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The recovery of rare earth by a novel extraction and precipitation strategy using functional ionic liquids

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ABSTRACT

A novel precipitation strategy grounded on [trihexyl(tetradecyl)phosphonium]$_2$[4,4′-isopropylidenebis(phenoxyacetate)] (abbreviated as [P_{66614}]$_2$[IOPAA]) was put forward for rare earth element (REE) recovery. The H_2IOPAA and [P_{66614}]$_2$[IOPAA] were synthesized and characterized by NMR, IR and elemental analysis. The factors in the precipitation process such as the equilibrium time, pH value of aqueous phase, concentration of salt-out agent and mole amount of IL were investigated. In addition, the precipitation mechanism of [P_{66614}]$_2$[IOPAA] for Pr(III) was proposed to be $2Pr^{3+}_{aq} + 6Cl^{-}_{aq} + 3\{[P_{66614}]_2[IOPAA]\}_{IL} = 6[P_{66614}]Cl_{IL} + Pr_2[IOPAA]_3\downarrow$. The process was successfully tested for the recovery of REE from simulated leaching solution of Nd-Fe-B scrap. After removing the iron ion with [P_{66614}]Cl, a high recovery rate (99.85%) of REE was obtained. Without saponification, organic diluent or oxalic acid, the proposed precipitation strategy has revealed the potential to be a sustainable process to the quantitatively recovery REE.

1. Introduction

Rare earth elements were defined as a group of 17 elements, including the 15 lanthanides plus Sc and Y [1,2]. The elements played important roles in many high-tech applications and green tech products, such as wind turbines, electric vehicles, NiMH batteries, lasers, fluorescent lamps and permanent magnets [3,4]. REE were irreplaceable for certain applications that took advantages of the f-orbital electrons [5]. Currently, the annual output of REE in China has contributed to >90% of world total production [6]. The demand for REE was estimated to grow by >8% per annum until 2020 [7]. Waste water, radioactive dust and air emission were the major environmental risks of rare earth mining. Therefore, the recycling of REE from scrap productions has been considered as an important strategy to overcome the supply risk of REE and reduce the environmental risks related to rare earth mining [8,9]. Recycling of REE not only could help to create a closed-loop system but also solve the problem of REE balanced utilization [10]. NdFeB magnets, generally contained Pr, Nd and small amounts of Tb, Dy. Over 80% of REE in NdFeB magnet was in the form of Pr and Nd [7]. It was expected that the highest growth rate of REE applications would be from NdFeB [11]. The highly criticality of Nd has made Pr as the substitution in a low cost [1]. Various methods, such as hydrometallurgy, molten salt extraction, gas phase extraction and liquid metal extraction, have been applied to recovery REE from NdFeB scrap [12].

The similarity of physical and chemical properties making REE difficult to be separated from each other to obtain individual REE with high purity [13]. Solvent extraction was one of the most common hydrometallurgical techniques for the separation and purification of REE [14]. The major advantages of solvent extraction were the continuous separation ability with a high throughput and relatively simple equipment. The extractant played an important role in solvent extraction process because it could transfer metal ions between two immiscible phases [15]. Up until now, some kinds of extractants have been used for separating the REE, i.e., organic phosphorus acid, carboxylic acid, tertiary and quaternary amines, sulphoxide, etc. [16,17] However, some problems in solvent extraction still need to be considered. For example, the acidic extractants usually needed to be saponified using $NH_3 \cdot H_2O$, NaOH or $Ca(OH)_2$ to facilitate the REE extraction processes, which would inevitably release the wastewater containing ammonia-nitrogen, Ca^{2+} or Mg^{2+} into the environment [18,19].

The stripping acid for extraction, oxalic acid for REE precipitation together with the resulting acidic wastewater polluted the surrounding nature water and soil [20]. Thus, the development of simple, cost-effective and environment-friendly strategy for REE recovery has been important and necessary. Chemical precipitation was an effective method to recovery metal ion, it has so far become the most widely used process in industry because of its simple operation and low cost [21]. The conventional deposition mechanism was achieved by reacting

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chemicals with metal ions to form insoluble precipitates, then the formed precipitates could be separated by using sedimentation or filtration from the aqueous phase [22]. Although widely used, traditional hydroxide and sulfide precipitations existed some limitations, such as the evolution of toxic H_2S fumes in acid conditions and disposal problems. Some attractive findings about the chemical precipitation in combination with other methods, including nanofiltration, ion-exchange treatment and electro-fenton process were reported [23,24]. Nowadays, considerable attentions have been paid to design and synthesize chelating precipitants, i.e., Papadopoulos et al. found that the removal rate of nickel reached 94.2%–98.3% by using the combination of ion-exchange and precipitation process, while only 74.8% was obtained by using individual ion-exchange [25]. Xu and Zhang developed a new organic heavy metal chelator-dipropyl dithiophosphate. The chelator could remove over 99.9% of lead, cadmium, copper and mercury from the feed solution containing 200 mg/L metal ions at pH 3–6 [26].

