Separation of Ce, La and Nd in rare earth hydroxide (REOH) by oxidation with potassium permanganate and precipitation

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Abstract. The present work describes the development of an efficient and relatively simple process to obtain high grade Ce(OH)₄ from REOH (Rare earth hydroxide). The Rare earth hydroxide was obtained through base digestion of monazite. The steps investigated in the process for obtaining Ce(OH)₄ were: (i) dissolution RE hydroxide (REOH) with HNO₃ and oxidation of Ce⁴⁺ to Ce⁵⁺, (ii) selective precipitation of Ce(OH)₄ with Na₂CO₃, (iii) selective precipitation of Nd(OH)₃ with ammonium hydroxide (iv) precipitation of La with oxalic acid. The main variables affecting the cerium oxidation were: the ratio of the KMnO₄/REOH, temperature and oxidation time. A ratio of 1.25/10 of KMnO₄ / REOH was necessary for full cerium recovery. The recovery of cerium increases as temperature and oxidation time rises, the purity of the product Ce(OH)₄ at the pH above 4. The process conditions were achieved in the use of 1.25/10, KMnO₄/REOH ratio, at the 120 °C and the oxidation time of 75 minutes. The composition of the final product Ce(OH)₄ was 97.98 wt.% Ce(OH)₄, in a process yielding a recovery of Ce greater than 93%, were obtained. The composition of the final product Nd(OH)₃ was 37 wt.% Nd(OH)₃, in a process yielding a recovery of Nd greater than 98%, were obtained. The composition of the final product La₂(C₂O₄)₃ was 90 wt.% La₂(C₂O₄)₃, in a process yielding a recovery of La greater than 93%, were obtained. The oxidation of Ce³⁺ to Ce⁴⁺ using KMnO₄ follows first order reaction. The value of reaction rate constant of Ce was 0.0291 minutes⁻¹.

Keywords: REOH, oxidation, KMnO₄, precipitation

1. Introduction

The rare earth elements (REE) find application in many fields associated with modernity such as green energy, high performance magnets, lighting and consumer electronics, medical equipment as well as in more traditional industries including glass, ceramics and catalysis [1]. The supply of REE to the world market is predominantly from China, resulting from the processing of ionic clays and high grade mineral concentrates such as bastnasite, monazite and xenotime [2][3]. In recent years, a relatively high supply risk index has been assigned to the REE by a number of countries [4]. This has spurned interest in the production of REE from mineral concentrates of lower grade and varying sources. To satisfy the demands of these alternative resources the application of new separation methodologies is of interest.
The monazite ores are known to contain significant quantities of REEs and therefore processing of monazite ores for REEs has become more prominent recently [5]. Rare earths hydroxide (REOH) was a monazite process products containing REE elements namely Ce, La, Nd, Pr, Y, Sm and Gd [6]. Youcai et.al, 2017, studied extraction and recovery of cerium(IV) and thorium(IV) from sulphate medium by an α-aminophosphonate extractant to extract cerium(IV) and thorium(IV) from sulphate medium by an α-aminophosphonate extractant. A solvent extraction process to extract and recover cerium and thorium from bastnasite leaching was proposed, in which the purities of cerium and thorium products reached 99.9% and 99% with yield of 92% and 98%, respectively. Aminophosphonate extractant was very expensive, while the chemicals used in precipitation or in this process were very cheap [7].

In alkaline solutions, the trivalent cerium is readily oxidized to the tetravalent ceric ion either by bubbling oxygen during the RE-hydroxide precipitation or afterwards by drying the RE-hydroxide in the presence of air [8]. In acid solutions, the oxidation of Ce$^{3+}$ to Ce$^{4+}$ may occur by chemical oxidation with strong oxidants such as persulphate, permanganate, bismuth, lead dioxide or silver oxide are used; by electrochemical oxidation or by photochemical oxidation [9].

