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# A sustainable $[P_{6,6,6,14}]_2$ [OPBOA]-based separation process of rare earth and transition metal in waste NiMH battery



MINERALS ENGINEERING

Xiang Su<sup>a,b,c</sup>, Wenqi Xie<sup>c</sup>, Xiaoqi Sun<sup>a,c,d,\*</sup>

<sup>a</sup> Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China

<sup>b</sup> School of Chemistry and Environmental Engineering, Pingdingshan University, Pingdingshan, Henan 467000, PR China

<sup>c</sup> Fujian Research Center for Rare Earth Engineering Technology, Xiamen Institute of Rare Earth Materials, Haixi Institute, Chinese Academy of Sciences, Xiamen, Fujian

361021, PR China

<sup>d</sup> Ganzhou Rare Earth Group Co., Ltd., Ganzhou, Jiangxi 341000, PR China

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#### ABSTRACT

The separation of rare earth (RE) and transition metals is a critical step in the recycling of nickel-metal hydride (NiMH) battery. From the point of environmental and practical issues, an ionic liquid (IL) [trihexyl(tetradecyl) phosphonium]<sub>2</sub>[2,2' -(1,2-phenylenebis(oxy))dioctanoate] ([P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA]) was newly synthesized for the separation of RE from transition metals in NiMH batteries leachate. The separation factors of  $\beta_{Nd/Co}$  and  $\beta_{Nd/Ni}$  could arrive at 5.2 × 10<sup>3</sup> and 5.4 × 10<sup>3</sup>, respectively. Meanwhile, the extracted Ni(II) and Co(II) could be effectively scrubbed and stripped by 0.5 mol/L sodium chloride (NaCl) solution without loss of RE. The loaded Nd(III) in [P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA] could be quantitatively stripped by 0.014 mol/L hydrochloric acid (HCl), 0.016 mol/L sodium oxalate (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) or 0.022 mol/L sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>). [P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA] could be recycled without regeneration when Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> were used as stripping agents and larger precipitated particle size could be obtained by low-concentration Na<sub>2</sub>CO<sub>3</sub> solution, the recovery efficiency and purity of RE in NiMH batteries could still reach more than 96.4% and 99.8 wt% by using NaCl and Na<sub>2</sub>CO<sub>3</sub> for stripping, respectively. As characterized by XRD, the recovered RE oxides could be easily obtained by calcinations.

## 1. Introduction

NiMH battery is a type of rechargeable battery with good performance. Due to their advantages of higher energy density, no memory effect and environmentally-friendly property, NiMH battery has gradually replaced nickel-cadmium (Ni-Cd) battery for extensive applications in various technological purposes during the past years (Al-Thyabat et al., 2013; Swain and Mishra, 2019). With the increasing demands of electronic equipment (for example digital cameras and personal computers) and hybrid vehicles, the consumptions of NiMH batteries have been significantly increased. It was pointed out by European Commission that the annual consumption of consumer, industrial and automobile NiMH batteries was about 160000, 190000 and 800000 tons in 2017, respectively (Innocenzi et al., 2017). Owing to short service life (average: two years), a large number of NiMH batteries were wasted, especially the wastes of metal elements.

NiMH batteries usually contained RE elements (La, Ce, Pr, Nd) and other metal elements (Ni, Co, and Mn, ect) (Maroufi et al., 2018).

Although NiMH batteries not including lead, cadmium and other elements that caused greater harms to the environment, the accumulations of these metals in the environment have negative impacts on the life safety of organisms, including human beings. Meanwhile, the metals contained in NiMH batteries are very important resources. Among them, RE and Co are critical raw materials in EU report 2014 (European Commission, 2014). China, known as the country with the richest resources of RE, had already strictly controlled the quotas on RE exports because of the environmental pollutions from RE production processes. Thus, a growing number of countries have paid attention to the importance of these raw materials (Ilankoon et al., 2018; Powell, 2011). Developing substitute material is the solution to meet the continuous supplies of these materials, but it will take a lot of time. Furthermore, the exploitation of new resource has the risk of environmental pollution. Above all, the recycling uses of RE from waste resources (such as NiMH batteries) seem to be an effective solution (Wang et al., 2017).

