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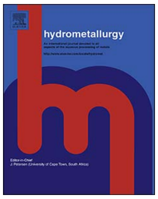

Extraction of rare earths using bubbling organic liquid membrane with un-saponified P507

Jie Liu[a], Kun Huang[a,b,*], Xiaohong Wu[a], Wenqian Liu[a], Weiyuan Song[b], Huizhou Liu[a,b]

[a] *CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266100, PR China*
[b] *CAS Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China*

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ABSTRACT

Extraction and enrichment of low-concentration rare earths from the in-situ leaching solutions of ion-absorbing type rare-earth ores using bubbling organic liquid membrane with un-saponified P507 was investigated. Experimental results revealed that saponification of P507 extractant are unnecessary for extraction of rare earths using bubbling organic liquid membrane. The equilibrium pH of the aqueous solutions flowing out from the extraction column would not decrease obviously, because the total volume of un-saponified P507 contacting with the aqueous phase in the column was very small, and the aqueous-to-organic phase ratios could be very large. Therefore, the loading capacity of rare-earth ions in the organic phase have no obvious changes, compared to that using saponified P507. Scale-up experiments in the pilot-scale columns connected in cascade for continuous countercurrent extraction of low-concentration rare earths about 100 mg/L in the leaching solutions demonstrated that, the final residual concentrations of rare earths remained below 3.0 mg/L, while total recovery of rare earths after extraction and stripping processes could reach above 90%. Bubbling organic liquid membrane extraction is in fact an interfacial chemical reaction of rare-earth ions with un-saponified P507 adsorbing at the surface of organic liquid membrane. During countercurrent extraction processes, shearing interaction of the aqueous solutions with dispersed organic bubbles rising in the extraction column would result in continuous exposure of fresh surface of organic bubbles, which is a main driving force to promote the mass transferring and enrichment of rare-earth ions into the organic liquid membrane layer.

1. Introduction

The ion-adsorption type rare earth ores in Southern China are famous for its high content of middle and heavy rare earth elements (Chi and Tian, 2006, 2008). Nowadays, in-situ leaching the ion-absorbing ores by acidic ammonium sulfate solution and then followed by precipitation with ammonium bicarbonate have been widely employed in industries to extract and enrich rare earths (Tian et al., 2010; Wang et al., 2014). During the processes, severe ammonia-nitrogen pollution towards local environments is usually not avoidable. After years of over-exploiting, a large amount of leaching tailing ores remained (Tian et al., 2013a). Rare earths flow away with rainwater into the rivers and were lost. It was reported the concentrations of rare earths in the in-situ leaching solutions of tailing ores were generally $<$ 300 mg/L, or even less (Li et al., 2012). Enrichment and recovery of rare earths from such a kind of low-concentration solutions by traditional chemical precipitation are extremely difficult and not economic (Chi et al., 2003; Chi and Tian, 2006). In order to improve the precipitation efficiency of rare earths, excessive ammonium bicarbonate must be added, which not only results in co-precipitation of non-rare earths impurity ions, but also increases the ammonia-nitrogen pollution (Tian et al., 2011). The Chinese government has issued strict reduction policies to control the ammonia-nitrogen pollution emissions. It is urgent to develop green sustainable and economic method to treat the low concentration rare-earth leaching solutions of the ion-absorbing ores (Wang et al., 2013).

Solvent extraction is a main method for enrichment and separation of rare earths (Xu, 2002; Feng et al., 2012; Jha et al., 2016). However, traditional liquid-liquid extractor, including mixer-settler, extraction tower or column, and centrifugal extractor, are not suitable for extraction of metal ions with very low concentrations. Generally, the required aqueous-to-organic phase ratios (A/O ratios) in traditional extractor are low, and dispersion of organic phase with very small volume into a large volume of in-situ leaching solutions for enrichment of low-concentration rare earths is extraordinarily difficult (Chi et al., 1995; Wang and Chen, 2001). It is hard to avoid the dissolution loss of organic extractant in flowing-out aqueous solutions during operations at large

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[*] Corresponding author at: CAS Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Bei'er Jie No.1, Zhongguan cun, Haidian, Beijing 100190, PR China.
E-mail address: khuang@ipe.ac.cn (K. Huang).

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A/O ratios using traditional extractors. Discharge of the raffinates containing emulsion oil droplets would result in severe environmental pollution (Huang et al., 2015). On the other hand, saponification of organic extractant is usually necessary for those traditional acidic phosphorus extractants, such as P507 and Cyanex 272, extensively employed in rare-earth solvent extraction and separation (Xiao et al., 2015a,b). Extraction of rare-earth ions by un-saponified P507 would result in an increase of H$^+$ ion concentrations in raffinates, so that prevent the progressing of the extraction reaction, and the extraction loading capacity of rare earths in the organic phases would decrease. However, the saponification processes would unavoidably bring about a large amount of ammonia-nitrogen wastewaters with high content of salts, which was difficult to be treated using traditional methods (Yang et al., 2013; Xiao et al., 2013, 2015a,b). This has become a serious challenge to the sustainable development of rare-earth industries.