This study proposes a methodology which consists of: (i) dissolution RE hydroxide (REOH) with HNO$_3$ and oxidation of Ce$^{3+}$ to Ce$^{4+}$, (ii) selective precipitation of Ce(OH)$_4$ with Na$_2$CO$_3$, (iii) selective precipitation of Nd(OH)$_3$ with ammonium hydroxide at pH 8.5. (iv) precipitation of La with oxalic acid to La oxalate. The effects of the main variables involved in the precipitation and purification of cerium, the process variables assessed were: molar of KMnO$_4$, time and temperature of oxidation reaction were investigated.

1.1. Theory

The separation of cerium from the RE elements can be carried out by selective dissolution of the trivalent RE-hydroxides, by keeping the cerium (IV) hydroxide in its insoluble form or through its selective precipitation from the acid solution. In either case, the cerium separation occur given the solubility difference between the Ce(IV)-hydroxide ($K_{sp} \sim 10^{-54}$) and the RE(III)-hydroxide ($K_{sp} \sim 10^{-22}$). Oxidation through permanganate solution leads to simultaneous precipitation of Ce(OH)$_4$ and MnO$_2$, as we see in equations (1) (2) and (3).

\[
RE(OH)_3 + 3 HNO_3 \rightarrow RE(NO_3)_3 + 3 H_2O
\]

\[
Ce(OH)_3 + 3 HNO_3 \rightarrow Ce(NO_3)_3 + 3 H_2O
\]

\[
2 KMnO_4 + 2 Ce(NO_3)_3 + 2 HNO_3 \rightarrow K_2O + 2 MnO_2 + 2 Ce(NO_3)_4 + H_2O
\]

Mixing of KMnO$_4$ and Na$_2$CO$_3$ at the oxidation process has been done by Renata, et al. (2010). In this work, Na$_2$CO$_3$ was used as a precipitating agent after oxidation [10]. The reaction of Na$_2$CO$_3$ with Ce(NO$_3$)$_3$ was following Equation (4) and Equation (5).

\[
Na_2CO_3 + 2H_2O \rightarrow 2NaOH + CO_2 \uparrow + H_2O
\]

\[
Ce(NO_3)_4 + 4NaOH \rightarrow Ce(OH)_4 \downarrow + 4NaNO_3
\]

Separation of La and Nd by precipitation with NH$_4$OH at pH 8.5. In the hydroxide form the value of $pK_{sp}$ of La(OH)$_3$ ~ 22.3, the $pK_{sp}$ of Ce(OH)$_3$ ~ 19.82 and $pK_{sp}$ of Nd(OH)$_3$ ~ 23.3.

\[
(Nd. La) (NO_3)_3 + NH_4OH \rightarrow Nd(OH)_3 (s) + NH_4NO_3 + La(NO_3)_3 (liquid)
\]

The last filtrate was La Nitrate, when oxalic acid was added, La oxalate (La$_2$(C$_2$O$_4$)$_3$) was precipitated. Reaction of La Nitrate with oxalic acid solution according to Equation (7).

\[
2 La(NO_3)_3 + 3 H_2C_2O_4 \rightarrow La_2(C_2O_4)_3 (s) + 3HNO_3 (liquid)
\]
1.2. Kinetics of oxidation reaction
As shown by the stoichiometric reaction, full oxidation of one mole of a target compound requires N moles of potassium permanganate. Typically, second-order reaction rate constants for the oxidation of VOC compounds by permanganate have been obtained using a pseudo-first-order approach by assuming that either the contaminant or permanganate concentration is constant.

2. Methodology
2.1. Materials & Equipment
The materials used were rare hydroxide (REOH) product from PTBGN, technical HNO$_3$, water, filter paper, KMnO$_4$, oxalic acid and ammonium hydroxide. All reagents used in this work were of technical grade and their solutions were prepared with distilled water.

Glass equipment, analytic scales, Ikamag heater stirrers, thermometers, ovens, and x-ray spectrometers (XRF) are used in this study.

2.2. Cerium Recovery
In the cerium recovery step, the RE nitrate solution was prepared by dissolving the RE-hydroxide in a nitric acid solution (14 mol L$^{-1}$). Solution sodium carbonate was prepared by dissolving the two salts in distilled water.

