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Co and Ni extraction and separation in segmented micro-flow using a coiled flow inverter

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HIGHLIGHTS

- Segmented micro-flow extraction is developed using a CFI and a phase separator.
- Shorter time and better extraction efficiency are obtained in microflow.
- Regular segments are formed at slow velocity and in- and outlet match.
- Specific interfacial area are measured from the recorded slug dimension.
- Mass transfer performance are identified from experimental results.

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ABSTRACT

The segmented micro-flow extraction and separation of the adjacent elements of Co from Ni sulphate solution with Cyanex 272 is developed using a micro-scale coiled flow inverter (CFI). This is compared with the conventional batch extraction in parallel. Continuous operation of a process involving liquid-liquid extraction and then two-phase separation is achieved instantly. For the latter a micro-scale separator is used. Compared with batch extraction, the segmented micro-flow extraction process shows order-of-magnitude faster extraction times, higher extraction ability for Co, lower extraction for Ni, and then a better selectivity between Co and Ni at industrial-matching concentration. Regular columnar slugs are observed at low flow rates and found to be a Gaussian function of the flow rates. Matched in- and outlet flows indicates that extraction in micro-flow is dependent on mass transfer by molecular diffusion. Extraction efficiency is enhanced by the internal circulation flow generated within slugs. Additionally, the characteristic parameters, overall volumetric mass transfer coefficient $k_L\alpha$ and overall mass transfer coefficient k_L, are measured to determine the mass transfer performance. Compared with batch, much higher $k_L\alpha$ of Co (0.26–0.017 s^{-1}) and smaller of Ni (0.053–0.013 s^{-1}) are investigated in CFI. Meanwhile, 4.5 times increasement of the k_L value of Co to Ni is observed in CFI indicating the asynchronous extraction between Co and Ni.

1. Introduction

Cobalt and Nickel are amongst the most important nonferrous metals [1]. Because of the similar physicochemical properties, the adjacent elements Co and Ni always coexist in nature. One significant source of Co is as a by-product of the hydrometallurgical treatment of nickel sulphide and nickel laterite ores in sulphate media. The separation and recovery of Co from Ni have mainly been conducted through direct solvent extraction (SX) using phosphinic acid derivatives, e.g. diisooctylphosphinic acid (Cyanex 272) [2–4]. It is estimated that 40% of cobalt in western hemisphere is produced by SX with Cyanex 272 [4]. Mixer-settler is one of the most common equipment in the conventional extraction industry process. However, the contradictory operation, i.e. mixing by mechanical agitation and coalescence by gravity, leads to some disadvantages in mixer-settler, such as long mixing time, huge plant footprint for coalescence, a third phase crud and emulsion droplets formation, mechanical entrainment, etc., [5,6] Therefore, it is nec-

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Nomenclature

C	mass concentration of metal ions, g/l
ΔC_{ln}	logarithmic mean concentration difference, g/l
W_s	slug width, m
L_f	wall film length, m
L_{UC}	unit cell length, m
L_s	slug length, m
ID	channel inner diameter, m
J	mass transfer flux, g m^{-2} s^{-1}
α	interfacial area, m^2/m^{-3}
k_L	overall mass transfer coefficient, m s^{-1}
$k_L\alpha$	overall volumetric mass transfer coefficient, s^{-1}
t	residence time, s
Q	volumetric flow rate, ml s^{-1}
V_c	volume of microchannel, ml

Subscripts

aq	aqueous phase
org	organic phase
in	at inlet
out	at outlet
eq	at equilibrium
Co	cobalt
Ni	nickel

essary to seek a new extraction technology of "greener, smaller, better, faster, and cheaper" to overcome above problems.

In recent years, along with the progress in microfabrication, microflow devices display many advantages for liquid-liquid extraction and are proposed as a potential substitute for mixing-settling SX [7–10]. A decrease in the channel dimension in the range of 50–1000 μm in a microreactor can induce a high specific surface area and short diffusion length [11]. Consequently mass/heat transfer is strongly enhanced by promoting contact between very thin fluid layers and realized rapid micromixing. Additionally, the increasing throughput by numbering-up gives new possibilities at macro scales out of reach for micro-flow processing [10]. As liquid-liquid mass transfer depending on concentration gradients, specific interfacial area and residence times, enhancement of extraction efficiency for reaction and separation can be expected in such micro scales.

