Extraction of cerium and terbium from hydrochloric acid solutions obtained from leaching of fluorescent lamp phosphors

L. Bumhira[a], C. Dorfling[a]*, and G. Akdogan[a]

[a]*Department of Process Engineering, Stellenbosch University, Private Bag X1, Matieland, 7602, South Africa*
**Corresponding author: dorfling@sun.ac.za*

ABSTRACT

Hydrometallurgical recovery of rare earth elements from phosphors obtained from end-of-life fluorescent lamps involve leaching followed by extraction of dissolved metals from solution. The similar properties of rare earth elements make selective recovery of individual elements challenging. The aim of the paper was to investigate the extraction of primarily Ce and Tb from a hydrochloric acid leach solution also containing other REEs (Y and Eu) as well as impurity metals (Ca and Al). Batch solvent extraction tests were performed with di-(2-ethylhexyl) phosphoric acid (DEHPA) at various extractant concentrations, pH conditions and organic-to-aqueous ratios. Extraction isotherms and separation factors for the range of conditions tested in the project are presented in the paper. Separation of individual REEs was not possible at the conditions investigated, but a mixed REE product can be obtained in a single extraction stage operated at a pH of 0.5 using 1 M extractant at an O/A ratio of 1; these conditions resulted in complete Y and Eu, 95 % Ce and 99 % Tb extraction with Ca and Al co-extraction below 7 %. A better quality mixed REE product can be produced by operating at lower pH and extractant concentration conditions, but this would require a larger number of extraction stages.

Keywords: Cerium, fluorescent lamps, phosphors, rare earth elements, solvent extraction, terbium

1. Introduction

1.1. Background

Recovery of rare earth elements (REEs) present in the phosphor powders recovered from end-of-life fluorescent lamps presents an important opportunity for local REE beneficiation, maintaining market balance, and moving towards a circular economy. The hydrometallurgical process route typically proposed for REE recovery from phosphors involves one or more leaching stages followed by metal separation and recovery from the resultant pregnant leach solutions.

Separation of individual REEs in solution is challenging because of the very small differences in properties such as ionic radii between the elements. In addition to REEs, phosphors contain metal impurities such as Ca and Al which further complicates the extraction process. Solvent extraction has become the most suitable industrial technology for separating REEs when handling large volumes of leach solutions (Xie *et al.*, 2014). During solvent extraction, the aim is to selectively extract REEs of interest from the aqueous phase (leach solution) to an immiscible organic phase. Selectivity of solvent extraction of individual REEs relies, amongst other factors, on the reduction in ionic radius across the lanthanide series. This results in differences in formation coefficients of the rare earth-extractant complexes, thereby permitting preferential extraction of specific complexes into the organic phase (Rydberg, 2004). Heavy elements of the lanthanide series form stronger bounds with extractant molecules than lighter members (Nash, 1993). As a result, the selectivity order for REE extraction generally follows the following sequence: Lu > Yb > Tm > Tb > Eu > Pm > Pr > Ce > La (Peppard and Wason, 1961; Wang *et al.*, 2002). The extraction of REEs by cationic exchange from aqueous solutions is given by Equation 1, where RE and H_2A_2 denote the trivalent rare earth element and the dimeric form of the organic acid (extractant), respectively (Morais and Ciminelli, 2004; Gupta and Krishnamurthy, 2005). Some of the most commonly used cationic exchangers in REEs extraction are discussed in Section 1.2.

$$RE^{3+}_{(aq)} + 3H_2A_{2(org)} \rightarrow RE(HA_2)_{3(org)} + 3H^{+}_{(aq)} \quad (1)$$

The aim of the current study was to investigate the extraction of REEs (primarily Ce and Tb) from hydrochloric acid leach solutions produced during the leaching of phosphor powder recovered from end-of-life fluorescent lamps. The effect of operating parameters on REE and impurity extraction was determined to evaluate the possibility of selective extraction of REEs from the leach solution.

