Extraction of neodymium(III) from aqueous solutions by solvent extraction with Cyanex® 572

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Abstract: The present research aims at studying the extractability of Nd(III) by Cyanex® 572 as a new extractant form from nitrate solutions. The effects of contact time, the concentration of nitrate ion, hydrogen ion, and extractant, and type of diluent were discussed, suggesting that the extraction of neodymium with Cyanex 572 was found to be a cation-exchange mechanism releasing three H⁺ ion during the extraction. Cation-exchange mechanism of Nd(III) with Cyanex 572 was studied using slope analysis. Hydrogen ion concentration strongly influences the extraction behavior of Nd(III) in the solvent extraction. Results showed that three moles of Cyanex 572 are incorporated in the extraction process of one-mole neodymium(III) from the aqueous solutions. The concentration of nitrate ion in the aqueous solution has positive effect on the extraction efficiency of neodymium due to the salting out effect. The type of diluent influences the extraction efficiency of Nd(III). Results indicated that non-polar diluents were suitable solvents for the extraction of neodymium(III).

Keywords: liquid-liquid extraction, neodymium(III), cyanex 572, diluents

1. Introduction

Rare earth metals (REMs) have wide uses in different industries such as catalysts, alloys, used in magnets, lasers, phosphors, and solar panels (Allahkarami & Rezai, 2021). Neodymium(III) and its compounds have widely used in laser crystals, colorant for glass, and permanent magnets (Zepf, 2013). The most important application of Nd(III) is magnet generating 37% of the total value of the REEs market. These magnets are neodymium-iron-boron (NdFeB) with 25-30% neodymium, 3-4% dysprosium, 60-70% iron, 1% iron, and 1-4% of other REEs (Tunsu et al., 2015). Given its physicochemical properties, neodymium(III) has attracted a large number of researchers to use different techniques for the neodymium(III) extraction from aqueous solutions. There are different techniques for the extraction of neodymium(III) from aqueous solutions, including adsorption (Kanani-Jazi et al., 2020; Park and Tavlarides, 2010), ion exchange (Spedding et al., 1947), pyrometallurgy (Sepahvand et al., 2020; Yoon et al., 2014), and solvent extraction (Kao et al., 2006). The advantages and disadvantages of these method were explained in the literature (Allahkarami and Rezai, 2019). To extract neodymium(III) from different resources, different acids such as HCl, HNO₃, and H₂SO₄ are used. After leaching, the anion part of acid can form a complex with neodymium(III). These complexes have different constant stability resulting in different extraction behavior in solvent extraction. Furthermore, the use of these acids for changing anion concentration can be led to variation of H⁺ ion concentration which can affect the extraction behaviour of metal (Rice and Smith, 1975). The concentrated acid can damage to process equipment. The use of dilute acids can prevent from damaging to process equipment. Different extraction systems have been applied for the recovery of neodymium(III), such as organophosphorus acids (Banda et al., 2012; Bina Gupta et al., 2003; Kumari et al., 2019; Riaño et al., 2020), organophosphorus esters (Kao et al., 2006; Zhang et al., 2015), and high molecular weight amines.
The combination of Cyanex 272 with different amine extractants was investigated by Liu et al. (Liu et al., 2014) for the extraction of praseodymium(III) and neodymium(III) from aqueous solution. Among them, the best synergistic enhancement factors for Pr(III) and Nd(III) were obtained 14.2 and 12.2, respectively when a mixture of Cyanex 272 and Alamine 336 was used during the extraction. Rho et al. (Rho, Sun, & Cho, 2020) applied trioctylphosphate oxide (TOPO) as an extractant for the extraction of praseodymium(III) and neodymium(III) from nitrate-based leachate of permanent magnet. Their results indicated that these metals were selectively stripped with HCl solution. Organophosphorus solvents have been commercially used for liquid-liquid extraction of rare earth elements (El-Hefny and Daoud, 2004; B. Gupta et al., 2002; Saji and Reddy, 2003; Sun et al., 2005). The advantages of organophosphorus extractants in liquid-liquid extraction (LLE) processing are including their chemical stability, good extraction kinetics, good loading and stripping characteristics.

