

THE EFFECT OF PC88A SOLVENT EXTRACTION PARAMETERS AND ITS STRIPPING BEHAVIOR TO THE RECOVERY OF YTTRIUM

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ABSTRACT

Yttrium (Y) is one of the elements major in heavy rare earth elements (HREE) used in various industries such as metallurgy, steel, laser, electronics, optics, superconductors, magnets, color television (TV) tubes and others applications. In nature, the rare earth elements (REE) are associates in fairly multifaceted combination and because of chemical properties likeness and difficult to isolate REE into single elements. These could be the biggest hurdle in the recovery and extraction of yttrium from xenotime minerals. Therefore, solvent extraction of yttrium from chloride solution using organic extractant 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A) diluted in kerosene and modified with isodecanol was investigated in this study. Based to a solvent extraction study, the best conditions for recovering yttrium using an organic combination consisting of 34% PC88A, 6% isodecanol, and 60% kerosene were 1.0 g of yttrium chloric hexahydrate in 0.2 M hydrochloric acid (HCl) with a ratio organic to aqueous of 1:3 and 30 minutes contact time. Additional research on the behavior of stripping was also differentiated and considered. It was discovered that nitride acid (HNO₃) were more effective in yttrium stripping than HCl and sulfuric acids (H₂SO₄).

Keywords: PC88A, Solvent Extraction, Stripping, Yttrium

INTRODUCTION

Although yttrium was discovered in the late 1800s (Voncken, 2018), it wasn't commercially available until the last few decades (Singh et al., 2015) in the fields of chemistry, physics, computer technology, energy, medicine, and other fields (Grate et al., 2020). Tin-tailing, or xenotime sand, comes from the tin mining sector in peninsular Malaysia, primarily in the state of Perak, Selangor, Pahang and Negeri Sembilan (Meor Sulaiman, M. Y., 2010). This sand contains yttrium. Yttrium is a metal that is very valuable for the advancement of new materials, since yttrium has very unique properties and profitable. To acquire yttrium with high purity, the mineral needs to be purified with few steps of process, namely cracking/digestion of xenotime, leaching, selective precipitation, crystallization, chemical treatment, heat treatment and extraction (Biyantoro et al., 2002).

Solvent extraction is a well-known separation method in which a solute is transported from aqueous phase to another immiscible or partially miscible fluid (solvent) which is in interaction with the initial phase. Basically, there are three solvent extraction stages that is extraction, scrubbing and stripping. In hydrometallurgy, the aqueous phase comprises element of interest to be extract into the organic phase. Solvent extraction is a part of analytical chemistry techniques that able to concentrate elements by an extractant reagent in the organic phase from diluted aqueous solutions. Industrial solvent extraction is a technique that was pioneered by the nuclear industry and utilized for the purification and separation of metals, including plutonium preparation in 1942. Diethylether,

a solvent, and diluted uranyl nitrate were utilized in this extraction process. This was a significant advance in solvent extraction applications, leading the way not just in the nuclear sector but also in the extraction of other elements (Hudson et al., 1982). Currently, solvent extraction is commercially practice for a varied of minerals to obtained valuable elements.

The need of splitting REE from mineral after the cracking or digestion process led to the advancement in solvent extraction with selective complexation. Solvent extraction methods are normally need good extraction kinetics. Regarding its chemical stability, optimum loading and stripping characteristics, low solubility in the aqueous phase, versatility in the extraction of various metal ions, and availability for use in industrial settings. Previously, numerous fundamental researches on the yttrium extraction with di-(2-ethylhexyl) phosphoric acid (D2EHPA) (Biyantoro et al., 2002, Mohammadi et al., 2015, Perwira et al., 2018 and Sapiee et al., 2019) and Tributyl Phosphate (TBP) (Azhar et al., 2020) have been studied. In 1957, Peppard et al., detailed the use of D2EHPA as a capable extractant for REE. In that study the lanthanides distribution coefficient were showed. D2EHPA as extractant was dependent on the influence of D2EHPA concentration in the equilibrated organic phase, however contradicting to H^+ concentration in the aqueous phase. Additionally, if the solute concentration in the organic phase was too concentrated, a third phase emulsion was forming leading to incomplete extraction process (Anticó et al., 1996). These studies collectively highlight effective methods for high yttrium recovery through solvent extraction processes. Additionally, factors such as extraction time (Nicol et al., 2022), solvent choice based on physicochemical properties and dissolution capabilities (Chandaliya et al., 2012), and operating parameters like agitation rate and settling time (Poole, 2020) significantly impact the yield and quality of the extracted product.