Recent years, some non-saponification synergistic extraction systems (Fan et al., 2010; Tian et al., 2013b; Zhu et al., 2015; Ma et al., 2017) were suggested in order to eliminate the ammonia-nitrogen wastewater pollution originated from the saponification of acidic organo-phosphorus extractants. Xiao et al. (2015b) suggested a double-solvent extraction system, composed of P507 and N235, for non-saponification extraction, based on the ability of P507 to extract rare earths and simultaneously N235 to extract H$^+$ ions released out by P507, so that the equilibrating aqueous pH could remain at a constant value, which is favor of improving the extraction capacity of acidic phosphorus extractants towards rare-earth ions. Bifunctionalized ionic liquid extractants composed of tricaprylmethylammonium cations ([A336]$^+$) and phosphoric acid or carboxylic acid anions were also reported successfully in separation of rare earths without saponification (Sun et al., 2010; Wang et al., 2011; Quinn et al., 2017). An inner synergistic effect was observed by combining the cation of A336 with the phosphoric acid group in acidic phosphorus extractants as anions, which exhibit different separation ability and selectivity for different rare-earth ions, and therefore traditional saponification operation of organic phosphoric acid can be avoidable (Guo et al., 2014; Chen and Chen, 2016; Yang et al., 2016). Although those reported technologies prevent ammonia-nitrogen contamination to some extent, they are only applicable to treat high concentration rare-earth aqueous solutions in traditional extractors. Partially dissolution loss of organic phosphorus extractant or ionic liquid cations still exists in the flowing-out aqueous solutions during operations at large A/O ratios.

Our previous works suggested a bubbling organic liquid membrane extraction technique for extraction and enrichment of low-concentration rare earths from the in-situ leaching solutions of ion-adsorption ores (Huang et al., 2015; Liu et al., 2017). The organic extractant with very small volume can be dispersed by gas bubbles thoroughly, due to their surface activity, and covered on the surface of gas bubbles to form a layer of organic liquid membrane. Those organic bubbles covered with organic extractant membrane ascend in the extraction column and contact counter-currently with aqueous feed solutions, so that rare-earth ions with very low concentration in the solutions can be extracted and enriched into the surficial organic liquid membrane layer of those gas bubbles. Pilot experiments demonstrated that the A/O volume ratios of continuous aqueous phase versus dispersed organic liquid membrane on bubbles within per unit of mass-transfer height of the extraction column could reach > 600:1 (Huang et al., 2015). The extraction of low-concentration rare earths could be intensified because the extraction reaction occurs on the organic liquid membrane layer covered on the surface of those dispersed gas bubbles. The interfacial effect promote the mass transferring, and the rare-earth ions in the aqueous solutions can be rapidly enriched into the organic liquid membrane layer (Liu et al., 2017). However, previous works found that the saponification degree of organic phosphoric acid extractant is one of the main factors that affect the stability of the organic liquid membrane layer on the surface of the gas bubbles. The dissolution loss of organic phosphorus extractant in the raffinates flowing-out from the extraction column would increase correspondingly, if the saponification degrees of organic extractants were not controlled properly. Meanwhile, separation of aqueous and organic two phase might become difficult at high saponification degrees. Severe emulsion and axial mixing might occur in the extraction column when operation at large volume flow ratios.

The aim of present work is to explore whether it is feasible using un-saponified P507 to perform such a bubbling organic liquid membrane extraction for extraction and enrichment of low-concentration rare earths directly from the in-situ leaching solutions of the ion-absorbing ores. Experiments in pilot-scale extraction columns connected in cascade for countercurrent operation were performed using un-saponified P507, and compared with that using saponified P507.

2. Experimental

2.1. Chemicals and reagents

The experimental feed aqueous solutions were the in-situ leaching solutions of the ion-absorbing type rare-earth ores in Dongjiang, Longnan, Ganzhou, Jiangxi, PRC, kindly provided by Ganzhou Rare Earth Group Co., Ltd. Before using, the in-situ leaching solutions were filtered with an industrial microporous filter (0.45 μm) to remove the tiny mineral particles suspended in them. The chemical analysis of the in-situ leaching solution is given in Table 1.

Industrial-grade of 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester (P507), purchased from Xiamen Pioneer Technology Co. Ltd., was used as the organic extractant. Kerosene, purchased from China Petrochemical Corporation (Sinopec Group), was used as the diluent. All of the organics were used as received, without further purification.

The stock organic solutions were prepared by mixing P507 with kerosene. The molar concentrations of P507 in the stock organic solutions were 1.5 mol/L. Industrial-grade of hydrochloric acid and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd. The other chemicals were of analytical grade.

2.2. Procedures

2.2.1. Lab-scale experiments in a small model extraction column

2.2.1.1. Both the aqueous solution and organic phase passed through circularly into and out of the column. 1.5 L of stock un-saponified P507 organic solutions and 4.5 L of feed aqueous solutions were employed for performing bubbling organic liquid membrane extraction in a small model extraction column. First, air was blown into the extraction column from the air inlet at the bottom of the column. The volume flow rate of air was 10.0 L/h. And then, 4.5 L of feed aqueous solutions was pumped into the extraction column from the feed aqueous solution inlet at the top of the column. The aqueous solution passed through the column, flowed out of the column from the bottom outlet, and then return back into the top inlet of the column circularly for further extraction round and round. The volume flow rate of the feed aqueous solutions was 3.0 L/h. When gas bubbles were blown out from the top end of the gas needles stably, the organic phase was pumped into the organic bubble film generator from the organic phase inlet at the bottom of the extraction column, so that the organic bubbles, i.e. gas

Table 1
Chemical analysis of the in-situ leaching solution of the ion-absorbing type rare-earth ores.

Elements	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Conc./mg·L^{-1}	64.09	3.47	0.51	1.63	9.06	5.26	< 0.1	10.13	1.53
Elements	Dy	Ho	Er	Tm	Yb	Lu	TRE[a]		
Conc./mg·L^{-1}	8.36	1.75	5.12	0.76	4.62	0.40	116.68		

[a] TRE: Total concentrations of rare earths in the in-situ leaching solutions. The aqueous pH value of the leaching solutions was 4.45.