In recent years, the potential applications of phosphinic and phosphonic acids in the recovery of REEs from different aqueous solutions have received considerable attention. The new product of Cytec Industries named Cyanex 572 includes equal amounts of phosphinic and phosphonic acids (Industries, 2015). The results of Wang et al. (2015) indicated that Cyanex 572 has higher stripping efficiency and lower acid requirement compared to PC88A solvent, and it also can be effectively used for separating heavy REs. The advantage of Cyanex 572 is that it reduces the acid consumption in the stripping process, but it requires bigger process equipment (Quinn et al., 2015). Pavon et al. (2018) evaluated the extractability of Cyanex 572 and Cyanex 272 for the separation of neodymium(III) from a mixture containing Nd(III), Tb(III), and Dy(III) elements by pertraction. They found that hydrochloric acid concentration of 1.2 M with pH 2 and pH 1.5 were optimum conditions for the extraction of neodymium(III) by Cyanex 272 and Cyanex 572, respectively. Their experimental results showed that Cyanex 572 was more suitable that Cyanex 272 for transferring three mentioned metals through membrane.

In the state of our knowledge, there is not any systematic study about neodymium(III) extraction by Cyanex 572. This research examines the influence of time, the concentration of nitrate ion, solution pH, extractant concentration, and the type of diluents on neodymium(III) extraction. Also, the values of thermodynamic parameters for this mixture were calculated. Finally, the extraction reaction of neodymium with Cyanex 572 was identified using slope analysis.

2. Materials and methods

A stock solution of Nd(NO$_3$)$_3$ was prepared by dissolving the desired quantity of Nd(NO$_3$)$_3$$\cdot$6H$_2$O (99.99%, Sigma Aldrich) in double-distilled water to prepare the synthetic solution. The extractant Cyanex 572 (Content: 100%) was kindly supplied by Cytec and it was used as received. The extractant was dissolved in kerosene to the desired concentration. The kerosene solvent, from Fluka, was mainly used in the experiments as a diluent. All the other chemical reagents were of analytical reagent grade. Equal volumes (5.0 mL each) of aqueous and organic solutions were mixed in a glass beaker and shaken at ambient temperature using a mechanical shaker. Dilute ammonium hydroxide (NH$_4$OH) and nitric acid (HNO$_3$) solutions were used to adjust the solution acidity to the desired value. After equilibration, the mixture of organic and aqueous solutions was transferred to a separatory funnel which the phases were allowed to separate. The determination of neodymium(III) ion concentration in the aqueous phases was carried out by ICP-AES analysis (Agilent Company’s (Australia) LIBERTY-RL model).

Distribution ratio (D), Percentage extraction (E%), and stripping percentage (S%) are obtained as follows:

\[
D = \frac{[\text{Nd(III)}]_{\text{aq, eq}} - [\text{Nd(III)}]_{\text{aq, init}}}{[\text{Nd(III)}]_{\text{aq, eq}}} 
\]

\[
E(\%) = \frac{D}{D + \frac{v_{\text{aq}}}{v_{\text{org}}}} \times 100
\]

\[
S(\%) = \frac{[\text{Nd(III)}]_{\text{org}}}{[\text{Nd(III)}]_{\text{aq, eq}}} \times 100
\]
where \([\text{Nd(III)}]_{\text{init}}\) and \([\text{Nd(III)}]_{\text{eq}}\) represent the initial and equilibrium concentration of neodymium(III) ion in the aqueous solution. \([\text{Nd(III)}]_{\text{aq}}\) and \([\text{Nd(III)}]_{\text{org}}\) are the equilibrium concentration of neodymium(III) in the stripping stage and the initial concentration of neodymium in the organic phase, respectively. \(V_{\text{aq}}/V_{\text{org}}\) is the ratio of aqueous phase to organic phase. In this research, the ratio of \(V_{\text{aq}}/V_{\text{org}}\) is equal to 1.