In the extraction process, it was intentionally to separate yttrium from other REE. In order to acquire high yttrium content, thorough study in yttrium extraction and purification from xenotime mineral is necessary. To our knowledge, there hasn't been any published research on the extraction of yttrium using PC88A solvent, despite the fact that there have been several studies on the extraction of REE using various extractants. Therefore, it is essential to define best conditions for yttrium extraction such as of hydrochloride acid concentration, organic to aqueous ratio, contact time, loaded amount of yttrium (III) chloride Hexahydrate (g/l), speed and solvent content. Besides, stripping process parameters (acid suitability, acid concentration, and stripping duration) also been studied in this research.

METHODOLOGY

Experimental

Stock solutions (aqueous) of yttrium chloride were prepared by dissolving the respective yttrium (III) chloride Hexahydrate (99.9%) supplied by Aldrich in diluted HCl (37%, Merck). The organic extractant 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A) (Laurice Labs, Maharashtra, India) was diluted in 30% kerosene (R&M Chemicals) to desire concentration and modify with isodecanol (Laurice Labs, Maharashtra, India). All reagents used were analytical grade. The two stages of the experimental work that were done were solvent extraction and stripping. Solvent extraction experiments were carried out in a glass beaker positioned on a magnetic stirrer plate at room temperature. Mixture of aqueous and organic solvent were vigorously stirred. After 30 minutes, the mixture was transferred into a separatory funnel and waited until a stable, two-layer immiscible solution formed. Then, the aqueous raffinate and extracted organic phase were flushed out into different sample bottle. Different solvent extraction batches were done to study different

extraction parameter such as HCl concentration, organic to aqueous ratio, contact time, loaded amount of yttrium (III) chloride Hexahydrate (g/l), speed, and solvent content.

In stage two, extracted yttrium in organic phase from previously solvent extraction experiment were used for stripping steps. The extracted organic phase was stripped with different molarity of HCl, HNO₃ (65%, R&M Chemicals) and H₂SO₄ (95%, R&M Chemicals) for 30 minutes at room temperature. Then, it was allowed to form two phases: the aqueous phase and the organic phase. Then the best condition for acid concentration was selected to study the effect of stripping duration. Figure 1 shows experimental flow chart.

Characterization

In order to identify the yttrium contained in organic and aqueous solution from solvent extraction and stripping process, the EDXRF Spectroscopy was used to analyse the samples by EDX7000, Shimadzu. This analytical instrument also able to determine the composition of the elements in the sample solution by measuring the fluorescence intensity converted into yttrium concentration in part per million (ppm).

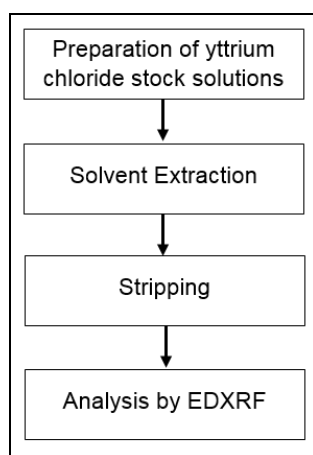


Figure 1. Experimental flow chart

RESULTS AND DISCUSSION

Effect acid molarity on yttrium extraction

HCl with concentration of 0.1 M, 0.2 M, 0.5 M, 1.0 M, 1.5 M and 2.0 M were selected to study the effect the HCl molarity on yttrium extraction and the results were shown in Figure 2. Molarity acid was believed to influence the coefficient distribution, efficiency, and separation factor of yttrium extraction. Higher acid molarity (> 0.2 M HCl) showed a decrease in the percent of yttrium recovery from 80% to 0%. This is due to the PC88A solvent preferring H⁺ ion exchange in the low acid molarity of HCl to bind complex organic mixtures to the Y³⁺ ion. Basuki and colleagues also reported that even by increasing acid concentration in solvent extraction process can increase the reactivity of the H⁺ ion formation but the extraction could be lowered as high acidity will reduce the ability of solvent (Basuki et al., 2019). The optimum concentration to gain the highest extraction of yttrium was 0.2 M HCl.