1.2. Solvent extraction for REE separation

Di-(2-ethylhexyl) phosphoric acid (DEHPA) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEHEHP) have been widely employed as extractants in rare earth recovery from leach solutions (Xie *et al.*, 2014). HEHEHP in kerosene was used to extract Eu, Tb, and Y from nitric acid leachates (Nakamura *et al.*, 2007); 97.8 % Y, 58.1 % Tb, and 52.8% Eu recoveries were reported. Abreu and Morais (2014) investigated the use of different organophosphorus acids (DEHPA, Cyanex 272 and Ionquest 801 / PC-88A) for the extraction of Tb and Y from hydrochloric acid solutions. Cyanex 272 was the least effective of the three cationic exchangers. DEHPA gave the highest extraction (41.4 % Tb and 81.3 % Y) in both mediums. A DEHPA concentration of 1 M and an aqueous solution pH of 0.3 were used.

Although DEHPA is the most commonly used extractant in REEs extraction industries, HEHEHP is known to give higher separation factors for REEs separation. HEHEHP also requires less acid in the aqueous phase during stripping (Song *et al.*, 2009). However, the extraction efficiency achievable with HEHEHP decreases when the viscosity of the organic phase increases. Higher extraction efficiencies can also be obtained with DEHPA (Song *et al.*, 2009; Abreu and Morais, 2014), and DEHPA is relatively cheap compared to HEHEHP (Huang *et al.*, 2008).

In order to address the shortcomings of the conventional single extractant solvent extraction process studies have been conducted on the use of mixtures of reagents as the extractant in solvent extraction processes. Wang *et al.* (2006) found that heavy rare earth extraction is highest for a mixture of HEHEHP and DEHPA, followed by HEHEHP and Cyanex 301, HEHEHP and HHEOIPP (isopropylphosphonic acid 1-hexyl-4-ethyloctyl ester), HEHEHP and Cyanex 302, and HEHEHP and Cyanex 272, in that order. The HEHEHP and DEHPA mixture and the HEHEHP and Cyanex 272 mixtures were the only two that exhibited synergistic extraction effects. For the current study, DEHPA was selected as extractant because of the relatively high extraction efficiencies achievable and low costs compared to other extractants.

1.3. Solvent extraction performance

The distribution coefficient, percentage extraction and separation factor help in understanding and quantifying the performance of various extractants (Habashi, 1999). The ratio between the concentration of the targeted solute (solute A) in the extractant ($[A]_{org}$) and the aqueous phase ($[A]_{aq}$) at equilibrium is known as the distribution ratio (D), as shown in Equation 2:

$$D = \frac{[A]_{org}}{[A]_{aq}} \tag{2}$$

The percentage of metal ions extracted can be determined from the distribution ratio according to Equation 3, where V_{org} is the organic phase volume and V_{aq} is the aqueous phase volume:

$$\%E = \frac{100 \times D}{{V_{aq}}/{V_{org}} + D} \tag{3}$$

The separation factor showing the extent of separation between solutes A and B is given by Equation 4. Separation between solute A and B is only possible if $\alpha_{(A/B)}$ is significantly larger or smaller than unity (Gupta and Krishnamurthy, 2005).

$$\alpha_{A/B} = \frac{D_A}{D_B} \tag{4}$$

2. Experimental

2.1. Leach solution preparation

The hydrochloric acid leach solution used for the solvent extraction tests was prepared by performing multiple leaching steps on phosphor powder recovered from end-of-life fluorescent lamps. The waste fluorescent phosphor powder was obtained from a lamp recycling and mechanical processing facility in South Africa. The received powder was obtained from typical waste fluorescent lamps which were treated to remove hazardous mercury; the elemental composition of the as-received powder is summarized in Table 1. The major phases identified were quartz (SiO_2), magnesium cerium terbium aluminum oxide ($(Ce,Tb)MgAl_{11}O_{19}$), hydroxylapatite ($Ca_5(PO_4)_3(OH)$), yttrium europium oxide ($Y_2O_3:Eu^{3+}$), monazite ($(Ce,La,Nd,Th)(PO_4,SiO_4)$), barium silicon oxide ($BaSiO_3$), tetracalcium bis(phosphate(V)) oxide ($Ca_4(PO_4)_2O$), and calcium phosphate silicate.