The experiments were carried out in beakers, under magnetic agitation, at 25 ± 1 °C temperature. A volume of 100 mL of a rare earth nitrate solution was used (10 grams of RE hydroxide in 25 mL HNO$_3$). The oxidation of Ce(III) to Ce(IV) through the addition of KMnO$_4$ (0.25 – 1.25 grams). The time of reaction was 15 – 75 minutes and temperature of reaction was 90 – 120 °C.

The precipitation of Ce(IV) was accomplished with Na$_2$CO$_3$ solution (15 wt.%). The pH control (pH = 4) throughout the experiment was carried out through manual addition of a Na$_2$CO$_3$ solution (15 grams /100 L). After precipitation, the solid was filtered and was washed with distilled water and then dried at 105 °C.

2.3. Separation of Nd and La
The neodymium was selectively precipitated from the filtrate as neodymium hydroxide with the addition of an ammonium hydroxide solution (15 wt.%) at a controlled pH 8,5. After precipitation, the solid was filtered and the filtrate was precipitated as lanthanum oxalate through the addition of an oxalic acid solution (15 wt.%). The neodymium hydroxide and lanthanum oxalate then dried at 105 °C. In all the stages of the experiment, the concentration of the rare earth elements was determined by X-ray spectrometer. In all the stages of the experiment, the concentration of the rare earth elements was determined by X-ray spectrometer.

3. Results and Discussion
The results of the composition of REOH (Feed) using XRF were presented in Table 1. In general the largest element content in REOH was Ce, followed by La and Nd.

| Component | Y$^{3+}$ | La$^{3+}$ | Ce$^{3+}$ | Pr$^{3+}$ | Nd$^{3+}$ | Sm$^{3+}$ | Gd$^{3+}$ | Dy$^{3+}$ |
|-----------|---------|---------|---------|---------|---------|---------|---------|---------|
| wt. %     | 2.14    | 17.12   | 31.15   | 0.36    | 11.38   | 6.72    | 1.01    | 0.47    |

3.1. Effect of KMnO$_4$/REOH ratio
3.1.1. Recovery of cerium hydroxide. The recovery of cerium through the investigated technique comprises two phenomena, namely, the oxidation of Ce(III) to Ce(IV) by MnO$_4^-$ (Eq. (3)), and the precipitation of Ce(IV) as hydroxide. As a strong oxidant agent, in nitrate medium, MnO$_4^-$ is capable of oxidizing the nitric ion to NO$_2$ according to Equation (8):

$$2\text{KMnO}_4 + 2\text{HNO}_3 \Leftrightarrow K_2\text{O} + 2\text{NO}_2 + 2\text{MnO}_2 + \text{H}_2\text{O} + 4\text{On} \hspace{1cm} (8)$$
To avoid competition between this reaction and the cerium oxidation reaction represented by Equation (5), the pH and the NO$_3^-$ concentration in the RE Nitrate solution must be controlled. At this point of the study, the influence of the weight of KMnO$_4$ or the KMnO$_4$/REOH ratio and the reaction time and temperature of the cerium oxidation were investigated.

Recovery of element (\%) = \frac{\text{weight of element in the product}}{\text{weight of element in the feed}} \times 100\% \hspace{1cm} (9)

Element : Ce, La and Nd
Product : Ce(NO$_3$)$_4$, Nd(OH)$_3$ concentrate and La$_2$(C$_2$O$_4$)$_3$

Weight of element in the feed = wt,\% \times \text{weight of REOH} \hspace{1cm} (10)
Weight of element in the product = wt,\% \times \text{weight of product} \hspace{1cm} (11)