Based on the advantages of no high temperature, lower energy consumption, no harmful gas generation and higher recovery rate,

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<sup>\*</sup> Corresponding author at: Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China. *E-mail address*: xqsun@fjirsm.ac.cn (X. Sun).

hydrometallurgy has been widely used to recover the critical materials from waste NiMH batteries (Fernandes et al., 2013; Innocenzi and Vegliò, 2012; Larsson and Binnemans, 2014; Lupi and Pilone, 2002). Usually, leaching and metals separation are critical two parts in the recovery process. In the previous investigations, three mineral acids (nitric acid, hydrochloric and sulfuric) could effectively dissolve the waste (Holmberg, 2017). However, the previous research have shown that nitric acid was not suitable for the dissolution of cathode hydrogen storage alloy (Larsson et al., 2013). As for sulfuric acid leaching process, it founded that the formation of double salt between RE and nickel or alkali metal could affect the recovery of RE (Yang et al., 2014). Compared with nitric acid and sulfuric acid, the hydrochloric acid could avoid the above mentioned shortcomings.

Metals separation could be realized by chemical precipitation or solvent extraction. For example, Mei et al proposed a method of sulfuric acid leaching and sodium sulfate precipitation to recover the RE from waste NiMH battery in 2008 (Mei et al., 2008), but the formation of double salt between RE and sodium sulfate affect the quality of recycled RE. Yang et al developed a method of hydrochloric acid leaching and oxalic acid precipitation to recover RE in 2014 (Yang et al., 2014). But the purity of the obtained RE oxides (99%) need to be further improved. Solvent extraction is another commonly used method for metal separation and recovery. Several extractants (such as D<sub>2</sub>EHPA, TBP and Cyanex 923) have been used to extract and separate the RE elements from acid leaching solutions (Fernandes et al., 2013; Larsson et al., 2012; Li et al., 2009). However, volatile organic diluents were always needed when these traditional extractants were used. Meanwhile, the higher concentrations of acid, alkali or salt were necessary in the stripping step, which was obviously not an environmentally friendly process.

Ionic liquid (IL) has the properties of higher thermal stability, lower vapor pressure and lower flammability, ect (Singh et al., 2018). The investigation on IL based extraction could be traced back to 1990s (Dai et al., 1999; Huddleston et al., 1998). The separation of metal elements using IL from waste NiMH battery leachate has been studied by some scholars. For example, trihexyl(tetradecyl)phosphonium nitrate ( $[P_{6,6,6,14}][NO_3]$ ) was used to separate lanthanum (La) from nickel (Ni) with the high concentration of nitrate by Hoogerstraete et al. in 2014 (Hoogerstraete and Binnemans, 2014). Trioctyldecylamine chloride (Alamine 336) was used to remove cobalt (Co) from hydrochloric acid leaching solution of waste NiMH battery by Fernandes et al in 2013 (Fernandes et al., 2013). Unfortunately, the recovery processes were operated under higher acid concentration or higher salt conditions.

Because of the tunability of anions and cations in ILs, many bifunctional ILs with excellent properties have been obtained by optimizing the structures of anions and cations (Azizi and Larachi, 2018; Dong et al., 2016a; Fischer et al., 2011). Trihexyl-(tetradecyl)phosphonium chloride (CyphosIL101, [P<sub>6.6.6.14</sub>]Cl) is more cheap and environmentally friendly than fluorine-containing ILs, which has been industrialized (Bradaric et al., 2003; Wellens et al., 2012) and often used as a source of cations for bifunctional ILs (Dong et al., 2016b; Mahandra et al., 2017; Zhao et al., 2017). The acidity of phenoxycarboxylic acid was indicated to be stronger than that of naphthenic acid due to the introduction of phenoxy group, resulting in better demulsification resistance and better separation abilities (Zhang et al., 2003). According to our previous reports, the ILs formed by CyphosIL101 and phenoxycarboxylic acid have been provided with the properties of good separation ability and easy-stripped (Dong et al., 2016a). OPBOA has been used as an extraction-precipitant in our previous work to selectively enrich and recover RE from magnesium-rich RE feed solution, which showed a pretty result (Su et al., 2019). In this work, a novel ionic liquid ([P<sub>6.6.6.14</sub>]<sub>2</sub>[OPBOA]) based on OPBOA was synthesized to selectively separate Nd(III) from Co(II) and Ni(II), aiming to develop a novel, sustainable and efficient liquid-liquid extraction method for recovering RE from waste NiMH battery. NiMH battery alloy powder was used to verify the effect of this separation strategy for its potential application.