The first leaching stage was aimed at dissolution of yttrium and europium, which are present in the readily soluble red phosphors (Y_2O_3:Eu^{3+}); sulfuric acid was preferred as lixiviant because of the expected suppression of calcium dissolution. The first stage leach was performed for a period of 6 hours with 2 M H_2SO_4 at 25°C and a solid-to-liquid ratio of 10 % (w/v). At these conditions, 98 % Y and 89 % Eu leached with insignificant Ce and Tb dissolution. The solid residue recovered from the first leaching step was subjected to alkali fusion: the leach residue and sodium hydroxide were mixed in the ratio 1:1.5 (mass basis). Sintering was performed in a muffle furnace at a temperature of 800 ± 3°C for 120 minutes. The fusion product was washed to remove soluble material such as sodium aluminate (Liu *et al.*, 2014). The insoluble material was filtered prior to drying in an oven for 24 hours at a temperature of 60°C.

The dried alkali fusion product was pulverized before being leached for 45 minutes using 5 M HCl at 60°C and a solid-to-liquid ratio of 5 % (w/v); this resulted in more than 96 % Ce and 98 % Tb leaching, respectively. The leach solution recovered from this second leaching step, the composition of which is summarized in Table 2, was used as leach solution for the solvent extraction tests.

Table 1.

Metal content in as-received waste fluorescent lamp phosphor powder.

Metal	Average metal content (g/kg)	Metal	Average metal content (g/kg)
Al	12.19 ± 2.1	Fe	5.6 ± 0.2
B	0.55 ± 0.03	Gd	0.8 ± 0.03
Ba	1.2 ± 0.09	La	2.2 ± 1.3
Ca	231 ± 7.1	Mg	2.9 ± 0.04
Ce	2.1 ± 0.5	Tb	1.8 ± 0.2
Cu	0.6 ± 0.03	Y	42.3 ± 0.02
Eu	2.9 ± 0.02	Zn	7.1 ± 3.9

Table 2.

Second stage hydrochloric acid leach solution (aqueous phase) composition.

Metal content (ppm)					
Al	**Ca**	**Ce**	**Eu**	**Tb**	**Y**
1246	9506	195.6	42.3	203.5	129.3

2.2. Method

Batch solvent extraction tests were performed in 100 mL glass beakers. Mixing of the organic/aqueous dispersion was done using magnetic stirrer set at a mixing speed of 300 rpm. After every 2 minutes of mixing, the aqueous phase pH was measured and adjusted using 5 M NaOH until the pH stabilized at the desired value, indicating that extraction equilibrium had been achieved. After agitation, the dispersion was transferred to a separation funnel for phase separation to take place; the collected aqueous phase was filtered using 0.22 µm syringe filters to remove trace amounts of the

organic phase. Metal content of the aqueous samples was determined using inductively coupled plasma optical emission spectrometry (ICP-OES).

The effects of equilibrium pH, organic-to-aqueous (O/A) ratio and extractant concentration on metal extraction were investigated according to a full factorial experimental design using di-(2-ethylhexyl) phosphoric acid (DEHPA) as extractant in kerosene as diluent. The levels for the respective process conditions were: extractant concentrations of 0.5 and 1 M; O/A ratios of 1, 1.5, 2, 2.5 and 5; and pH values of 0.25, 0.5, 1, 1.5 and 2.

2.3. Materials

Sulfuric acid (98 wt%) and hydrochloric acid (32 wt%) used as lixiviants in the first and second leaching stages, respectively, were supplied by Kimix, who also supplied NaOH pellets for alkali fusion and preparation of stock NaOH solutions. Demineralized water was used to dilute the concentrated acid to the desired concentration and to prepare stock solutions. DEHPA and kerosene used to prepare the organic phase for solvent extraction experiments were supplied by Hong Kong Guokang Bio-Technology Co. Ltd. and Kimix, respectively.

