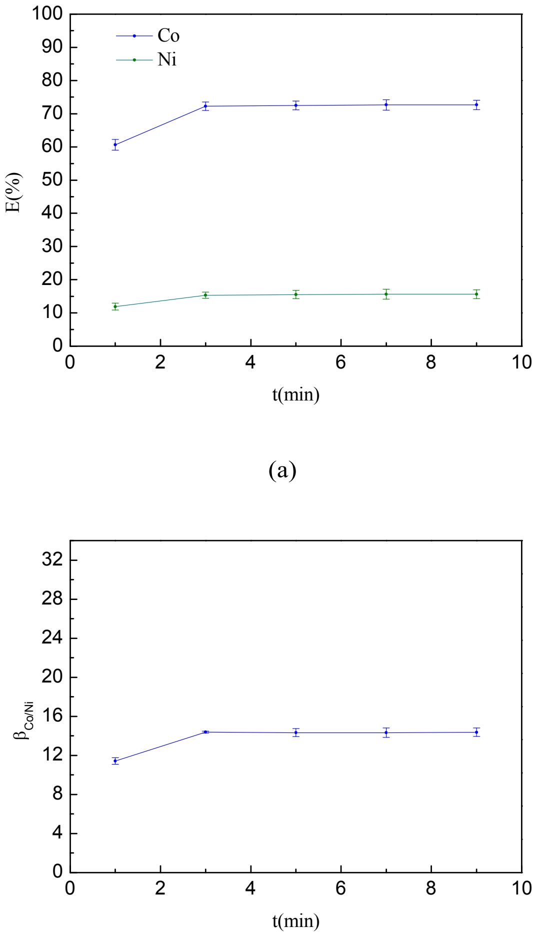


(a)

(b)

Fig. 4 Effect of flow rate on the extraction of Co and Ni in microfluidic extraction

Since the internal volume of the microreactor is on the order of 8 μL (volume of the chamber), residence times were less than 0.019s at the flow rate of 25 mL·min^{-1}. Despite these extremely short residence time, the thermodynamic equilibrium could also be reached. The results of batch extraction was shown in Fig. 5. In these batch experiments, the extraction equilibrium was reached when the contact time was more than 3 minutes, this time was much larger than that in the microreactor .



(a)

(b)

Fig. 5 Effect of contact time on the extraction of Co and Ni in batch extraction

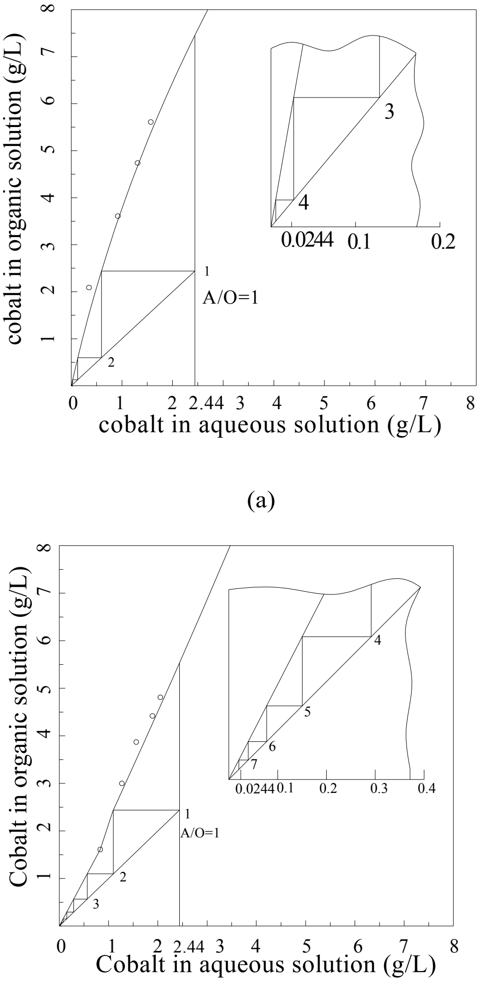
In microfluidic extraction, since the residence time “t” is inversely related to the volume flow, one would expect maximum extraction efficiency at low flow rates. However, the results were in the opposite direction. According to Benz et al.,[25] the diffusion (diffusion coefficient, D) from a sphere of radius, r, into a well-stirred volume was a complex function of time, t, described by two parameters:

$$\frac{C}{C_0} = f\left[\frac{Dt}{r^2}, \frac{k \cdot V_E}{V_R}\right] \tag{6}$$

With k being the partition coefficient and V_E/V_R the ratio of extract to raffinate volume, which was set to one. In this function, only the first parameter, Dt/r^2, was time dependent.

The droplet diameter, 2r, as a measure of diffusional length, almost linear decreased with increasing flow rate, and the mass transfer surface area greatly increased. Although the residence time was shorter, the mass transfer efficiency was linear increased. Furthermore, it was expected that at very high flow rates the drop size approached a minimum value, and hence, the diffusional length was not further decreased. As a result, the extraction efficiency reached a maximum value at high flow rates as shown in Fig. 4(a). In this case, the extraction efficiency had a maximum at intermediate to high flow rates and decreased again at very high flow rates.

3.3. Cobalt extraction isotherm



(a)

(b)

Fig. 6 Mc-Cabe Thiele plot for cobalt extraction
(a) microfluidic extraction, (b) batch extraction.

To determine the number of stages required at a chosen volume phase ratio, the Mc-Cabe Thiele diagrames were constructed with fresh aqueous solution to simulate the first stages of counter-current extraction (fresh aqueous solution to meet loaded organic solution). Both in microfluidic and batch extraction tests, the same organic with 70% saponified 20% v/v PC88A was contacted with fresh aqueous solution with A/O ratio1:1 at pH 5.0. In batch extraction, the shak-out time of these two phases was 5min at every tests, and the microfluid flow rates of these two phases were both 25 $mL\cdot min^{-1}$. From the extraction isotherm, shown in Fig. 6(a), it was observed that quantitative extraction of Co (＞99.9%) was achieved in seven stages in batch extraction, and that was achieved in four stages in microfluidic extraction, shown in Fig. 6(b). The results showed that it reduced extraction stages of cobalt by using microfluidic technology.

4. Conclusions

Microfluidic extraction had shown great promise for extraction and separation of cobalt from nickel in sulphate solutions. The main conclusions were summarized as follows:

(1) In all the same equilibrium pH from 3.8 to 5.4, the cobalt percentage extraction and separation factor in microfluidic extraction were much greater than that in batch extraction. The co-extraction of nickel was not negligible both in these two experiments.

(2) The Co extraction was significantly affected by the flow rates of micromixer, compared to conventional batch extraction, and extraction equilibrium was achieved less than 0.02s.

(3) It reduced extraction stages of cobalt by using microfluidic technology. Quantitative extraction of Co (＞99.9%) was achieved in seven stages in batch extraction, but that was achieved in four stages in microfluidic extraction.

Acknowledgements

The authors gratefully acknowledge the Joint Funds of the National Natural Science Foundation of China for financial support of this research.

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