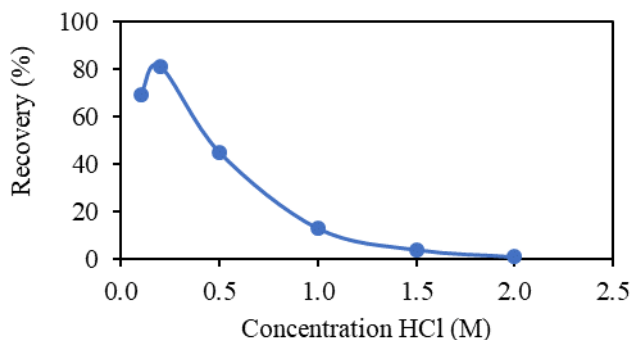


Figure 2. Effect HCl molarity on yttrium extraction.

Effect of solvent amount on yttrium extraction

The solvent amounts of the extraction mixture used to study its effect on the extraction of yttrium under constant conditions were 25%, 33%, 40%, 50%, and 67%. The results are shown in Figure 3. The optimum organic to aqueous ratio to get higher percent recovery of yttrium was 1:3. 25% solvent yielded a high percentage of yttrium extraction, probably because the concentration of H^+ ion in the mixture was higher to enhance the ability of yttrium to form the Y^{3+} ion. Thus, the interaction between the Y^{3+} ion and the PC88A organic ligand will form a complex organic mixture.

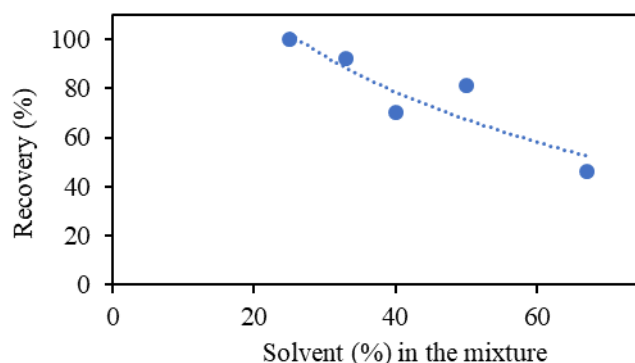


Figure 3. Effect of organic to aqueous ratio to recover yttrium.

Effect of contact time between aqueous and organic phase to extract yttrium

From the data in Figure 4, we can see the effect of the extraction time between the aqueous phase feed and solvent on the distribution of yttrium into the organic phase. The longer the contact between phases during extraction, the higher the concentration of yttrium bound to PC88A. The yttrium solutes extracted into the organic phase will increase by prolonging the stirring duration, which will also increase the mass transfer from the aqueous phase to the organic phase. Thus, the extraction efficiency increases as a result. The amount of yttrium solute extracted will remain constant after attaining the ideal value, and additional stirring time has no further significance. Also, prolong the stirring time will decreased the extraction due to the solvent's optimum ability. However, if the reaction continue for more than 30 minutes, the extraction of yttrium lesser may be due to back-extraction process of yttrium into aqueous phase. Therefore, the optimum separation time to obtain relatively high purity yttrium was obtained at 30 minutes.

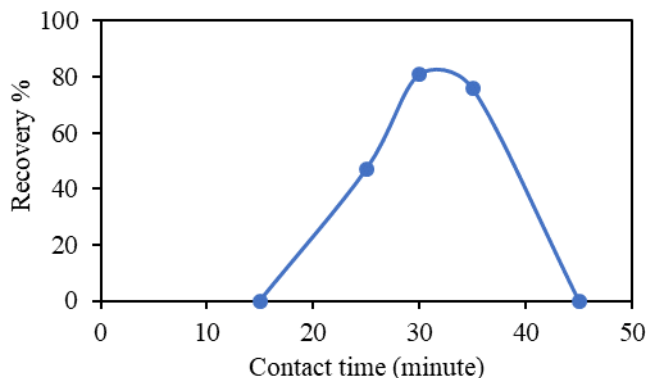


Figure 4. Effect contact time between aqueous and organic phase on yttrium extraction.

Effect of initial Y (III) ion concentration

In order to achieve high efficiency in yttrium extraction, different loads of yttrium (III) chloride hexahydrate were introduced to the feed stock solution (aqueous). The yttrium extraction decreased with increasing feed concentration (Figure 5). It is because the organic phase was saturated, which decreased the amount of yttrium that diffused into the organic phase. This finding was in line with Basuki et al.'s (2020). From the data below (Figure 5), 0.3 g yttrium (III) chloride hexahydrate in 25 ml solution or 12 g/L is the optimum value to get higher percent recovery of yttrium. A high concentration of yttrium in an aqueous solution would hinder the extraction of yttrium because it's surrounded and encapsulated by organic solvent. Thus, the organic solvent could not hold the Y^{3+} ion and developed an emulsion. Therefore it can be said that the separation of the solute (yttrium) is relative to their solubility in the two phases (Li, et al., 2021).