#### 2. Materials and methods

#### 2.1. Chemicals

Methyl 2-bromooctanoate ( $\geq$ 95%) and sodium hydride (60%) were purchased from Adamas Reagent Co., Ltd, China, while 1, 2-dihydroxybenzene ( $\geq$ 98%) was purchased from Chengdu Xiya Reagent Chemical Technology Co., Limited (China). Sodium hydroxide ( $\geq$  96%), hydrochloric acid (36%), sodium chloride (greater than99.5%), cobalt chloride hexahydrate (CoCl<sub>2</sub>· $6H_2O$ ,  $\geq$  99.0%), nickel chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O,  $\geq$  98.0%), tetrahydrofuran ( $\geq$  99.5%), cyclohexane  $(\geq 99.7\%)$ , anhydrous ethanol ( $\geq 99.7\%$ ), petroleum ether (60 ~ 90°C,  $\geq$  90%) and ethyl acetate ( $\geq$  99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Trihexyl(tetradecyl)phosphonium chloride  $(\geq 95.0\%)$  was provided by Cytec Industries Inc. NdCl<sub>3</sub> solutions were prepared by dissolving the corresponding oxides (greater than 99.99%) with hydrochloric acid, then diluting with deionized water. NiMH battery alloy powder was purchased from Xinxiang Heluilida Power Material Co., Ltd (China). All the chemicals were used as received without further purification.

#### 2.2. Instrumentation

The content of  $[OPBOA]^{2-}$  in aqueous phase was determined by Ultraviolet–Visible (UV–Vis) spectra (Agilent Cary 5000 UV–Vis Spectrophotometer). Thermoscientific iCAP 6500 series inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to measure the concentration of metal ion and  $[P_{6,6,6,14}]^+$  in aqueous phase. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra (AV III-500 BRUKER spectrometer) of ILs were obtained in *d*imethylsulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>, C<sub>2</sub>D<sub>6</sub>OS). IR spectra and the pH value were obtained with a Nicolet iS50 spectrometer and a PHS-25 digital pH meter, respectively. The morphology of solid particle was observed by scanning electron microscope (SU-1510, Hitachi, Japan), while the particle size date was given by Brookhaven NanoBrook Omni, USA. XRD spectra were obtained with a Miniflex 600 X-ray diffractometer in the range of 5–90 degree (20).

## 2.3. Synthesis of [P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA]

2,2'-(1,2-phenylenebis(oxy))dioctanoic acid (OPBOA) was synthesized in reference to our previous work (Su et al., 2019). OPBOA and [P<sub>6,6,6,14</sub>]Cl were used to prepare [P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA] by ion-exchange and neutralizing reactions (Sun and Waters, 2014), the structures of OPBOA, [P<sub>6,6,6,14</sub>]Cl and [P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA] were shown in Fig. 1. Finally, light yellow viscous liquid in a yield of 97.13% was obtained. The NMR characterization of the IL is as follows: <sup>1</sup>H NMR (500 MHz, DMSO)  $\delta$  6.66 (dd, J = 5.8 Hz, 3.7 Hz, 2H), 6.56 (dd, J = 5.8 Hz, 3.6 Hz, 2H), 3.96 (t, J = 5.7 Hz, 2H), 2.18 (m, 16H), 1.74–1.65 (m,



Fig. 1. Molecular structure of OPBOA,  $[P_{6,6,6,14}]$ Cl and  $[P_{6,6,6,14}]_2$ [OPBOA].

4H), 1.53–1.14 (m, 112H), 0.93–0.83 (m, 30H).  $^{13}\mathrm{C}$  NMR (DMSO- $d_6$ , ppm)  $\delta$  14.32–33.94, 80.81, 114.13, 119.07, 149.45, 173.29.

## 2.4. Extraction and stripping experiments

5 mL of aqueous phase containing NdCl<sub>3</sub>, CoCl<sub>2</sub> or NiCl<sub>2</sub> and  $[P_{6,6,6,14}]_2[OPBOA]$  were fully contacted in a 15 mL centrifuge tube for 60 min at 25°C. The pH of the initial feed liquid was controlled at 4.4, sodium chloride was used as a salting out agent. All the separation of IL and aqueous phases was performed in a centrifugation (4000 rpm, 5 min). The experimental conditions of stripping and extraction were the same. In the stripping process of precipitation, 1 mol/L hydrochloric acid was used to dissolve the precipitate for ICP test in order to determine the efficiency of stripping. Extraction efficiency (E%), distribution ratio (D), separation factor ( $\beta$ ) and stripping percentage (S%) are used as the indicators of results in the process of extraction and stripping, whose calculation equations are given in the **Supplementary materials** (Eq. (S1-S4)).

