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Extraction and back-extraction behaviors of 14 rare earth elements from sulfuric acid medium by TODGA☆

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ABSTRACT

The unique physical and chemical properties of rare earth elements lay the foundation for their extensive application. N,N,N′,N′ Tetra-octyl-3-oxopentanediamide (TODGA) is excellent in its ability of extracting rare earth elements and it is favored for green initiative. In this paper, the extraction and back-extraction of 14 rare earth elements by TODGA were studied. Experiments show that in conditions of 6 mol/L sulfuric acid, the extraction temperature of 25 °C, the phase ratio of 1:1 and 0.04 mol/L TODGA (aviation kerosene as the diluent), the extraction rates of 14 rare earth elements including lanthanum, cerium, praseodymium, neodymium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, and yttrium were 99.00%–99.73%. Mixed with hydrochloric acid and nitric acid (HCl 3.5 mol/L, HNO_3 0.5 mol/L), the recoveries of the 14 rare earth elements are 91.52%–99.91% when the extraction temperature is 25 °C and the ratio is 1:1. The following application is based on the optimum conditions above with practical samples (from the roasting production line of China North Rare Earth High-tech Company Limited) for extraction and back-extraction experiments. Experiments show that TODGA has excellent enrichment effect on 14 rare earth elements, the extraction rates are 91.36%–99.80%, the back-extraction rates are 87.29%–99.64% and the total recoveries are 81.19%–99.44%.

1. Introduction

The rare earths or rare-earth elements (REEs) are a group of 17 chemically similar metallic elements (15 lanthanides, plus scandium and yttrium). They are becoming increasingly important in the transition to a green, low-carbon economy.[1] Rare earth materials are widely used in high tech fields and national defense construction, for their excellent performance in electrical, magnetic, optical, biological and other aspects. Thus, rare earth elements are well known as “industrial vitamins” and “twenty-first century industrial gold”.

Scientists have been working hard on the study and innovation of the process of enriching and separating rare earth elements (REEs) from rare earths, and have obtained some good rare earth separation methods.[2] At present, the industrial extraction of REEs mainly 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (P507) and di(2-ethylhexyl) phosphate (P204) are used, which are welcomed in their effective separation and the low cost, but it is difficult to strip heavy rare earth metals,[3] meanwhile, P507 and P204 can pollute the environment to some extent, so they are not ideal extractants. The extraction and separation of heavy rare earths by organophosphinic acid has been reported.[4] Nonsymmetric phosphinic acid may be a superior extractant for extraction and separation of heavy rare earths (REs),[5] but it is also a phosphorus-based extractant, which can cause pollution to some extent. Therefore, research on exploring new extraction agent to improve the rare earth separation process is extremely critical and we found that TODGA has a good extraction effect on heavy rare earth through our tests.

TODGA was proved to be a new type of amide pod ether extraction agent developed in recent years,[6] with a purity of 98% or more. TODGA, contains only C, N, O, H four elements, similar as

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malonamides that can be completely incinerated, which implies that the amount of secondary waste could be reduced significantly.[7] TODGA as a new extraction agent, is effective for its excellent performance and low environmental hazard and it is very welcome for rare earth separation process.[8] TODGA was focused on distribution behavior of metal ions from simulated high level liquid waste as extractant.[9–13] It was found that TODGA could effectively extract nitrate in nitric acid medium,[14,15] and the extraction ability of lanthanide and actinide metal ions in nitric acid medium was good.[16–19]

In nitric acid system, rare earth element extraction by TODGA research has been reported.[20] However, in the sulfuric acid medium, with aviation kerosene as diluent, TODGA on the extraction and extraction of REEs has not been reported so far. In practical production, rare earth concentrate is roasted with sulfuric acid before water soaking, and then we can get rare earth sulfuric acid solution. After that, P204 and P507 as extraction agent, aviation kerosene as diluent are used for the following rare earth element enrichment and separation. The process is stable and widely used, but it produces large amounts of salt-containing wastewater and moreover, P204 and P507 can cause environmental pollution. Therefore, to make the process a clean production becomes a goal that the whole industry is pursuing. Based on the practical production, in this paper, sulfuric acid was used as the diluent in the sulfuric acid medium, and the environmental-friendly extraction agent TODGA was used to extract 14 REEs (lanthanum, cerium, praseodymium, neodymium, europium, gadolinium, terbium, dysprosium, thulium, ytterbium, lutetium and yttrium). A good enrichment was obtained during the extraction and back-extraction process. This study is of great significance for the development of rare earth clean production process.