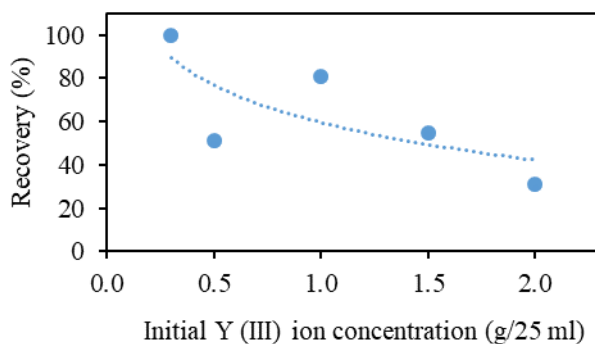


Figure 5. Effect of loaded organic amount in the pregnant solution.

Effect of stirring speed on yttrium extraction

From the data shown in Figure 6, the extraction of yttrium can only be done after vigorously stirring the mixture. However, the Y^{3+} ion extraction was reduced as the stirring speed was too high and the mixture tends to produce a third-layer phase, or emulsion. This phenomenon should prevail in order to extract most of the desired element of interest. Also, high stirring rates would produce excessive turbulence and air bubbles which could affect extraction precision. Hence, stirring speed of 6 units on scale is the optimum value to get higher percent recovery of yttrium.

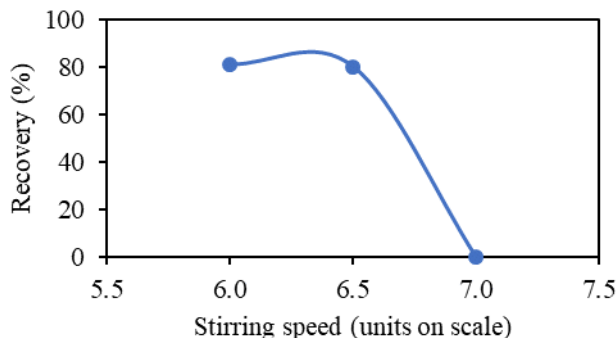


Figure 6. Effect of stirring speed on yttrium extraction

Effect of different composition PC88A and Isodecanol in solvent mixture on yttrium extraction

From Figure 7, the effect of extractant PC88A concentration and isodecanol in kerosene as an extraction factor in yttrium extraction. PC88A was used as extractant to pull out the REE in aqueous solution (in this case yttrium). Where as isodecanol was used as modifier in solvent extraction process to prevent the formation of third phase while during solvent extraction process. The result of the effect isodecanol content in yttrium extraction is shown in Figure 8. From the experiment, it was noticed that 35% PC88A and 6% isodecanol diluted in kerosene were the optimum compositions to extract yttrium from the aqueous phase.

Effect of acid concentration on yttrium stripping

The organic phase extracted from a 0.2 M HCl aqueous solution was used for the stripping process. Different concentrations of H₂SO₄, HNO₃, and HCl were studied. From the data in Table 1, the recovery of yttrium is very low (just 1.7%) upon 4 M H₂SO₄ stripping. As per record, stripping with higher than 4 M H₂SO₄, the emulsion tends to exist thus affect the stripping results. The emulsion occurs when 3 phases were exist in the solution. Therefore, H₂SO₄ is not suitable for yttrium stripping process.

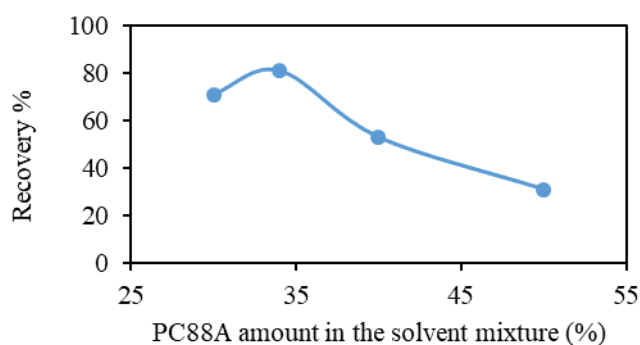


Figure 7. Effect of solvent different composition (PC88A) on yttrium extraction

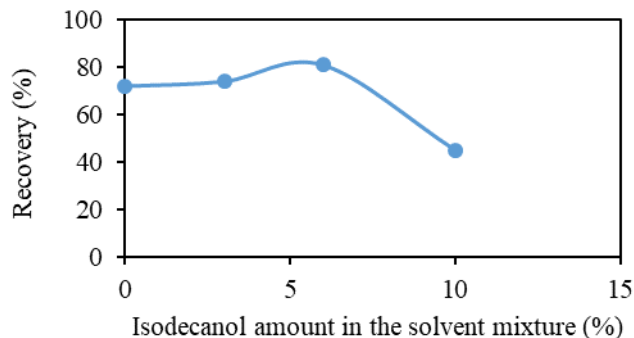


Figure 8. Effect of different composition Isodecanol in the organic mixture to extract yttrium