3. Results and discussion

3.1. Influence of contact time

To obtain the time of extraction equilibrium, a series of experiments were done at different contact time of aqueous and organic phases and at fixed values of pH and O/A. The results are shown in Fig. 1. The extraction efficiency of neodymium(III) increased from 45.17% to 95.24% with an increase in contact time from 1 min to 15 min. From Fig 1, it can be found that the optimum contact time for the neodymium(III) extraction was 8 min because the efficiency of extraction for Nd(III) metal kept constant at further increase in contact time. Thus, the contact time of 10 min was selected for the rest of the study.

![Fig. 1. Influence of contact time of aqueous and organic phases on the neodymium(III) extraction. \([\text{Nd(III)}] = 0.001 \text{ mol/L}, [\text{Cyanex 572}] = 0.2 \text{ mol/L}, \text{pH } 1.5, \text{ and O/A}=1\)](image)

3.2. Influence of solution pH

Hydrogen ion concentration is the important physicochemical parameter influencing the extraction behaviour of neodymium(III) during the extraction. The influence of solution pH on the extraction efficiency of neodymium(III) by Cyanex 572 is shown in Fig. 2. The extraction efficiency of neodymium(III) at pH 0.5 was only 0.17%. The extraction efficiency at pH 1.5 and higher up to 2 ranged from 68% to 87%. This behavior can be explained by the cationic exchange mechanism for neodymium(III) extraction with Cyanex 572. Similar results were obtained for the recovery of neodymium(III) using the mixture of D2EHPA and Oxine as an extractant in dodecane diluent (Roy, Basu, Anitha, & Singh, 2017).

![Fig. 2. Dependence between extraction efficiency of Nd(III) and pH solution. \([\text{Nd(III)}] = 0.001 \text{ mol/L}, [\text{Cyanex 572}] = 0.2 \text{ mol/L}, \text{ and O/A}=1\)](image)
3.3. Influence of nitrate ion concentration

The influence of nitrate ion concentration on the extraction behavior of neodymium(III) was investigated by varying it from 0.1 M to 0.5 M at pH 1.5 and O/A=1. The lowest extraction efficiency of neodymium(III) was 71.05% at 0.1 M nitrate ion concentration. Increasing nitrate ion concentration up to 0.5 M increased the extraction efficiency of neodymium(III) to 94.97%. This behavior may be attributed to the salting-out effect that is due to the common ion effect and water activity changes caused by the addition of potassium nitrate (KNO₃) (Kislik, 2012; Mishra and Sahu, 2016). As can be seen from Fig. 3, the slope value is about 1.

![Graph showing the dependence between logarithm distribution ratio and logarithm nitrate ion concentration.](image)

Fig. 3. Dependence between logarithm distribution ratio and logarithm nitrate ion concentration. [Nd(III)] = 0.001 mol/L, [Cyanex 572] = 0.2 mol/L, pH = 1.5, and O/A=1

3.4. Influence of Cyanex 572 concentration

Effect of extractant concentration on the neodymium(III) extraction was investigated in the range of 0.075-0.45 M at pH 1.5 and O/A=1. The lowest extraction was at a 0.075 M extractant concentration. Increasing extractant concentration from 0.075 to 0.45 M increased neodymium(III) extraction. Fig. 4 shows the variation of log D-3pH for Nd(III) versus Cyanex 572 concentration. From the plot of log D-3pH vs. extractant concentration, the slope value was found to be ~3, indicating the extracted neodymium(III) complex contains three molecules of Cyanex 572. Similar results were obtained by Nie et al. (Nie et al., 2018) for the extraction of scandium(III) from leaching solutions of tungsten residue.