3. Results and discussion

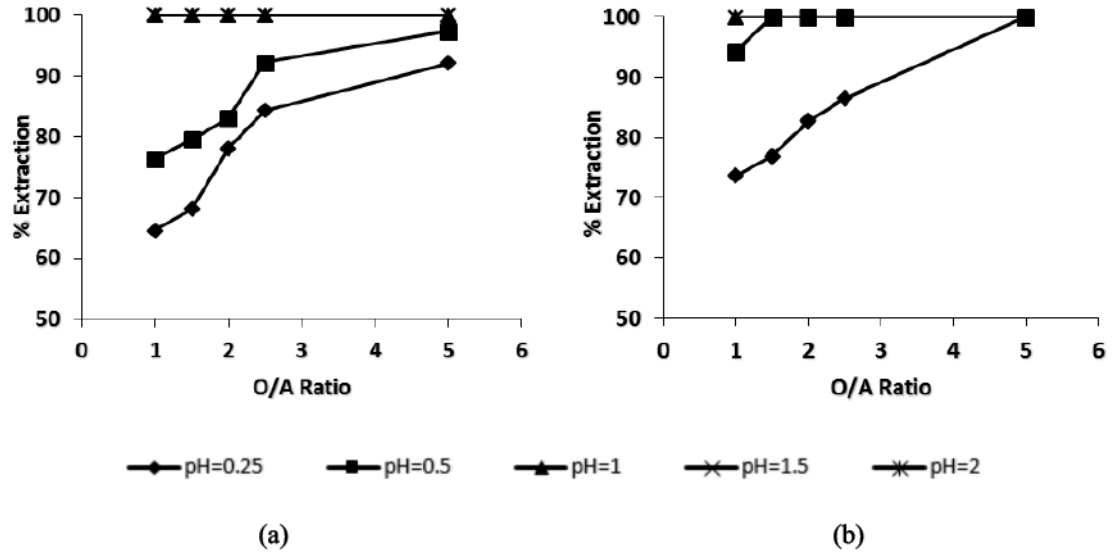
3.1. Effect of process variables on extraction

Figure 1 shows the effect of pH and O/A ratio on percentage extraction of Ce. Ce extraction was observed to increase with increasing pH and O/A ratio for both extractant concentrations. At the lowest extractant concentration and O/A ratio, over 99 % Ce extraction was only possible at pH 1.5 and beyond. For cationic exchangers, it is expected that the percentage extraction will increase with increase in pH as the decreasing H^+ concentration favors the forward extraction reaction (as shown in Equation 1). An increase in extractant concentration also caused an increase in percentage extraction as expected.

DEHPA showed a higher affinity for Tb than for Ce. At the lowest extractant concentration and O/A ratio, more than 99 % Tb was extracted even when operating at the lowest pH. These results confirm that DEHPA is a powerful extractant capable of extracting heavy rare earths even at low pH, as reported by Rydberg (2004) and Xie *et al.* (2014); the results are also in agreement with the selectivity series as discussed in Section 1.2. Heavy elements of the lanthanide series form stronger bounds with extractant molecules than lighter members (Nash, 1993). It was found that there was no significant increase in percentage extraction for Tb with increase in extractant concentration from 0.5 M to 1 M.

Y and Eu were co-extracted during the solvent extraction tests. Both rare earths were now present in relatively low concentrations in the leach solution since more than 90 % of these metals were dissolved in the first leaching step and reported to the sulfuric acid leach solution. After solvent extraction tests were performed with the second stage HCl leach solution, Y could not be detected in any of the remaining aqueous solutions using ICP-OES analysis. It was therefore assumed that complete extraction of the Y to the organic phase had occurred at all the investigated conditions. Similar to Tb, more than 90 % Eu extraction was found at pH 0.25 and O/A ratio of 1. The percentage extraction

increased with increasing O/A ratio and more than 99 % extraction was achieved at O/A ratio 2.5 and beyond. The extraction percentage was more than 99 % for all the other conditions. The similar extraction behavior of Eu and Tb is in agreement with the selectivity series, and can be explained at the hand of the close proximity of these elements in the lanthanide series.



(a) (b)

Fig. 1. Cerium percentage extraction at extractant concentrations of (a) 0.5 M and (b) 1 M.

The effect of pH and O/A ratio on the percentage extraction of impurities such as Ca and Al was also investigated. Figure 2 shows the extraction behavior of the main impurity (Ca) with respect to pH and O/A ratio at a fixed extractant concentration. An increase in aqueous phase pH resulted in an increase in Ca extraction to the organic phase. Percentage extraction was also found to increase with increase in O/A ratio. More than 99 % Ca extraction occurred at pH 1.5 and 2 when operating at an O/A ratio of 5. Similar results were observed for Al extraction.

Figure 3 specifically shows the effect of extractant concentration on the extraction of Ce and the main impurity Ca at pH 0.5. The graph shows a general increase in percentage extraction for Ce and Ca with increase in extractant concentration. More than 95 % Ce extraction could be achieved at an O/A ratio of 1 and 1 M extractant concentration against 76.4 % achieved at the same O/A ratio and 0.5 M extractant concentration. The results also show that there was no Ca extraction when operating at an extractant concentration of 0.5 M and O/A ratio of 1; Ca extraction only occurred when using 1 M extractant concentration, providing possible conditions for selective extraction / purification of REEs. The same extraction behavior was also observed for the other impurities and REEs except Y.