## 3. Results and discussion

## 3.1. Separation of Nd(III) from Co(II) and Ni(II)

NiMH batteries are mostly composed of especially RE (La, Ce, Pr and Nd) and transition metals (Co. Ni and Mn) (Innocenzi and Veglio, 2012: Xia et al., 2015), herein a stock solution of NdCl<sub>3</sub>, CoCl<sub>2</sub> and NiCl<sub>2</sub> was used as the simulating battery leachate to study the separation of RE and other metals. As shown in Fig. 2, with the increase of IL dosage, the extraction efficiencies of Co(II) and Ni(II) are always less than 5%, while the extraction efficiency of Nd(III) gradually increases. When the molar ratio  $(n_{II}/n_{Nd})$  is 4.0, the extraction efficiency of Nd(III) is close to 100%. The extraction mechanism of [P<sub>6.6.6.14</sub>]<sub>2</sub>[OPBOA]-Nd system was investigated (Supplementary material), and ion association was proposed by detecting the concentration of  $[P_{6,6,6,14}]^+$  and  $[OPBOA]^{2-}$ in aqueous phase (Fig. S1), as well as slope method (Fig. S2) and IR spectra (Fig. S3). Meanwhile, the  $\beta_{Nd/Co}$  and  $\beta_{Nd/Ni}$  reaches 5.2  $\times$  10<sup>3</sup> and 5.4  $\times$  10<sup>3</sup> respectively, being higher than the separation factors given in the previous research (Chen et al., 2018). The interesting separation factors of [P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA] provide potential for the separation of RE from transition metals in waste NiMH batteries.

## 3.2. Scrubbing and stripping of impurities

As can be seem in Fig. 2, the extraction efficiency for other metal is



Fig. 2. Effect of  $n_{IL}/n_{Nd}$  on the extraction efficiency (E, %) and separation factor ( $\beta$ ) of Nd(III), Co(II) and Ni(II) in aqueous phase. [NdCl<sub>3</sub>] = [CoCl<sub>2</sub>] = [NiCl<sub>2</sub>] = 0.005 mol/L, [NaCl] = 0.5 mol/L,  $n_{IL} = 0.25 \times 10^{-4} - 1 \times 10^{-4}$  mol,  $n_{IL}/n_{Nd} = 1.0-4.0$ .



Fig. 3. Stripping efficiency of Nd(III) and Ni(II) from loaded  $[P_{6,6,6,14}]_2$ [OPBOA] with different concentration of NaCl. [NdCl<sub>3</sub>] = [NiCl<sub>2</sub>] = 0.005 mol/L, n<sub>IL</sub> = 1 × 10<sup>-4</sup> mol, V<sub>NaCl</sub> = 5 mL.

much lower than that of RE. However, the content of Ni was much higher than that of RE in NiMH battery. A lower extraction efficiency could also bring a lot of Ni extraction, reducing the purity of recovered RE. Herein Ni(II) and Nd(III) were taken as examples to study how to selectively remove Ni(II) in the following experiments. In order to reduce the loss of Nd(III), mild stripping conditions were needed. In this paper, NaCl solution was used to selectively scrub and strip Ni(II) due to its different salting out effect for NiCl<sub>2</sub> and NdCl<sub>3</sub>. The stripping efficiency of Nd(III) and Ni(II) from loaded  $[P_{6,6,6,14}]_2[OPBOA]$  with different concentration of NaCl was shown in Fig. 3. With the increase of NaCl concentration, the stripping efficiency of Nd(III) and Ni(II) decrease due to the effect of salting out. When the concentration of NaCl is 0.5 mol/L, almost no Nd(III) can be stripped, while 21.8% of Ni(II) can be stripped. Obviously, 0.5 mol/L NaCl solution can be used to effectively remove Ni(II) by multi-step scrubbing without the loss of Nd(III).