Table 1. Effect of H₂SO₄ molarity on yttrium stripping from organic mixture

Concentration of H ₂ SO ₄ (M)	Yttrium recovery (%)
0.5	0.0
1.0	0.0
2.0	0.0
3.0	0.0
4.0	1.7

Figure 9 shows the effect of acid (HCl and HNO₃) concentration on yttrium stripping. From the graph, HNO₃ with concentration of 2 M was the optimum concentration to get high recovery of yttrium. The stripping efficiency start to decrease at 5 M because it is hard to break down the complex mixture organic solvent that form from extraction process. 2 M HNO₃ was capable to break down the bonding between Y³⁺ and organic complex and its ability to capture and thus pull yttrium from the organic extractant. In this research, H₂SO₄ and HCl have low efficiency to strip yttrium from organic phase and it can be conclude that the best stripping agents were HNO₃ > HCl > H₂SO₄ accordingly.

Effect of stripping duration to recover yttrium

Figure 10 showed the effect of stripping duration on yttrium into the aqueous phase. The longer the contact time between phases during extraction, the higher the concentration of yttrium bound to NO₃⁻. However, if the reaction prolong more than 45 minutes, the recovery become less showing that the yttrium reverse back to organic phase.

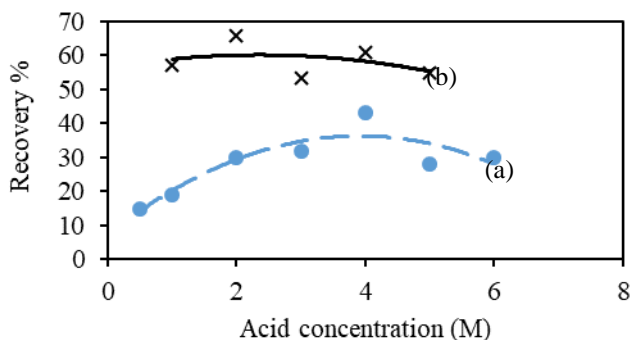


Figure 9. Effect acid concentration (a) HCl and (b) HNO₃ on yttrium stripping

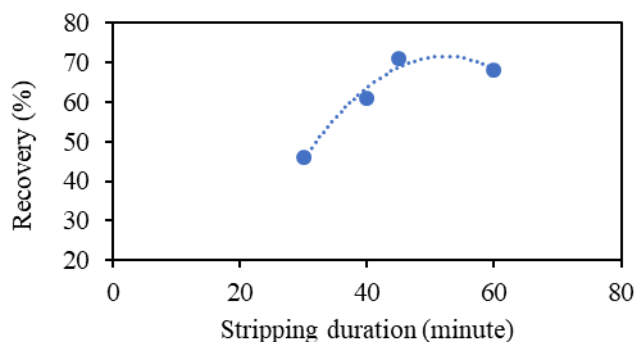


Figure 10. Effect of stripping duration using HNO_3 to strip yttrium.

In order to minimise the error during experiment, it is recommend to properly weighed the yttrium (III) chloride hexahydrate and ensure the cleanliness of all the apparatus used to measure the samples as it will affect the concentration of the sample during acid dilution. Also, noted to use same magnetic stirring plate and stir bar size for all experiments for results reliability.

CONCLUSIONS

Solvent extraction of yttrium from yttrium (III) chloride hexahydrate using extractant PC88A in kerosene was obtained in this study. It was found that the optimum condition to extract yttrium was 0.2 M HCl with a 30-minute contact time. Whereas 12 g/L of loaded yttrium (III) chloride hexahydrate in 34% PC88A and 6% isodecanol as a modifier in kerosene were used as solvents to extract the Y^{3+} ion. Complete extraction of yttrium was achieved from the 25% solvent phase contained in the extraction mixture. In addition, in the stripping study, it is suggested that yttrium stripping was preferred to occur with 2 M HNO_3 as the stripping agent for 45 minutes of contact time.

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