![Graph showing the influence of Cyanex 572 concentration on the distribution ratio of neodymium(III).](image)

Figure 4. Influence of Cyanex 572 concentration on the distribution ratio of neodymium(III). [Nd(III)] = 0.001 mol/L, pH = 1.5, and O/A=1

3.5. Stoichiometry of extraction

To obtain the stoichiometry of extraction, considering the main extractable species of Nd(III) is essential. As reported in the literature (Reddy et al., 1999), there are several hydrolysis species of Nd(III) in an aqueous nitric acid medium. Therefore, graphical analysis method was applied to establish the
neodymium(III) extraction equilibrium from nitrate solutions. However, the general equation of the formed species (Reddy et al., 1999) could be written as:

\[
\text{Nd}^{3+} + i\text{NO}_3^- \leftrightarrow \text{Nd(NO}_3)_i^{(3-)}.
\]  

(4)

In our present work, the Nd(III) extraction from nitrate medium may be presented as:

\[
\text{Nd}^{3+} + (3-i)\text{NO}_3^- + x(\text{HA})_{2(o)} \leftrightarrow \text{Nd(NO}_3)_{(3-i)}\text{H}_{2x+i}\text{A}_{2x(o)} + i\text{H}^+
\]  

(5)

The equilibrium constant and distribution ratio for the above reaction can be described as follows:

\[
K = \frac{[H^+][\text{Nd(NO}_3)_{(3-i)}\text{H}_{2x+i}\text{A}_{2x(o)}]}{[\text{Nd}^{3+}][\text{NO}_3]^{3-i}[(\text{HA})_2]^x}
\]  

(6)

\[
D = \frac{[\text{Nd(NO}_3)_{(3-i)}\text{H}_{2x+i}\text{A}_{2x(o)}]}{[\text{Nd}^{3+}]}.
\]  

(7)

By combining Eqs. (5) and (6), the dependence between the equilibrium constant \(K_{\text{eq}}\) and the distribution ratio \(D\) could be expressed by:

\[
K = \frac{[H^+][D]}{[\text{NO}_3]^{3-i}[(\text{HA})_2]^x}
\]  

(8)

\[
\log D = \log K + (3-i)[\text{NO}_3^-] + x[(\text{HA})_2] + i\text{pH}
\]  

(9)

To obtain the extraction reaction stoichiometry, the above studies can be applied to determine \(x\) and \(i\) values. In this context, slope analysis was applied to identify the dependence between logarithm distribution ratio (log \(D\)) and pH values. As shown in Fig. 5, the plot of log \(D\) of Nd(III) vs. log \([H^+]\) is a straight line with slope of about three, indicating that three hydrogen ions are involved in the chelates of Nd(III). Cation-exchange mechanism was also explained by Zhang et al. (Wang et al., 2015) for the extraction of heavy REEs by Cyanex 572. The slope value of log \(D\) versus pH solution for their study was about 3.

![Fig. 5. Dependence between logarithm distribution ratio and logarithm hydrogen ion concentration. [Nd(III)] = 0.001 mol/L, [Cyanex 572] = 0.2 mol/L, and O/A=1](image)

Dependence between the distribution coefficient of neodymium(III) and the concentration of Cyanex 572 on a log-log plot has presented in Fig. 4. The slope of this plot was found to be 2.73, which indicates three extractant molecules are incorporated in the chelates with Nd(III). According to the results and above discussion, the extracted complex of Nd(III) by Cyanex 572 is proposed as NdH\(_3\)A\(_6\).

3.6. Effect of temperature

The influence of temperature on the extraction of Nd(III) was evaluated at different experimental temperatures. The other variables were kept constant. The thermodynamic parameters of extraction, i.e., the enthalpy (\(\Delta H\)) and entropy (\(\Delta S\)) change can be determined according to the equation:

\[
\ln K_{\text{ex}} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}
\]  

(10)

where \(R\) is the universal gas constant, and \(T\) is the absolute temperature. \(\Delta H\) and \(\Delta S\) can be obtained from the slope and intercept of \(\ln K_{\text{ex}}\) versus \(1/T\), respectively. Plotting \(\ln K_{\text{ex}}\) versus [1000/T(K)] is...
shown in Fig. 6. Evidently, the distribution ratio increased with increasing temperature from 298 to 323 K. The values of ΔH and ΔS were found to be 14.350 kJ/mol and 9.507 J/mol K, respectively for the system under study. Temperature rise from 298 to 323 K at this process resulted in the positive value of ΔH, indicating the endothermic nature of the process. It can be found that the increase in temperature is favourable for the neodymium(III) extraction with this mixture.

