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An efficient and sustainable $[P_{6,6,6,14}]_2$[BDOAC] ionic liquid based extraction–precipitation strategy for rare earth recovery

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ABSTRACT

Ionic liquids are the key materials for the recovery of rare earths, which have attracted considerable attentions in the recent years. In this article, a novel ionic liquid [trihexyl(tetradecyl)phosphonium]$_2$[benzene-1,4-dioxydiacetate] ($[P_{6,6,6,14}]_2$[BDOAC]) has been developed for rare earth (RE) recovery. Experiments show that $[P_{6,6,6,14}]_2$[BDOAC] can form solid extracting complexes with rare earth ions from aqueous phase. The precipitation process of $[P_{6,6,6,14}]_2$[BDOAC] was investigated by IR and single-crystal X-ray diffraction analysis (SC-XRD), respectively. Nd$[BDOAC]_{1.5}(H_2O)_z$ is given as a proposed structure of the precipitate. The sizes of obtained precipitated particles are larger than those from conventional precipitation methods. Stripping of RE from the precipitate by 0.015 mol/L HCl is effectively achieved. $[P_{6,6,6,14}]_2$[BDOAC] can be regenerated in the RE recovery strategy. Because of bifunctional $[BDOAC]^{2-}$, the $[P_{6,6,6,14}]_2$[BDOAC] reveals better recovery capacity for RE. The recovery of RE from simulated waste NdFeB feed solution using $[P_{6,6,6,14}]_2$[BDOAC] was studied. The recovery rate of RE achieves 90.6%, and the purity of RE increases from 44.9% to 98.1%.

1. Introduction

Rare earth (RE) elements have played an essential role in permanent magnets, lamp phosphors, catalysts, membranes and other applications for their unique natures (Alonso et al., 2012; Anitha et al., 2015; Chen et al., 2017; Dupont and Binnemans, 2015). Concerns related to the significance of RE have been widespread discussed in the recent years. Monazite, bastnaesite, and xenotime are the most common ores among more than 200 kinds of minerals containing RE (Nassar et al., 2015; Phama et al., 2010). Up to now, more than 90% of the world's RE products come from China (Kanazawa and Kamitani, 2006; Turgis et al., 2016). Major environmental challenges such as wastewater, radioactive residue and geological problem in the process of RE mining are widely concerned. At the same time, RE minerals have being over-exploited. For overcoming the environmental problems and RE minerals shortage, more and more attentions have been paid to the utilizations of RE secondary resources. On the one hand, the recovery of RE contributes to overcoming their shortage by creating a closed-loop system. To some

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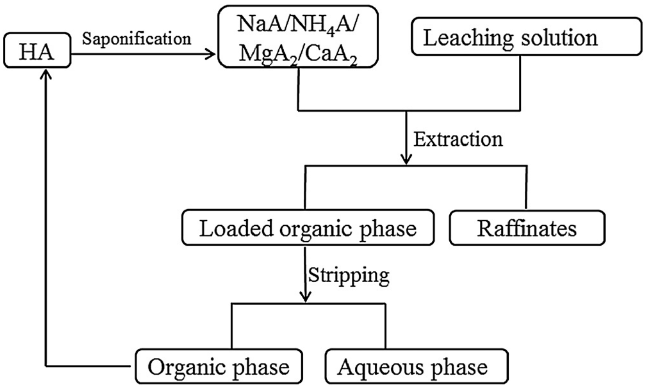

Fig. 1 – Solvent extraction of RE from leaching solution.

extent, the imbalance problem caused by the unwanted co-production of other RE can be also overcame (Binnemans et al., 2013). On the other hand, the recovery contributes to lowering the environmental burden from RE mining (Rademaker et al., 2013; Riaño and Binnemans, 2015; Sprecher et al., 2014).

Chemical precipitation (Bandara et al., 2016) has been widely implemented in the field of lanthanides recovering because of its simple and easy operation. However, the traditional chemical precipitation may not be an efficient green method. Oxalic acid and ammonium bicarbonate are always used as precipitants to precipitate rare earth. The toxicity of oxalic acid makes it necessary for recovery, but the water-solubility (14.3 g/100 g water at 30 °C) of oxalic acid makes its recovery difficulty (Chi and Wang, 1996). As for ammonium bicarbonate, it is difficultly to be recovered and separated because of the precipitated RE particles' fine sizes (Liu et al., 2017). On the other hand, a lot of impurities co-precipitate with RE ions in the rapid precipitation process. To a certain extent, the impurities reduce the purity of recycled RE and increase the cost of subsequent processing. Although extraction (Huang et al., 2017; Nakamura et al., 2007; Zhao et al., 2017) has been mature for industrial application, which still reveals some disadvantages. As depicted in Fig. 1, in order to eliminate protons and break the dimers in the acidic extractants and ensure a higher percent extraction for RE, the saponification is widely used in the RE industry for acidic extractants, i.e., P507 (HEH[EHP]), naphthenic acid and Cyanex272 (Dong et al., 2016; Song et al., 2014). Unfortunately, the saponification wastewaters containing high concentration of salt result in serious pollution (Liu et al., 2012). In addition, the uses of a large number of volatile organic solvents also increase the environmental burden. Therefore, it is necessary to develop a more efficient separation processing for the recovery of RE.