Ionic liquids (ILs) are molten salts with low melting points (below 100 °C) and consist entirely of ions. The applications of ILs in various fields, such as synthesis, catalysis, separation, electrochemical, were extensively investigated [27,28]. ILs have some properties including lower vapor pressure, thermal stability, lower flammability and negligible volatility, which made them particularly suitable for solvent extraction [29]. Organic solvents were commonly utilized as extractant or diluent in solvent extraction, however, they were toxic, volatile and flammable, causing safety and environmental issues [30,31]. IL-based extraction was indicated to be a relatively sustainable separation process, which used IL instead of organic solvent [32]. IL was called designer solvent because the properties of IL could be tuned easily by an appropriate choice of anion and cation [33,34]. Because of the excellent extractabilities, functionalized ILs containing functional groups in their cations and/or anions have aroused interests for the extraction and separation of metal ions [35,36]. Recently, several studies have evidenced the potentials of ILs for rare earth ore leaching and REE recycling. Literatures related to recovery REE using IL from waste NdFeB leaching solution were summarized in Table 1, it was found that various methods including leaching, extraction, membrane and electrodeposition have been applied to recovery REE. In this article, a new functionalized IL $[P_{66614}]_2[IOPAA]$ was synthesized and characterized. Also, the application of $[P_{66614}]_2[IOPAA]$ for REE recovery using a precipitation strategy for simulated Nd-Fe-B leaching solution was investigated.

2. Experimental

2.1. Materials

Trihexyl(tetradecyl)phosphonium chloride (>99.5%, Cyphos IL 101, $[P_{66614}]Cl$) was supplied by Cytec Industries Inc. An anion-exchange resin (Dowex Monosphere 550A (OH)) was obtained from Dow Chemical Company. Sec-octylphenoxy acetic acid (HSOPAA) was purchased from Luoyang Aoda Chemical Co., Limited (China). [Trihexyl (tetradecyl)phosphonium][sec-octylphenoxy acetate] ($[P_{66614}][SOPAA]$) was synthesized according to our previous study [43]. Bisphenol A (99%) was purchased from Xiya Reagent Company, Limited (China). $BrCH_2CO_2C_2H_5$ (98%) was purchased from Adamas Reagent Company. The aqueous solutions of rare earth ions were prepared by dissolving corresponding rare earth oxides (99.99%) in hydrochloric acid and diluting with deionized water. All the other chemicals in the study were used without further purification. Fig. 1 shows the structures and abbreviations of different chemicals used in this study.

2.2. Instrumentation

An elemental analysis (carbon, hydrogen, nitrogen) was performed on a CE Instruments EA-1110 element analyzer. Thermo scientific iCAP 6500 series inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to determine the concentration of REE in aqueous phase. IR spectra were recorded with a Nicolet iS50 spectrometer. The pH values of aqueous solutions were determined by PHSJ-4F made by INESA scientific instrument CO., Ltd. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra of H_2IOPAA and $[P_{66614}]_2[IOPAA]$ were obtained in DMSO-d6 with an AV III-500 BRUKER spectrometer. The energy dispersive spectrometer (EDS) was used to determine the elemental constituent of obtained complex precipitation.

2.3. Synthesis of H_2IOPAA and $[P_{66614}]_2[IOPAA]$

H_2IOPAA (molar mass = 344 g/mol) was synthesized in two steps from compound I according to Scheme 1. Compound II was synthesized directly from compound I by a nucleophilic substitution with bromo compound, and the compound III was obtained by alkaline hydrolysis of compound II. Detailed synthetic route of the dicarboxylic acid was listed in supplementary material. The yield and purity of H_2IOPAA were determined to be 72.0% and 99.8%, respectively.

$[P_{66614}]_2[IOPAA]$ (molar mass = 1310 g/mol) was prepared using the combination of ion exchange and neutralizing reaction [44]. Detailed synthetic route was also listed in supplementary material. Yield of $[P_{66614}]_2[IOPAA]$ was determined to be 96.1%.

2.4. Precipitation and extraction experiments

All the precipitation experiments were performed at 298 K in a thermostatic air bath oscillator for 1 h. Unless otherwise noted, 0.131 g (1×10^{-4} mol) of the undiluted $[P_{66614}]_2[IOPAA]$ was equilibrated with 4 mL of aqueous solution in a 15 mL centrifuge tube. 0.5 mol/L sodium chloride was selected as the salting-out agent. After complete precipitation, the IL phase and aqueous phase were separated by centrifugation at 4000 rpm for 10 min. The aqueous phase was separated, and the precipitation in aqueous phase was filtrated and washed with methanol for several times. After that, the precipitation was dried at 60 °C in oven for 5 h. Then the collected precipitation and upper organic phase after precipitation experiments were used to investigate the precipitation mechanism. To optimize the precipitation procedure, the efficiency of precipitation on Pr(III) was evaluated in terms of different parameters, such as the equilibrium time, effect of pH, concentration of salt-out agent and effect of mole amount of IL. Only one parameter was varied at the time while keeping the other variables constant. The concentration of metal ion in aqueous phase was measured by ICP-OES. The amount of metal ion precipitated by IL was calculated by mass balance. The precipitation efficiency (P) in the process of precipitation was

Table 1
REE recovery from waste Nd-Fe-B leaching solution using IL.

IL	REE	Recovery method	Ref.
$[Hbet][Tf_2N]$	Nd^{3+},Dy^{3+}	Combined leaching/extraction system	[37]
$DODGAA/[C_8mim][Tf_2N]$	Nd^{3+},Dy^{3+}	Supported liquid membrane	[38]
TBP/[P2225][TFSA]	Pr^{3+}, Nd^{3+},Dy^{3+}	Solvent extraction/electrodeposition	[39]
$[A336]NO_3$	Nd^{3+},Dy^{3+}	Selective leaching/solvent extraction/selective stripping with EDTA	[40]
$TBP/[A336]NO_3$	Pr^{3+}, Nd^{3+},Dy^{3+}	Combined wet and dry separation	[41]
$[P_{66614}]Cl$	Nd^{3+},Dy^{3+}	Combined selective leaching/extraction	[42]