Stratified and segmented (also called as slug and plug) flow are the most common flow patterns in microreactors. The latter provides better mass transport due to the internal recirculation within the segments and faster surface concentration renewal [12–14]. The stable flow patterns and uniform interfacial areas permit a precise tuning of the mass transfer processes and make a prior prediction of mass transfer coefficients feasible. Moreover, liquid-liquid phase separation after mixing can also be successfully achieved using different phase separators [15–17].

Microfluidic chip [18] and capillary microreactors [19] are most popular devices used in micro-flow processes. In order to realize even higher heat and mass transfer efficiency, some novel capillary channels with unconventional structure are observed in laboratory and industrial application, especially some helically coiled tubes have been proposed. Nigam et al. [20] firstly reported a novel microstructured coiled flow inverter (CFI) which has alternating equal distance 90°-bends. Compared to straight helically coiled tubes, 38.5% higher heat transfer coefficient, 3.5-fold enhancement in Sherwood number have been provided in CFI [21,22]. Kurt et al. [23] reported a CFI fabricated with different structures, including step-wise, zigzag, and frame-wise, to offer improved residence and thermal time distribution. In our previous work [24], the CFI was firstly applied to liquid-liquid extraction of an organic compound, which showed about 20% higher extraction performance than that in straight tube. However, there are, to our best knowledge, few reports concerning the process of metal ions extraction and separation on such micro-scale CFI.

In this work, we use a segmented flow in micro-scale CFI to study the extraction and separation performance of Co and Ni in industrial-matching sulfate solution by Cyanex 272. Meanwhile, a phase separator is adapted to achieve continuous operation of liquid-liquid extraction and then two-phase separation. A comparison is made with conventional batch extraction in parallel. Firstly, the effects of final pH, residence time, and extractant volume concentration on the extraction efficiency are studied to optimize the operation conditions. Then, flow patterns in CFI at different flow rates are recorded. The specific interfacial areas and mass transfer performance have also been investigated.

2. Experimental

2.1. Materials and analysis

The commercial extractant Cyanex 272 (Diisooctylphosphinic acid, $C_{16}H_{35}O_2P$, 90%) was provided by Sigma-Aldrich and used without any further purification. Prior to be used, it was pre-neutralized by adding stoichiometric amount of 10 mol/l NaOH to form a single phase. Organic phase was prepared by dissolving certain pre-neutralized Cyanex 272 in kerosene. The aqueous phase was prepared by dissolving stoichiometric amounts of CP grade $NiSO_4{\cdot}6H_2O$ and $CoSO_4{\cdot}7H_2O$ (both supplied by Alfa Aesar) in deionized water (produced by Millipore Elix UV-5 water purification system, 18.2 MΩ, Germany). The initial concentrations of Co and Ni were 2.578 and 66.34 g/l, respectively. Initial pH of the aqueous phase was 4.43 for all experiments.

The pH values in the aqueous phase were measured by a pH meter (PHM210, MeterLab). The concentration of Co in the aqueous solution before and after extraction was measured by a ICP-OES spectrometer (model: SPECTROBLUE-EOP, SPECTRO, Germany). The high Ni concentration in the aqueous phase was determined by complexometric titration using 0.02 mol/L Na_2EDTA standard solution with murexide as indicator agent. Both of Co and Ni concentrations in the organic phase were calculated according to the mass balance between the aqueous and organic phase.

2.2. Apparatus and extraction procedure

Fig. 1a shows the setup of continuous segmented micro-flow extraction system (hereinafter termed "micro-flow"). All the experiments were performed at room temperature (298 ± 2 K). A dual channel syringe pump (Fusion 200, Chemyx Inc. US) with two 25 ml gastight syringes was used to pump the green aqueous and light yellow organic phase at given flow rates. In order to get the phase volume ratio of organic and aqueous phase (A/O) of 1.0, the volumetric flow rates of both phases were equal for all experiments. The total flow rates were set at 24, 60, 120, 240, 360, 480 ml/h for 300, 120, 60, 30, 20, 15 s of the residence time in CFI, respectively. For generation of segmented flow, the organic and aqueous phases were joined to an orthogonal T-type joint