The effect of the KMnO$_4$/REOH ratio was investigated in the range between 0.25/10 and 1.25/10. In this range, the weight ratio of KMnO$_4$ in the oxidant solution is affect the cerium recovery or purity. The use of Na$_2$CO$_3$ in the precipitant solution enhances the stability of the permanganate solution, which is more stable in basic medium, when compared with its stability in acid or neutral medium. The composition (% weight) of cerium hydroxide (Ce(OH)$_4$) ranged from 70% to 94% when the KMnO$_4$/REOH ratio increased at the interval considered. The impurities in Ce(OH)$_4$ are La(OH)$_3$, Nd(OH)$_3$, water etc (Y, Dy, Gd, Mn). Thus, after an KMnO$_4$/REOH ratio 1.25/10, only a marginal rise was observed in the cerium recovery. However, the ratio of KMnO$_4$/REOH will not affect the purity of the cerium (Figure 1). The amount of KMnO$_4$ not too much because the formed MnO$_2$ will contaminate Ce(OH)$_4$.

![Figure 1](image_url). Influence of the KMnO$_4$/REOH ratio on the purity of the Ce(OH)$_4$

The recovery of cerium ranged from 47% to 89.0% when the KMnO$_4$/REOH ratio increased at the interval considered (Figure 2). The stoichiometric amount of KMnO$_4$ was 1.17 grams for 10 grams REOH or KMnO$_4$/REOH ratio was 1.17/10.
Renata, et al. (2010), the recovery of cerium ranged from 40% to 99.9% when the excess of permanganate increased at the interval considered. Thus, after an excess of 30%, only a marginal rise was observed in the cerium recovery [10]. However, the excess of permanganate did not affect the purity of the cerium.

3.1.2. Recovery of neodymium hydroxide concentrate. The neodymium was selectively precipitated from the filtrate as neodymium hydroxide with the addition of an ammonium hydroxide solution (15 wt.%) at a controlled pH 8.5. The filtrate was RE (La, Nd) Nitrate. Reaction of RE (La, Nd) with ammonium hydroxide solution at pH 8.5 according to Equation (9).

The lanthanum was still in the filtrate. Figure 3 shows the composition (% weight) of neodymium hydroxide (Nd(OH)₃) concentrate ranged from 20% to 25% when the KMnO₄/REOH ratio increased at the interval considered. The impurities in Nd(OH)₃ concentrate are La(OH)₃, Ce(OH)₃, water etc. (Y, Ce, La, Dy, Gd, Mn). Thus, KMnO₄/REOH ratio, only a marginal rise was observed in the cerium recovery. However, the ratio of KMnO₄/REOH will did not affect the purity of the neodymium (Figure 3). The cerium recovery in Ce(OH)₄ was not perfect so it precipitated in Nd(OH)₃. The % weight of cerium in Nd(OH)₃ concentrate was decrease with increase of KMnO₄/REOH ratio.

The recovery of neodymium ranged from 85% to 93% when the KMnO₄/REOH ratio increased at the interval considered (Figure 4).
3.1.3. Recovery of lanthanum oxalate. The composition (% weight) of lanthanum oxalate (La₂(C₂O₄)₃) ranged from 60% to 90% when the KMnO₄/REOH ratio increased at the interval considered. The impurities in La₂(C₂O₄)₃ are Ce₂(C₂O₄)₃, Nd₂(C₂O₄)₃, water etc. (Y, Dy, Gd, Mn). Thus, KMnO₄/REOH ratio, only a marginal rise was observed in the cerium recovery. However, the ratio of KMnO₄/REOH will did not affect the purity of the neodymium (Figure 5).

The recovery of lanthanum ranged from 53% to 70% when the KMnO₄/REOH ratio increased at the interval considered. The purity of lanthanum oxalate decreased with an increase in KMnO₄/REOH ratio, but the recovery increased with an increase in KMnO₄/REOH ratio (Figure 6).

