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RECOVERY OF NEODYMIUM AND DYSPROSIUM FROM ACETIC ACID LEACHING SOLUTION OF XENOTIME BY SOLVENT EXTRACTION

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ABSTRACT

Rare earth elements (REEs) have become increasingly influential in human lives due to their significant roles in various high-tech applications. The research on neodymium (Nd) and dysprosium (Dy) recovery from either primary or secondary REE sources has attracted the increasing attention of researchers because of their importance and indispensable in the manufacturing of neo magnet or NdFeB. Solvent extraction after acid leaching is commonly applied to extract and separate Nd and Dy from different sources. Therefore, a study was conducted to recovery Nd and Dy from local xenotime minerals through solvent extraction. This research aimed to determine the ability of acetic acid (CH_3COOH) as the leaching solution for the recovery of Nd and Dy using an organic solvent, 30% of Di-(2-ethylhexyl) phosphoric acid (D2EHPA) in kerosene as the extractant. The Nd and Dy concentrations before and after extraction were analysed using Energy Dispersive X-Ray Fluorescence (EDXRF). The study found that the highest extraction efficiency of Nd and Dy was 99.4% and 99.3%, respectively, at the leaching solution concentration of 1M and the volume ratio of the aqueous-to-organic (A/O) phase equal to 1. The best extraction temperature and time with the optimum extraction efficiency was at 30°C and 20 min. Therefore, this study proves that CH_3COOH is potentially be used as the leaching media of xenotime for the extraction of Nd and Dy with D2EHPA.

Keywords: Neodymium; Dysprosium; Xenotime; CH_3COOH

Abstrak

Unsur nadir bumi (REE) telah menjadi semakin berpengaruh dalam kehidupan manusia oleh kerana peranan pentingnya dalam pelbagai aplikasi berteknologi tinggi. Penyelidikan mengenai perolehan semula neodimium (Nd) dan disprosium (Dy) daripada sumber REE utama atau sekunder telah menarik perhatian para penyelidik kerana kepentingan dan keperluannya dalam pembuatan magnet neo atau NdFeB. Pengekstrakan pelarut selepas larut lesap asid biasanya digunakan untuk mengekstrak dan memisahkan Nd dan Dy daripada sumber yang berbeza. Oleh itu, satu kajian telah dijalankan dengan mengekstrak Nd dan Dy daripada mineral xenotim tempatan melalui teknik pengekstrakan pelarut. Kajian ini bertujuan untuk menentukan keupayaan asid asetik (CH_3COOH) sebagai larutan larut lesap untuk

mengekstrak Nd dan Dy dengan pelarut organik, Di-(2-etilheksil) asid fosforik (D2EHPA) dalam kerosin dengan kepekatan 30%. Kepekatan Nd dan Dy sebelum dan selepas pengekstrakan dianalisis menggunakan Pendarfluor Sinar-X Penyebaran Tenaga (EDXRF). Kajian mendapati kecekapan pengekstrakan tertinggi Nd dan Dy ialah 99.4% dan 99.3%, pada kepekatan larutan larut lesap 1M dan nisbah isipadu fasa akueus-kepada-organik (A/O) bersamaan dengan 1. Suhu dan masa pengekstrakan terbaik dengan kecekapan pengekstrakan optimum ialah pada 30°C dan 20 min. Oleh itu, kajian ini membuktikan bahawa CH_3COOH berpotensi digunakan sebagai media larut lesap xenotim untuk mengekstrak Nd dan Dy dengan D2EHPA.

Kata Kunci: Neodimium; Disprosium; Xenotim; CH_3COOH

INTRODUCTION

Rare earth elements (REE) are found in the Earth's crust at relatively low concentrations, with an estimated average concentration ranging from 150 to 220 parts per million (Qi, 2018). The most commonly mined REE-bearing minerals globally are bastnaesite, xenotime, and monazite, according to Balaram (2019). Due to their widespread use in the production of high-tech products such as computers, smartphones, permanent magnets, fluorescent lamp phosphors, electric vehicles, and renewable energy sources, REE have become a prominent area of focus in current research. Moreover, as they play a crucial role in the development of green technologies, more than 60% of REE demand is directed towards new applications and is expected to continue growing (Mancheri et al., 2019).