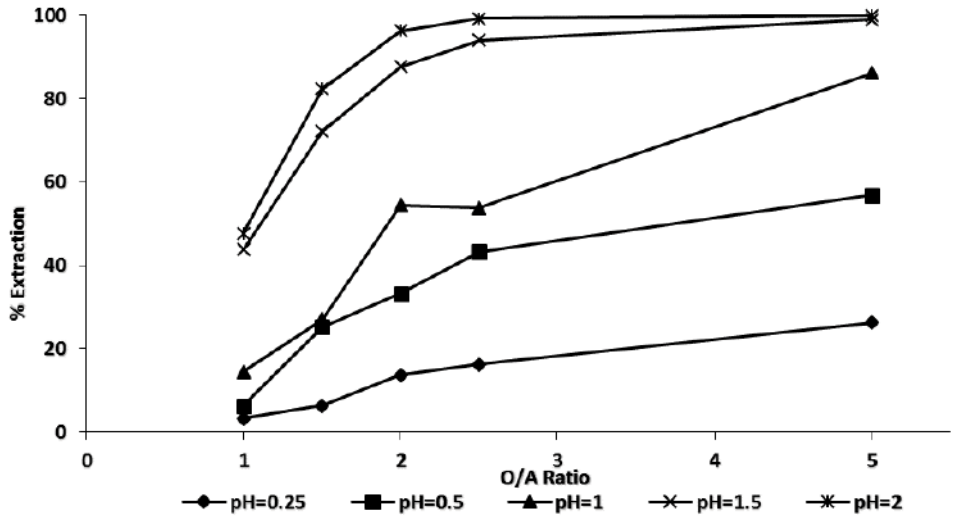


Fig. 2. Percentage extraction of Ca at an extraction concentration of 1 M.

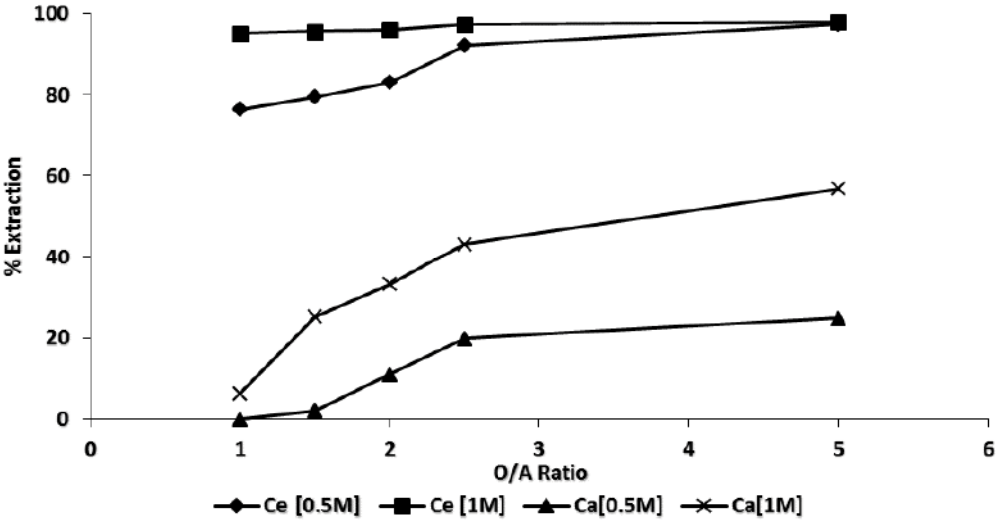


Fig. 3. Effect of extractant concentration on percentage Ce and Ca extraction at pH 0.5.

3.2. Separation efficiency

The separation factors of Tb and Ce relative to other elements in solution were determined using Equation 4. The separation factors obtained at an extractant concentration of 0.5 M are shown in Table 3. Separation factors that could not be determined due to complete extraction of one or both metals of interest into the organic phase are denoted by '-'. Separation factors for the two rare earth elements relative to Y could not be determined due to complete extraction of Y. Previous literature on rare earth recovery mostly focused on separation factors between adjacent rare earths (Michelsen and Smutz, 1971; Gschneidner Jr, 1980; Sato, 1989; Mishra *et al.*, 2000; Thakur, 2000; Abreu and Morais, 2014). There was no basis of comparison for separation factors of the REEs with impurities present.