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Figure 4. Influence of the KMnO₄/REOH ratio on the recovery of Nd(OH)₃

Figure 5. Influence of the KMnO₄/REOH ratio on the purity of the lanthanum oxalate

Figure 6. Influence of the KMnO₄/REOH ratio on the recovery of the lanthanum oxalate
3.2. Effect of the oxidation reaction temperature

3.2.1. Recovery of cerium hydroxide. The effect of the temperature was investigated at temperature variations from 90°C to 120°C through the addition of KMnO$_4/REOH$ ratio at 1/10. The highest temperature reached at the boiling point of 120°C. The composition (% weight) of cerium hydroxide (Ce(OH)$_4$) ranged from 70% to 90% when the temperature increased at the interval considered. The impurities in Ce(OH)$_4$ are La(OH)$_3$, Nd(OH)$_3$, water etc (Y, Dy, Gd, Mn). The oxidation reaction was complete when the temperature increased. The effect of temperature increased to the composition (% weight) of cerium hydroxide (Ce(OH)$_4$) was presented in (Figure 7).

![Figure 7](image1.png)

**Figure 7.** Influence of the temperature on the purity of the cerium hydroxide

The recovery of cerium ranged from 47% to 80.0% when the temperature increased at the interval considered. (Figure 8).

![Figure 8](image2.png)

**Figure 8.** Influence of the temperature on the recovery of the cerium hydroxide

3.2.2. Recovery of neodymium hydroxide. The composition (% weight) of neodymium hydroxide (Nd(OH)$_3$) concentrate ranged from 20% to 25% when the temperature increased at the interval considered. The impurities in Nd(OH)$_3$ concentrate are La(OH)$_3$, Ce(OH)$_3$, water etc (Y, Ce, La, Dy, Gd, Mn). Thus, the temperature, only a marginal rise was observed in the cerium recovery. However, the temperature will did not affect the purity of the neodymium (Figure 9). The cerium recovery in Ce(OH)$_4$ was not perfect so it precipitated in Nd(OH)$_3$. The % weight of cerium in Nd(OH)$_3$ concentrate was decrease with increase of temperature.

![Figure 9](image3.png)

**Figure 9.** Influence of the temperature on the purity of the Nd(OH)$_3$ concentrate

The recovery of neodymium is ranged from 95% to 90% when the temperature increased at the interval considered. (Figure 10).

![Figure 10](image4.png)

**Figure 10.** Influence of the temperature on the recovery of Nd(OH)$_3$ concentrate
3.2.3. Recovery of lanthanum oxalate. The composition (% weight) of lanthanum oxalate \((\text{La}_2\text{(C}_2\text{O}_4)_3)\) ranged from 60% to 95% when the temperature increased at the interval considered. The impurities in \(\text{La}_2\text{(C}_2\text{O}_4)_3\) are \(\text{Ce}_2\text{(C}_2\text{O}_4)_3\), \(\text{Nd}_2\text{(C}_2\text{O}_4)_3\), water etc (Y, Dy, Gd, Mn). Thus, temperature only a marginal rise was observed in the cerium recovery. However, the ratio of \(\text{KMnO}_4/\text{REOH}\) did not affect the purity of the lanthanum (Figure 11).

![Figure 11. Influence of the temperature on the purity of the \(\text{La}_2\text{(C}_2\text{O}_4)_3\)](image)

The recovery of lanthanum ranged from 51% to 65% when the temperature increased at the interval considered. (Figure 12).

![Figure 12. Influence of the temperature on the purity of the \(\text{La}_2\text{(C}_2\text{O}_4)_3\)](image)

3.3. Effect of the oxidation time

3.3.1. Recovery of cerium hydroxide. The effect of oxidation time was investigated at the interval between 15 and 75 minute, at 120 °C at amount of \(\text{KMnO}_4/\text{REOH}\) ratio 1/10. The composition (% weight) of cerium hydroxide \((\text{Ce(OH)}_4)\) ranged from 60% to 99% when the oxidation time increased at the interval considered. The impurities in \(\text{Ce(OH)}_4\) are \(\text{La(OH)}_3\), \(\text{Nd(OH)}_3\), water etc (Y, Dy, Gd, Mn). The oxidation reaction was complete when the oxidation time increased. The effect of oxidation time increased to the composition (% weight) of cerium hydroxide \((\text{Ce(OH)}_4)\) was presented (Figure 13).
The recovery of cerium ranged from 47% to 93% when oxidation time increased at the interval considered. (Figure 14). A cerium precipitation yield higher than 99% takes the oxidation time need 150 minutes [10]. After drying the precipitate at 110°C, the chemical composition was determined as: 69.2% CeO$_2$, 14.5% MnO$_2$, 0.05% Pr$_6$O$_{11}$, 0.06% Nd$_2$O$_3$ and 16.0% H$_2$O. The content of cerium in the solution was 0.008 g L$^{-1}$, indicating a cerium precipitation yield higher than 99%. In this the chemical composition was determined 65.95% Ce element or 97.98% Ce(OH)$_4$, 0.04% Nd element or 0.05% Nd(OH)$_3$ and 1.97% H$_2$O etc.