In Malaysia, xenotime is a commercially significant byproduct extracted from alluvial deposits, locally referred to as amang. This mineral is primarily found in the Kinta Valley of Perak State in Peninsular Malaysia.. Research by Hazan et al. (2019) has shown that local xenotime contains approximately 61.4% REEs with notable concentrations of yttrium (Y), ytterbium (Yb), dysprosium (Dy), erbium (Er), and neodymium (Nd) at 45.3%, 5.2%, 4.7%, 2.9%, and 1.6%, respectively. The growing demand for neodymium-iron-boron (NdFeB) permanent magnets, driven by the increasing use of electronic equipment and green energy technologies such as computers, wind turbines, and electric vehicles, has led to a surge in interest in extracting Nd and Dy from xenotime (Jowit et al., 2018). As a result, global production of NdFeB magnets is expected to experience rapid growth, driven by the rising demand for electronic devices and electric vehicles, according to Dushyantha et al. (2020). This trend is likely to have significant implications for the Malaysian mining industry, particularly in the extraction and processing of xenotime-rich amang deposits.

The extraction of Nd and Dy from xenotime typically involves a three-step process: digestion, separation, and extraction, as reported by Hazan et al. (2019). The initial step, digestion, aims to break down the orthophosphate mineral lattice into a byproduct called tri-sodium phosphate (Na_3PO_4). This process can be achieved through two methods: sulfuric acid baking or caustic digestion, as described by Farzaneh et al. (2017). However, a more recent approach has been using alkaline digestion with sodium hydroxide (NaOH) at high temperatures, also known as alkaline fusion digestion, which has been successfully applied to both xenotime and monazite processing (Hazan et al. 2019, Jacqueline et al. 2019, Azhar et al. 2020, Sanjit et al. 2021). This method is considered more effective for mineral decomposition, as it eliminates the need for evaporation and acid conversion, resulting in reduced liquid waste volumes, according to Mnculwane (2022).

Extraction of REE involves filtering a solution containing Na_3PO_4 to produce an insoluble REE hydroxide precipitate, followed by acidic leaching with non-organic acids such as sulfuric, hydrochloric, and nitric acids (Guan et al., 2022). Researchers have explored various methods for extracting REE from primary and secondary sources, including using organic acids like citric and acetic acid to leach waste materials (Gergoric et al., 2019; Stein et al., 2022). However, the application of organic acids for primary sources remains limited. For solvent extraction, reagents like D2EHPA, PC88A, and TOPO have been used extensively (Altansukh et al., 2021). D2EHPA is a popular choice due to its high extraction rate, selectivity, and stability (Pan-pan et al., 2018). This study investigated how factors such as acid concentration, aqueous-to-organic volume ratio, and temperature affect the extraction efficiency of neodymium (Nd) and dysprosium (Dy) using D2EHPA in kerosene as an extractant.

METHODOLOGY

Reagents And Instruments

This study used xenotime sand from Kinta Valley, Perak. Analytical-grade chemicals, including kerosene, NaOH, and CH_3COOH acid, were purchased from R&M Chemical while D2EHPA was obtained from Sigma Aldrich, Malaysia. The EDXRF (EDX-7000, Shimadzu) was used to analyze the sample's element concentrations before and after extraction. Deionized water was used for all experiments in this study.

Sample Digestion

A 100g xenotime sample was fused with 200g of NaOH pellets in a crucible at a temperature range of 300-400°C for 3 hours. The resulting sintered sample was then dissolved in 2000 mL of deionized water, stirred for 3 hours, and filtered using a vacuum filter. The precipitate was washed with deionized water until pH 7 was reached, and then dried in an oven at 70°C for 24 hours.

REE-Loaded Aqueous Solutions

A rare earth hydroxide (REOH) precipitate was obtained through drying. REE-loaded aqueous solution were prepared by leaching REOH into acetic acid with concentrations of 0.5, 1, 3, and 5 M. The solutions were stirred at a temperature range of 70-80°C for a specified period. The concentrations of Nd and Dy in the solutions before extraction were analyzed using EDXRF.

Solvent Extraction

A 30% extractant was prepared by dissolving a specific volume of D2EHPA in kerosene. The aqueous solutions were mixed with the extractant at ratios of 1:1 to 1:4 and stirred for 15 minutes at 30°C, 40°C, 50°C and 60°C. The mixture was then left to equilibrate for 20 minutes before separating into aqueous and organic phases. The composition of the organic phase was analyzed using EDXRF.