## 3.3. Stripping of Nd(III)

The stripping using HCl, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> was investigated. As shown in Fig. 4, NdCl<sub>3</sub> can be effectively stripped from [P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA] using HCl, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub>. The stripping efficiency reaches 62% by pure water due to the self-salting out effect (Dong et al., 2016a), while the stripping efficiency reaches 100% using 0.014 mol/L hydrochloric acid. The lower stripping acidity is more sustainable than common high acid stripping. However, there are still some problems concerned. It is reported that there is competition between RE and acid in the extraction system based on this type of bifunctional ionic liquids (Wang et al., 2011). Therefore, metal ions are easily recovered in the acid stripping process due to the protonation of carboxylic acid anions, but at the same time, the dissociation of original IL is produced (Parmentier et al., 2015a). As indicated in Fig. 4(B)-(b) and (C)-(b), 0.03 mol/L HCl can dissociate partial [P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA] into  $[P_{6,6,6,14}]$ Cl and OPBOA. The IR absorption peak of C = O stretching vibration in carboxyl group shifts significantly toward the higher wavenumber (1729 cm<sup>-1</sup>, unlike 1698 cm<sup>-1</sup> of OPBOA, as the hydrogen bond formation weakened by the resulting [P<sub>6,6,6,14</sub>]Cl (Su et al., 2019)). <sup>1</sup>H NMR spectra of -CH group from Fig. 4(C)-(b) is not identical with Fig. 4(C)-(a). Therefore, the dissociated [P<sub>6.6.6.14</sub>]<sub>2</sub>[OPBOA] needed to be further regenerated with alkali for the recycling of IL (Huang et al., 2017). Also the acquisitions of RE oxides were not fast and easy to be obtained using hydrochloric acid stripping (Parmentier et al., 2015b).

In view of the above problems, the precipitation stripping method was a good choice.  $Na_2C_2O_4$  and  $Na_2CO_3$  were commonly used as



**Fig. 4.** (A) Stripping efficiency of Nd(III) from loaded  $[P_{6,6,6,14}]_2$ [OPBOA] with different concentration of HCl, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub>. (B) IR spectra and (C) <sup>1</sup>H NMR spectra of (a)  $[P_{6,6,6,14}]_2$ [OPBOA], (b) stripped  $[P_{6,6,6,14}]_2$ [OPBOA] with HCl, (c) stripped  $[P_{6,6,6,14}]_2$ [OPBOA] with Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, (d) stripped  $[P_{6,6,6,14}]_2$ [OPBOA] with Na<sub>2</sub>CO<sub>3</sub>.

precipitants in industry due to their cheapness and readily available. The stripping efficiencies of Nd(III) with different concentrations of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> were shown in Fig. 4. 0.016 mol/L Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is sufficiently for 100% stripping of Nd(III) from Nd(III) loaded [P<sub>6.6.6.14</sub>]<sub>2</sub>[OPBOA], while 0.022 mol/L Na<sub>2</sub>CO<sub>3</sub> is needed for the full stripping. It can be seen from Fig. 4(B)-(c)-(d) and 4(C)-(c)-(d) that the IR and <sup>1</sup>H NMR of the fresh [P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA] and stripped [P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA] with Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> are almost the same, that is, the stripped [P<sub>6.6.6.14</sub>]<sub>2</sub>[OPBOA] can be used directly without regeneration. The properties of precipitated particles are especially important for phase separation. The formed solid particles under different concentrations of stripping agents were shown in Fig. 5. All extraction and stripping conditions were the same except for the type and concentration of the stripping agents in the process of obtaining precipitates. Fig. 5 reveals that the larger solid particles can be easily obtained using the stripping agents with lower concentrations. For example, the particles obtained from 0.01 mol/L Na2C2O4 are needle-like



Fig. 5. SEM photographs of stripped precipitates with different stripping agents. Stripping agents: (a) 0.01 mol/L Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, (b) 0.01 mol/L Na<sub>2</sub>CO<sub>3</sub>, (c) 0.1 mol/L Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, (d) 0.1 mol/L Na<sub>2</sub>CO<sub>3</sub>.

particles (24.3 µm). While 0.1 mol/L Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> gave fine needle-like particles (9.14 µm), although agglomerated together. Interestingly, massive particles (33.1 µm) obtained with 0.01 mol/L Na<sub>2</sub>CO<sub>3</sub> appears to be not only larger than the flaky particles (10.2 µm) obtained with 0.1 mol/L Na<sub>2</sub>CO<sub>3</sub>, but also larger than the particles produced by the same concentration of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. Compared with Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub> is less toxic and more environmentally friendly, and the better stripping property of Na<sub>2</sub>CO<sub>3</sub> makes it a promising stripping agent for [P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA] based system.