3.3.2. Recovery of neodymium hydroxide. The composition (% weight) of neodymium hydroxide (Nd(OH)$_3$) concentrate ranged from 30% to 35% when the oxidation time increased at the interval considered. The impurities in Nd(OH)$_3$ concentrate are La(OH)$_3$, Ce(OH)$_3$, water etc (Y, Ce, La, Dy, Gd, Mn). Thus, the oxidation time, only a marginal rise was observed in the cerium recovery. However, the oxidation time will affect the purity of the neodymium (Figure 15). The cerium recovery in Ce(OH)$_4$ was not perfect so it precipitated in Nd(OH)$_3$. The % weight of cerium in Nd(OH)$_3$ concentrate was decrease with increase of temperature.
3.3.3. Recovery of lanthanum oxalate. The composition (% weight) of lanthanum oxalate (La$_2$(C$_2$O$_4$)$_3$) ranged from 63% to 97% when the oxidation time increased at the interval considered. The impurities in La$_2$(C$_2$O$_4$)$_3$ are Ce$_2$(C$_2$O$_4$)$_3$, Nd$_2$(C$_2$O$_4$)$_3$, water etc (Y, Dy, Gd, Mn). (Figure 17).

The recovery of lanthanum ranged from 70% to 90% when the oxidation time increased at the interval considered. (Fig. 18).

3.4. Reaction order and rate reaction constant determination

The general form of a first and second-order reaction rate equation, as a function of the target compound and potassium permanganate concentrations in the aqueous phase, can be written as follows [11].

$$\frac{dC_A}{dt} = -kC_AC_B$$

We now reformulate Equation (12) in terms of consumed fraction of reactants, $X_A = (C_{A0} - C_A) / C_{A0}$ and $X_B = (C_{B0} - C_B) / C_{B0}$. Here, $C_{A0}$ is the initial concentration of target compound (M). The definition of $P = C_{B0} / C_{A0}$, we have: $X_B = N X_A / P$. Substitution of these definitions into:

$$\frac{dX_A}{dt} = kC_{A0}(1 - X_A)(P - N X_A)$$

Integration of Equation (13) gives the following general formula for the variation of $X_A$ with time:

$$\frac{1}{C_{A0}(P - N)} \ln \left[ \frac{P - N X_A}{P(1 - X_A)} \right] = kt \quad \text{where} \quad P \geq N$$

According to Equation (14), a plot of $1/C_{A0}(P - N)\ln[(P - NX_A) / P(1 - X_A)]$ vs. time should yield a straight line, with its slope being the second-order reaction rate constant k. The solution for $X_B$ follows from Eq. (15) by substituting $X_A = PX_B / N$ to obtain:
\[
\frac{P}{C_{B0}(P - N)} \ln \left[ \frac{N(1 - X_B)}{(N - PX_B)} \right] = kt \quad \text{where} \quad N \geq PX_B \quad (15)
\]

The assumption for the commonly used pseudo-first-order approach of constant concentration of one of the reactants is only valid if the amount of the target compound or permanganate is sufficiently high to neglect any change in the concentration during the course of an experiment. If permanganate is in excess, this means that P/N is much larger than unity. Therefore, Equation (16) for such conditions may be simplified to yield:

\[
\frac{1}{C_{B0}} \ln \left[ \frac{C_A}{C_{O}} \right] = -kt \quad \text{where} \quad P \geq N \quad (16)
\]

To estimate k using the pseudo-first-order approach, Eq. (16) can be used with a constant concentration of permanganate, equal to its initial value.