The extraction efficiency (%E) was calculated using Equation (1) to determine the percentage of solute that transfers from the aqueous to the organic phase. The equation defines extraction efficiency as the product of the distribution coefficient (D), and the volumes of the aqueous (V_A) and organic (V_O) phases.

$$\%E = \frac{D \times \frac{V_o}{V_A}}{1 + (D \times \frac{V_o}{V_A})} \times 100 \quad (1)$$

The distribution coefficient (D) in Equation (2) is defined as the ratio of the element concentrations in the organic to the aqueous phases at the equilibrium state where Co is the concentration of an element in the organic phase and C_A is the concentration of an element in the aqueous phase.

$$D = \frac{C_O}{C_A} \quad (2)$$

RESULTS AND DISCUSSION

Table 1 shows the concentration of REE before extraction in acid solution at the concentrations of 0.5, 1, 3 and 5M. The results showed that the concentrations of Dy and Nd in the xenotime samples were 5.19, 6.47, 6.57 and 6.89% and 0.59, 0.90, 1.19 and 1.06%, respectively. Notably, Dy concentrations were significantly higher than Nd concentrations due to xenotime's composition as a heavy rare earth element (HREE) phosphate. The solution also contained naturally occurring radioactive materials (NORM), with thorium (Th) and uranium (U) present at less than 1% composition each.

Table 1. REE concentration in acetic acid solution before extraction

REE	Atomic Number	REE Concentration (%)			
		0.5M	1M	3M	5M
HREE					
Y	39	69.55	71.46	66.86	68.26
Gd	64	2.30	2.73	2.35	2.32
Dy	66	5.19	6.47	6.57	6.89
Ho	67	1.18	1.78	1.48	1.65
Tm	69	1.21	1.32	1.38	1.03
Yb	70	4.60	4.77	7.33	7.00
LREE					
Nd	60	0.59	0.90	1.19	1.06
Sm	62	0.68	0.94	0.53	0.40
La	57	ND	0.44	0.63	0.66
NORM					
Th	90	ND	ND	0.15	0.14
U	92	0.55	0.99	0.29	0.22

Effect of CH_3COOH concentration

The effect of acid concentration on the extraction behavior of Dy and Nd was examined by varying the concentration of CH_3COOH from 0.5 M to 5 M at an O/A ratio of 1 and a temperature of 30°C. As shown in Fig. 1, the extraction efficiency increased when the acid concentration rose from 0.5 M to 1M, reaching 99.3% for Dy and 99.4% for Nd. According to Tang et al. (2019), the increase in extraction efficiency is attributed to the insufficient acid concentration, which fails to meet the process requirements. However, as the acid concentration continued to increase, the extraction efficiency of Dy and Nd decreased slightly to 95.1% and 92.9%. The results indicate that the extraction of Dy and Nd no longer increases when the concentration exceeds 1M, suggesting that the acid is sufficient to consume major elemental oxides and react with rare earth compounds at higher concentrations. Notably, partially encapsulated Nd and Dy have limited opportunities to interact with the acid, even when recovery is no longer limited by the lack of hydrogen ions (H+) (Cao et al. 2018).

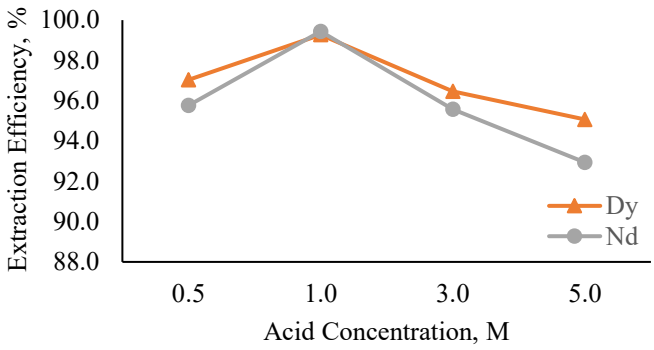

Figure 1. Effect of acid concentration on extraction efficiency

Effect of Aqueous-to-Organic Ratio

The aqueous-to-organic phase ratios (A/O) of 1:1, 1:2, 1:3, and 1:4 was examined to investigate their impact on the extraction of Dy and Nd under constant conditions. The results showed that the highest extraction efficiency was achieved at an A/O ratio of 1:1, with extraction yields of 99.3% for Dy and 99.4% for Nd. However, as the A/O ratio increased to 1:2, the extraction efficiency began to decline, as depicted in Figure 2. Specifically, at A/O ratios of 1:3 and 1:4, the extraction efficiencies for Dy and Nd were 95.5% and 95%, and 95% and 94%, respectively.