## 3.4. IL recycling

To verify the recyclability of  $[P_{6,6,6,14}]_2$ [OPBOA] stripped with Na<sub>2</sub>CO<sub>3</sub>, a series of extraction – stripping – extraction experiments were carried out. Considering the easy emulsifying of ILs under low salinity conditions, 0.03 mol/L Na<sub>2</sub>CO<sub>3</sub> was used in the following experiments, and the excessive Na<sub>2</sub>CO<sub>3</sub> could be recycled to use in the next stripping process by adding solid Na<sub>2</sub>CO<sub>3</sub>. The [P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA] loaded with Nd(III) was directly stripped with Na<sub>2</sub>CO<sub>3</sub> solution for one-time stripping. After centrifugation, the organic phase was gently



Fig. 6. Extraction efficiency of Nd(III) with regenerated  $[P_{6,6,6,14}]_2[OPBOA].$  [NdCl<sub>3</sub>] = 0.005 mol/L, [NaCl] = 0.5 mol/L,  $n_{\rm IL}$  = 0.75  $\times$  10 $^{-4}$  mol,  $V_{\rm Na2CO3}$  = 5 mL.



**Fig. 7.** Visual representation of ionic liquid phase during recovery process: (a) before shaking; (b) after shaking; (c) after standing; (d) after 4 times washing with NaCl solution.

washed twice with a small amount of pure water and directly used in the next extraction experiment. As revealed in Fig. 6, the extraction efficiency of Nd(III) with  $[P_{6,6,6,14}]_2[OPBOA]$  with 10 cycles remains basically unchanged, indicating that the potential of Na<sub>2</sub>CO<sub>3</sub> in stripping from  $[P_{6,6,6,14}]_2[OPBOA]$ -Nd(III) system.

#### 3.5. Recovery of RE in NiMH battery

The actual leachate of NiMH battery alloy was obtained by dissolving the commercial NiMH battery alloy powders with 1 mol/L hydrochloric acid, then diluting with deionized water and adjusting pH with sodium hydroxide. In the initial stage, 5 mL was used for exploratory experiment, and the results are listed in the in Supplementary materials (Table S1, Table S2). Here, 500 mL feed solution at a magnification of 100 times was used to further explore the application prospect of [P<sub>6.6.6.14</sub>]<sub>2</sub>[OPBOA] (Fig. 7). The pH and total RE concentration of obtained feed solution was 4.4 and 7.83  $\times$  10<sup>-3</sup> mol/L, respectively. The main metal composition of the feed solution was shown in Table 1 (the content of other metals such as Al and Fe was relatively lower, which had little effect on the separation of RE from other transition metals, therefore, it's no longer listed here and separately removed). Considering the high concentration of Ni(II) and other impurities, 13.7  $\times$  10  $^3$  mol  $[P_{6,6,6,14}]_2 [OPBOA]$   $(n_{IL}/n_{RE}$  = 3.5) was used to handle 500 mL feed liquid, and recovery efficiency of RE reached more than 96.4%.

In order to obtain RE product with higher purity, the selective scrubbing and stripping of impurities was performed by 0.5 mol/L NaCl solution for some times. The stripping efficiency of transition metal (Ni (II), Co(II) and Mn(II)) and the loss of RE ((La(III), Ce(III), Pr(III) and

 Table 1

 Composition of NiMH battery alloy powder and RE products (wt.%).

Ingredients	La	Ce	Pr	Nd	Ni	Co	Mn	Purity (RE)
Feed solution	23.7	2.35	0.519	8.37	52.7	7.06	5.35	34.9
Product 1*	66.7	5.38	1.66	23.0	2.88	0.317	0.132	96.7
Product 2*	67.8	5.73	1.59	24.6	0.233	0.00	0.00	99.8

\* "**Product 1**" was obtained without scrubbing by NaCl solution, "**Product 2**" was obtained by scrubbing with NaCl solution.

Table 2			
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Stripping efficiency (S%) of transition metal and loss of RE in each step
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Stripping step	S% of transition metal (%)			Loss of RE (ppm)			
	Ni	Со	Mn	La	Ce	Pr	Nd
1	70.6	83.3	88.8	17.6	1.01	0.0124	2.05
2	20.0	14.3	11.2	11.6	0.531	0.0193	1.55
3	5.14	2.11	_*	8.84	0.359	-	1.21
4	1.77	0.312	-	7.56	0.336	-	0.987
Total	97.5	100	100	45.6	2.24	0.0317	5.80

\* The element was not detected in the stripping solution.