Table 3.

Separation factors of Tb and Ce relative to other elements at an extractant concentration of 0.5 M.

pH	O/A	Tb/Ce	Tb/Al	Ce/Al	Tb/Ca	Ce/Ca	Tb/Y, Ce/Y	Tb/Eu	Ce/Eu
0.25	1	217.9	-	-	20489	94.0	-	12.2	0.06
	1.5	94.4	14493	153.5	6610	70.0	-	6.6	0.07
	2	88.2	38148	432.3	2535	28.7	-	4.1	0.05
	2.5	116.7	4128	35.4	3601	30.9	-	3.5	0.03
	5	101.4	6663	65.7	2374	23.4	-	2.3	0.02
0.5	1	181.8	-	-	-	-	-	-	-
	1.5	69.3	-	-	13217	190.6	-	-	-
	2	45.0	5355	119.0	1789	39.8	-	-	-
	2.5	9.4	1089	116.0	448.8	47.8	-	-	-
	5	3.0	2071	701.1	332.3	112.5	-	-	-
1	1	10.3	1138	110.5	3997	388.2	-	-	-
	1.5	10.8	749.7	69.6	481.0	44.7	-	-	-
	2	9.2	880.3	95.4	569.2	61.7	-	-	-
	2.5	9.2	320.9	35.0	373.5	40.8	-	-	-
	5	5.9	151.7	25.7	141.4	24.0	-	-	-
1.5	1	-	112.8	-	1279	-	-	3.3	-
	1.5	-	92.9	-	768.1	-	-	1.0	-
	2	-	54.5	-	131.0	-	-	0.2	-
	2.5	-	-	-	-	-	-	-	-
	5	-	-	-	-	-	-	-	-
2	1	-	-	-	-	-	-	-	-
	1.5	-	60.4	-	210.7	-	-	-	-
	2	-	7.9	-	113.4	-	-	-	-
	2.5	-	8.4	-	99.2	-	-	-	-
	5	-	0.3	-	2.1	-	-	-	-

Referring to Table 3, it is evident that the separation factors of Tb to Ce decrease with increase in pH and O/A ratio. The greatest separation was observed to occur at the lowest pH investigated where almost all the Tb (>99 %) was extracted and Ce extraction was relatively low. This behavior was expected since DEHPA has a higher affinity for heavier rare earths (Tb) compared to lighter ones (Ce). The separation factors at an operating pH of 1.5 and 2 could not be determined since both rare earth elements were below the detection limit of ICP-OES. It was therefore assumed that complete extraction had occurred for both rare earth elements and therefore no separation was achieved.

Although an increase in pH was observed to favor the extraction of lighter rare earths (Ce and Eu), impurities co-extraction also increased. This is in support of the fact that selective separation of metals decreases with increasing pH when using DEHPA as reported by Abreu and Morais (2014). The separation factors of Tb and Ce relative to Al and Ca were therefore found to decrease with increasing pH. The separation factors of Tb relative to Al and Ca were greatest (>2000) when operating at pH 0.25 meaning these impurities will not be problematic in achieving Tb of high purity at such conditions.

However, operating at higher pH (above pH 1.5) would result in co-extraction of the undesired impurities.

Separation of individual rare earth elements was found to be unfeasible at the investigated conditions since Y was completely extracted at all conditions. Separation factors of Tb relative to Eu were also low hence it was found that it is only possible to obtain a mixed product. When operating at a pH of 2, more than 99 % Y, Eu, Ce and Tb extraction was achieved. This is in agreement with what Rydberg (2004) reported, namely that all rare earths above Eu are extracted at pH 2. Separation factors were the lowest at this pH hence the mixed rare earth product obtained was highly contaminated with impurities. A large number of equilibrium stages would be required to obtain high purity rare earths.

The separation factors at an extractant concentration of 1 M were relatively lower than the separation factors obtained when operating at an extractant concentration of 0.5 M. However, despite the decrease in separation factors, the same extraction behavior as that found at extractant concentration of 0.5 M was observed.