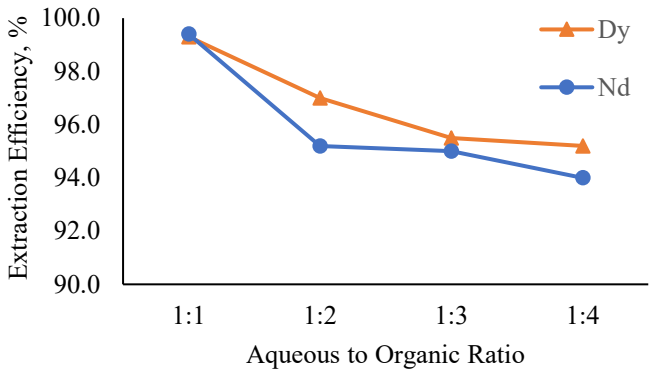

Figure 2. Effect of aqueous-to-organic ratio on extraction efficiency

The decrease in extraction efficiency is attributed to the solvent's saturation point being reached or exceeded, as suggested by Pusporini et al. (2021). Consequently, the declining trend in extraction efficiency observed in this study is due to the limitation of D2EHPA's ability to extract Dy and Nd at higher A/O ratios.

Effect of Temperature

The impact of temperature on extraction efficiency was examined at 30°C, 40°C, 50°C, and 60°C. The results showed that the extraction efficiency of Dy and Nd decreased from 99.3% and 99.4% to 90.2% and 90.1%, respectively, as the temperature increased from 30°C to 60°C as shown in Fig.3. This trend is consistent with findings from other studies (Arellano et al. 2020, Altansukh et al. 2021, Pan et al. 2022), which have reported that extraction activity using a temperature of 30°C is optimal for RE elements. Pan et al. (2022) also emphasized the importance of avoiding high temperatures above 35°C, as they can cause degradation of the extracted material, leading to decreased extraction efficiency and yield.

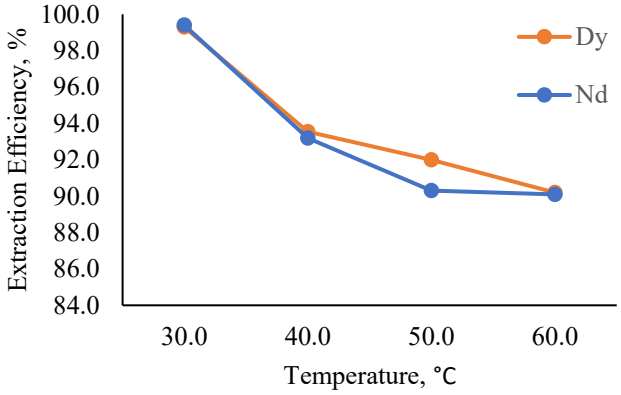

Figure 3. Effect of temperature on extraction efficiency

Therefore, selecting the suitable extraction temperature is crucial to maintain the stability of the extracted material, as excessive temperatures can destroy the structure and activity of the extraction process. As a result, increasing the extraction temperature does not significantly improve the extraction yield of Dy and Nd in this experiment.

CONCLUSION

This study demonstrates the successful extraction of Dy and Nd from an acetic acid leached solution of xenotime using 30% D2EHPA through solvent extraction. The results show that the leached solution concentration, aqueous-to-organic ratio, and temperature significantly impact the extraction efficiency of Dy and Nd. The optimal conditions for extraction were found to be a leached solution concentration of 1M, an extraction temperature of 30°C, and an aqueous-to-organic volume ratio of 1:1, resulting in extraction efficiencies of 99.3% for Dy and 99.4% for Nd. Overall, this study suggests that acetic acid has potential as a mineral leaching medium for the extraction of rare earth elements, providing a promising approach for the recovery of these valuable materials.

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