The application of ionic liquid (IL) instead of volatile organic compound (VOC) as extractant and/or diluent has been a booming technology for RE separation in the past decades (Parmentier et al., 2016; Sun et al., 2011). Carboxylic acid as one of the extractants is always used to recovery RE. Due to the changes of carboxyl groups involved in the coordination mode, rare earth carboxylate complexes can form in various forms. These complexes play an important role in the separation and determination of RE elements (Yang et al., 2014). Very recently, a novel extraction and precipitation strategy based on functional ionic liquids has been developed for RE recovery in this lab (Zhou et al., 2018). Efficient RE recovery, easy-to-use, and a more sustainable process are advantages of the proposed process. To further develop an extraction and precipitation system, herein the novel ionic liquid from solid benzene-1,4-dioxydiacetic acid (H_2BDOAC) has been prepared. H_2BDOAC is a common ligand for RE (Deng et al., 2009; Qiu et al., 2007), which can be easily prepared by Williamson reaction. The raw materials for H_2BDOAC preparation are inexpensive and available (Mirci, 1990; Wei et al., 1996). Accordingly, the IL based precipitation strategy with $[P_{6,6,6,14}]_2[BDOAC]$ for RE recovery without volatile dilute is proposed in this article, also some interesting properties of $[P_{6,6,6,14}]_2[BDOAC]$ for RE recovery are investigated.

Among the secondary resource utilizations, the recovery of RE from NdFeB magnets is important. NdFeB magnets usually contain two critical RE elements, i.e., Neodymium (Nd) and Dysprosium (Dy). As the NdFeB market expands rapidly, the demands for Nd and Dy are also increasing. In addition, Praseodymium (Pr) is generally added to replace Nd at a lower cost, sometimes Terbium (Tb) is also added. The above mentioned RE elements have been all considered as 'critical metals' (Alonso et al., 2012; Rademaker et al., 2013). There are some reports on the recovery of RE from NdFeB, for example, the extraction of Nd from waste Nd–Fe–B alloys by the glass slag method (Saito et al., 2003), the use of hydrogen to separate and recycle NdFeB-type magnets from electronic waste (Walton et al., 2015), and a method of using a combined leaching/extraction system to recycle RE from NdFeB magnets (Dupont and Binnemans, 2015). Recently, a strategy of recycling of used NdFeB magnets in deep-eutectic solvents to improve extraction selectivities and efficiencies has been raised (Riano et al., 2017). Herein the IL based extraction and precipitation strategy with $[P_{6,6,6,14}]_2[BDOAC]$ for RE recovery from simulated NdFeB leaching solution is investigated. Compared with our recent study (Zhou et al., 2018), the novelty of this work lies in: (1) A novel dicarboxylic acid is prepared, its synthesis method is simple (one-step method) and the irritating ethyl bromoacetate can be avoided by using safer and cheaper sodium chloroacetate. (2) The prepared $[P_{6,6,6,14}]_2[BDOAC]$ reveals stronger precipitation ability for light RE, which is significant for the recovery of RE from NdFeB. (3) A new crystal of $[Nd(BDOAC)_{1.5}(H_2O)_2]\cdot 3H_2O$ is produced by using $[P_{6,6,6,14}]_2[BDOAC]$ as the precipitant, which is of great significance for investigating the extraction and precipitation process. (4) Recovery of dicarboxylic acid is studied instead of calcining it during the recycling process based on $[P_{6,6,6,14}]_2[BDOAC]$, which is more favorable to the environment. (5) Some other interesting properties such as the larger particle size of precipitate and the higher recovery capacity of RE are also presented.

2. Experimental

2.1. *Reagents and apparatus*

Hydroquinone (99%) and sodium chloroacetate (99%) were purchased from Xiya Reagent Company, Limited (China) and sodium hydroxide (>96%), hydrochloric acid (36%), sodium chloride (>99.5%), hydrogen peroxide (30%), methanol (>99.5%) and toluene (>99.5%) were purchased from Sinopharm Chemical Reagent Co., Limited. Sec-octylphenoxy acetic acid (HSOPAA) and di(2-ethylhexyl) hydrogen phosphate (DEHPA) were purchased from Luoyang Aoda Chemical Co., Limited (China). Trihexyl(tetradecyl)phosphonium chloride (>99.5%, CyphosIL101, $[P_{6,6,6,14}]Cl$) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272, HBTMPP) were provided by Cytec Industries Inc. All chemicals were used as received without further purification. An anion-exchange resin (Dowex Monosphere 550A (OH)) was obtained from Dow Chemical Company. [Trihexyl(tetradecyl)phosphonium][sec-octylphenoxy acetate] ($[P_{6,6,6,14}][SOPAA]$) was prepared according to our recent study (Dong et al., 2016). Individual RE stock solutions including La-Lu plus Y were prepared by dissolving the corresponding oxides (>99.99%, obtained from Fujian Changting Golden Dragon Rare-Earth Company, Limited (China)) with hydrochloric acid, then diluting with deionized water. The original waste NdFeB ingredients list was provided by Ganzhou Rare Earth Group Co., Ltd (China). The structures of H_2BDOAC and $[P_{6,6,6,14}]_2[BDOAC]$ were given as Fig. 2. The structures of studied extractants, i.e., $[P_{6,6,6,14}]Cl$, DEHPA, HSOPAA, HBTMPP and $[P_{6,6,6,14}][SOPAA]$ were given in Supplementary materials, Fig. S1.

2.2. *Instrumentation and analysis methods*

Thin layer chromatography (TLC) method was applied to monitor whether there was residual raw material during