3.3. Extraction isotherms

Extraction isotherms for Ce displayed in Figure 4 show a net positive increase in extraction to the organic phase with an increase in pH for both extractant concentrations; the complete extraction achieved in a single stage at pH values of 1.5 and 2 are also reflected by the extraction isotherms. From the isotherms it can be determined that a single extraction stage is adequate to recover more than 95 % Ce from solution at a pH of 0.5 and above. The extraction isotherms of Tb are omitted because more than 99 % extraction was achieved at all pH levels, indicated that only one equilibrium stage is required to extract more than 99 % Tb at the investigated pH levels.

The solvent extraction results show that it is only possible to obtain a mixed rare earth product at the investigated pH levels. Even at pH 0.25, Ce recovery was in excess of 64 % at the lowest O/A ratio. The other rare earths that were present in the initial aqueous phase were Y and Eu. Y was extracted to completion before Tb. From the results, it is clear that operating at a low pH and low extractant concentration suppresses the extraction of the impurities Al and Ca. It is therefore suggested to perform the solvent extraction at a pH of 0.5 and extractant concentration of 1 M where more than 95 % Ce and more than 99 % Tb were extracted to produce a mixed REE product. Complete Y and Eu extraction was also achieved at these conditions, while Ca and Al extraction was below 7 %. A better quality / more pure mixed REE product can be produced by operating at lower pH and extractant concentration conditions, but this would require a significantly larger number of extraction stages.

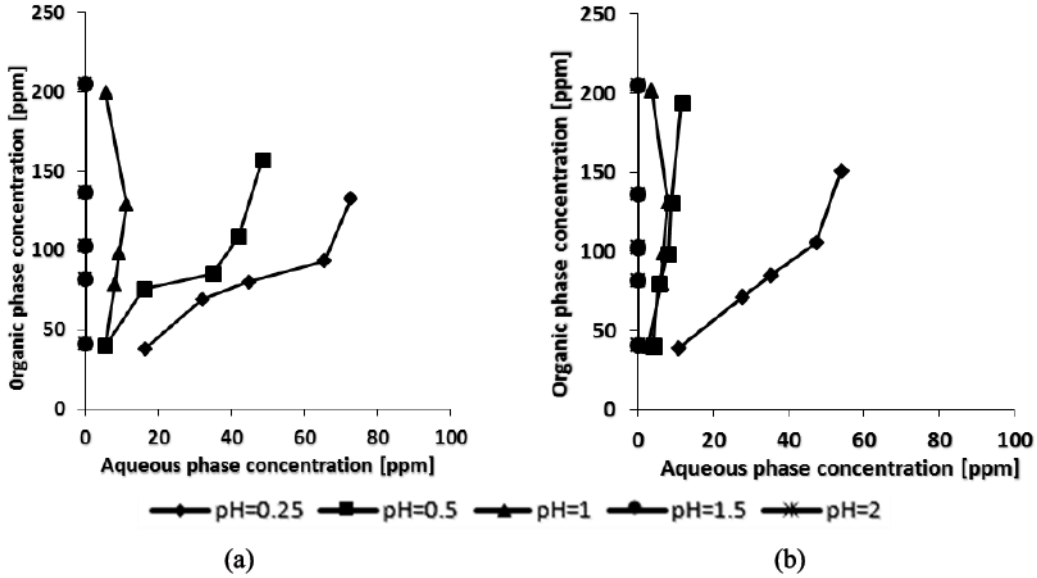


Fig. 4. Ce extraction isotherms at extractant concentration of (a) 0.5 M and (b) 1 M.

4. Conclusions

Solvent extraction tests showed that DEHPA could be used as extractant to recover rare earth elements from hydrochloric acid solutions obtained after the second stage leaching of fluorescent lamp phosphors. Ce and Tb solvent extraction results showed that all the targeted rare earths could only be recovered as a mixed product at this stage. A mixed rare earth product was produced using 1 M DEHPA, a pH of 0.5, O/A ratio of 1 and a temperature of 25°C. Complete extraction of Y and Eu was assumed at these conditions since both rare earths could not be detected in the remaining aqueous solution. More than 95 % Ce and 98 % Tb were extracted in a single stage solvent extraction process. The rare earths can undergo stripping using 5 M sulfuric acid prior to precipitation and calcination to recover the metals as rare earth oxides.

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