2. Experimental

2.1. Materials and analytical measurements

TODGA was synthesized by our laboratory, the synthetic process is shown in Fig. 1.

The specific synthetic steps are as follow:

2.1.1. Preparation of diglycolic acid

300 mL of 10 mol/L concentrated nitric acid was added to a 500 mL three-necked flask and heated to 55 °C with stirring in a water bath. When the temperature rose to 90–95 °C and the system became stable, the drop of 1 mL ethanol was added to initiate the reaction. Diethylene glycol was added and the speed of dropping was controlled so that the temperature of the reaction system could be maintained at 60–70 °C, and the reaction continued for 1 h after the dropwise addition.

2.1.2. Preparation of diglycolic anhydride

50 g diglycolic acid was dissolved in 140 mL acetic anhydride. Then, a few drops of phosphoric acid was added as initiator and the temperature rose to the boiling point of acetic anhydride (139 °C). After stirring for 1 h and most of the solvent evaporated, the residue was recrystallized from toluene. The yield was about 90%.

2.1.3. Synthesis of oxopentanediamide

58.5 g of diglycolic anhydride was dissolved in 450 mL of 1,4-dioxane (1000 mL three-necked flask) and was stirred until the solid was completely dissolved. 87.5 mL of di-n-octylamine and 40.6 mL of pyridine was mixed and added dropwise into the flask (using dropping funnel) with 3 h stirring. After the completion of the reaction, dioxane evaporated and 1:1 hydrochloric acid was added dropwise to the residue, and the crystals were precipitated. A suction flask was used to obtain mono-substituted oxo-pentanamide crystals. The yield was about 87%.

2.1.4. Synthesis of TODGA

67 g of the product above was dissolved in 34 mL of thionyl chloride (stirred and heated). After cooling to the indoor temperature, 600 mL of diethyl ether was added with stirring, and 100 mL of di-n-octylamine +50 mL of pyridine +40 mL of ether were slowly added dropwise under ice-bath. Reaction had continued for 3 h before filtration started. The filtrate was washed twice with 1 mol/L HCl and deionized water, and the organic phase was dried with anhydrous sodium sulfate to obtain a crude product.

After completion of the reaction, 10 mL of water was added to the flask, and the yellow residue left by the residual organic solvent was distilled off by a rotary evaporator. Then 100 mL of water was added to the residue, observing the upper layer of orange viscous liquid and the lower layer was light yellow turbid liquid. Separated by a separating funnel, the lower liquid was extracted twice with 10 mL of petroleum ether. The following extraction was repeated by 15 mL H_2O, 2 × 15 mL 1 mol/L HCl, 15 mL H_2O and 6 × 20 mL 5% $NaHCO_3$. The lower part of separation was the waste (latex-like) that should be abandoned. And then remove the excess petroleum ether and other solvent in the supernatant with a rotary evaporator to obtain the product TODGA 35.2 g. The yield was about 85%.

The practical sample was produced by the acid roasting production line of China North Rare Earth High-tech Company Limited. Lanthanide oxides (reagent grade) for further analysis and purification were all prepared by deionized water. TODGA (synthesized by ourselves purity ≥98.0%), was used as extractant, aviation kerosene (wide fractions aviation kerosene), sulfuric acid (analytical grade, Beijing Chemical Works, Beijing, China), diluent PH conditioning agent respectively; nitric acid (analytical purity, Beijing Chemical Works, Beijing, China), hydrochloric acid (analytical purity, Beijing Chemical Works, Beijing, China) and deionized water

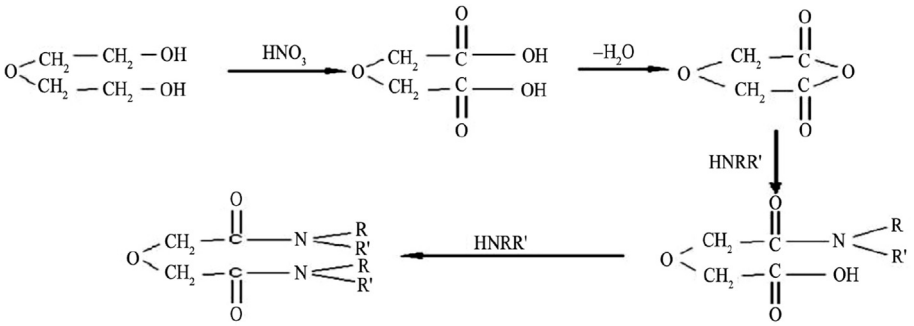

Fig. 1. Synthetic process of N,N,N',N' tetra-octyl-3-oxopentanediamide.