In the calculation of reaction rate constant with first order reaction, it was needed the graph of time correlation with \(-\ln (1-X)\) where X was conversion (mole) or recovery. Based on the equation (13), first order reaction was experimented for finding the reaction constants. The reaction rate was the overall reaction rate constant with the assumption that the concentration of HNO\(_3\) was constant because its amount tends to approach 1, therefore it could be mentioned that the occurring reaction was first order. The calculation results could be seen in Figure 19. Calculation of the second order reaction rate constant required the time versus \([1/C_{A0}(P - N)] \ln[(P - NX_A) / P(1 - X_A)]\) correlation graph in Figure 20.

**Figure 19.** Correlation between time and \(-\ln(1-X)\) for determining k value and linearity of first order reaction

**Figure 20.** Correlation between time and \([1/C_{A0}(P - N)] \ln[(P - NX_A) / P(1 - X_A)]\) for determining k value linearity of second order

Linear regression values were obtained from square root of R\(^2\) as shown in Table 2.

|          | First order reaction | Second order reaction |
|----------|----------------------|-----------------------|
| La       | y = 0                | y = 0                 |
|          | R\(^2\) = #N/A       | R\(^2\) = #N/A        |
| Ce       | y = 0.0291x + 0.0288 | y = 0.0879x + 0.0237  |
|          | R\(^2\) = 0.9697     | R\(^2\) = 0.9674      |
| Nd       | y = 0                | y = 0                 |
|          | R\(^2\) = #N/A       | R\(^2\) = #N/A        |
Linearity values ($R^2$) of first order reaction (Table 2) were greater when compared to the linearity values ($R^2$) of second order reaction (Table 3), so it could be stated that the reaction was first order. The value of reaction rate constant of Ce was 0.0291 minutes$^{-1}$, the value of reaction rate constant of La and Nd were not applicable. The results showed that the oxidation rate of ethanol and toluene by permanganate, rather than employing the common pseudo-first-order kinetic analysis, we used a more realistic and accurate second-order formulation for the oxidation of target.

Ferdowsi et al. 2017, did and optimizing and kinetics of leaching process of cerium, lanthanum and neodymium elements of apatite using nitric acid. The maximum leaching efficiency of which were 66.1%, 56.8% and 51.7% respectively for Ce, La and Nd, achieved under the optimum leaching conditions with nitric acid concentration of 18%. 0.06 ratio of solid to liquid and leaching time of 38 minutes, the activation energy of Ce of 6.54 kJ/mole [12].

4. Conclusion
The potassium permanganate as strong oxidator could be used to oxidize Ce$^{3+}$ to Ce$^{4+}$. The main variables affecting the cerium oxidation were: the ratio of the KMnO$_4$/REOH, temperature and oxidation time. A ratio of 1.25/10 of KMnO$_4$/REOH was necessary for full cerium recovery. The recovery of cerium increases as temperature and oxidation time rises, the purity of the product Ce(OH)$_4$ at the pH above 4. The process conditions were achieved in the use of 1.25 / 10 KMnO$_4$/REOH ratio, at the 120°C and the oxidation time of 75 minutes. The composition of the final product Ce(OH)$_4$ was 97.98 wt.% Ce(OH)$_4$, in a process yielding a recovery of Ce greater than 93%, were obtained. The composition of the final product Nd(OH)$_3$ concentrate was 37 wt.% Nd(OH)$_3$, in a process yielding a recovery of Nd greater than 98%, were obtained. The composition of the final product La$_2$(C$_2$O$_4$)$_3$ was 90 wt.% La$_2$(C$_2$O$_4$)$_3$, in a process yielding a recovery of La greater than 93%, were obtained. The oxidation of Ce$^{3+}$ to Ce$^{4+}$ using KMnO$_4$ follows first order reaction. The value of reaction rate constant of Ce was 0.0291 minutes$^{-1}$.

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