Fig. 8. XRD pattern of the RE product.

Nd(III)) were given in Table 2. As shown in Table 2, the stripping efficiency of Ni(II) reaches 97.5% after four times scrubbing and stripping (an improved value can be obtained by using larger volume of stripping solution or more steps), while Co(II) and Mn(II) can be completely removed after scrubbing and stripping. After four times of scrubbing and stripping, the total loss of La(III), Ce(III), Nd(III) is 45.6 ppm, 2.24 ppm, 5.80 ppm, and only 0.0317 ppm Pr(III) could be detected in the stripping solution.

After several times of scrubbing and stripping, the RE ions were finally stripped with 0.03 mol/L Na<sub>2</sub>CO<sub>3</sub> solution. The compositions of produced RE carbonates were also shown in Table 1. As can be seen in the Table 1, RE carbonates with a purity of 99.8 wt% can be obtained in only one step of extraction and stripping when scrubbed with 0.5 mol/L NaCl solution, while only a purity of 96.7 wt% is obtained without NaCl solution. Furthermore, RE oxides could be obtained simply by calcining the above RE carbonate at 850°C for 3 h, and the oxides were characterized by X-ray diffractogram (Fig. 8, La2O3 05-0602; Ce2O3 23-1048; Pr<sub>2</sub>O<sub>3</sub> 47-1111; Nd<sub>2</sub>O<sub>3</sub> 65-6729). The complete recycling process for RE from waste NiMH batteries alloy powders by [P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA] is shown in Fig. 9. Obviously, this is a sustainable and efficient process of selective recovery and separation RE from transition metal in waste NiMH battery, not only because NaCl is cheap and less harmful to the environment, but also the NaCl solution can be reused in the dilution process of preparing the feed solution. In addition, using low-concentration Na<sub>2</sub>CO<sub>3</sub> as a stripping agent for RE is conducive to the continuous operation of IL.



Fig. 9. Flowsheet for the separation and recovery of RE from transition metals in NiMH battery.

#### 4. Conclusions

In this paper, a sustainable [P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA]-based separation process of RE and transition metal in waste NiMH batteries was proposed. The extraction efficiency of Nd(III) reached nearly 100%, while the extraction efficiencies of Ni(II) and Co(II) could be controlled within 5%.  $\beta_{Nd/Co}$  and  $\beta_{Nd/Ni}$  could reach 5.2  $\times$   $10^3$  and 5.4  $\times$   $10^3$ when the molar ratio of IL to Nd(III) was 4. 0.5 mol/L NaCl could be used for effectively scrubbing and stripping transition metal ions from the loaded IL. Full stripping reached by using 0.014 mol/L HCl, 0.016 mol/L Na2C2O4 or 0.022 mol/L Na2CO3, respectively. The larger RE precipitation particle obtained by Na<sub>2</sub>CO<sub>3</sub> was conducive to phase separation. As for RE recovery from NiMH battery, a 500 mL feed solution was used, and the recovery efficiency of RE could reach 96.4% with the purity of 99.8 wt% by scrubbing with 0.5 mol/L NaCl solution four times and stripping with 0.03 mol/L Na<sub>2</sub>CO<sub>3</sub>. Compared with the previous work of RE separation from transition metal, the proposed strategy have exhibited some advantages: (1) mild conditions and no organic diluent were used; (2) higher separation efficiency of RE vs. transition metal could be reached; (3) 0.5 mol/L NaCl solution could be effectively used to remove transition metal without the loss of RE, also the used NaCl solution could be recycled; (4) RE could be quantitatively stripped and larger particle of stripping precipitate could be formed with lower concentration of Na<sub>2</sub>CO<sub>3</sub>; (5) [P<sub>6,6,6,14</sub>]<sub>2</sub>[OPBOA] could be recycled without further regeneration. Overall, the developed [P<sub>6.6.6.14</sub>]<sub>2</sub>[OPBOA]-based process has revealed potential for sustainable and efficient separating RE from transition metal in waste NiMH batteries.

## 5. Credit author statement

Xiang Su and Xiaoqi Sun designed the research, analyzed the data, and wrote the paper; Xiang Su performed the research; Xiang Su, Wenqi Xie, Xiaoqi Sun participated in data collection and discussion.

## **Declaration of Competing Interest**

The authors declared that there is no conflict of interest.

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## Appendix A. Supplementary material

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