![Graph showing the dependence between ln K and 1000/T(°K) for the neodymium(III) extraction: [Nd(III)] = 0.001 mol/L, [Cyanex 572] = 0.2 mol/L, and O/A=1](image)

**Fig. 6.** Dependence between ln K and 1000/T(°K) for the neodymium(III) extraction: [Nd(III)] = 0.001 mol/L, [Cyanex 572] = 0.2 mol/L, and O/A=1

### 3.7. Stripping property

The loaded organic phase was stripped using different acidic solutions. Table 1 presents the stripping percentages obtained using different mineral acids such as HCl, H₂SO₄, and HNO₃. The maximum stripping performance was obtained for nitric acid compared with that of sulphuric acid and hydrochloric acid. It is noted that some precipitation was observed with the use of sulphuric acid. The effect of the stripping solution acidity was also investigated at different concentrations of the mentioned acids. As presented in Table 1, the increase in acid concentration increased the stripping percentage of neodymium. Therefore, HNO₃ was a highly effective reagent for the neodymium(III) stripping.

<table>
<thead>
<tr>
<th>Stripping agent</th>
<th>Concentration (M)</th>
<th>Stripping efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>0.01</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>77.12</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>90.34</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0.01</td>
<td>16.87</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>81.98</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>91.13</td>
</tr>
<tr>
<td>HNO₃</td>
<td>0.01</td>
<td>40.56</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>90.24</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>97.11</td>
</tr>
</tbody>
</table>

### 3.8. Effect of the nature of organic diluents

Diluents play an important role in solvent extraction. The diluents improve the dispersion and coalescence properties of the extractants and reduce their viscosity. Diluents with important properties such as low volatility, high physical stability, low solubility in aqueous phase, low surface tension, and high flash point are good diluents. In this regard, a series of experiments were done using 0.2 M Cyanex 572 diluted in several diluents and aqueous phase containing 0.001 M Nd(III), at pH 1.5 and O/A = 1 and the results are presented in Table 2.

This research clearly reveals that the polarity of diluent has a significant effect on neodymium(III) extraction. The extraction efficiency of neodymium(III) decreased with an increase in the dielectric constant of the diluent. The experimental results indicated that the extraction efficiency of
neodymium(III) using Cyanex 572 diluted in chloroform and Cyanex 572 diluted in kerosene were 41% and 70%, respectively under the same conditions of extraction. Non-polar diluents were suitable solvents for the extraction of neodymium(III) (Kokare et al., 2010).

Table 2. Effect of diluents on the neodymium(III) extraction. [Nd(III)] = 0.001 mol/L, [Cyanex 572] = 0.2 mol/L, pH = 1.5, and O/A=1

<table>
<thead>
<tr>
<th>Diluents</th>
<th>Dielectric constant</th>
<th>Extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>4.81</td>
<td>41</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.39</td>
<td>52</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.27</td>
<td>61</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>2.23</td>
<td>60</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>2.02</td>
<td>66</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>1.92</td>
<td>68</td>
</tr>
<tr>
<td>Kerosene</td>
<td>1.8</td>
<td>70</td>
</tr>
</tbody>
</table>

4. Conclusions

In this research, the extraction of neodymium(III) with Cyanex 572 was successfully demonstrated for synthetic solutions. The solvent extraction of Nd(III) happens fast. Extraction for this metal is favored at pH>1.5, while the extraction of Nd(III) under low pH conditions (pH<1.5) is very poor. The extraction reaction of neodymium with Cyanex 572 was found to be cation-exchange mechanism releasing three H+ ion during the extraction. Results showed that three moles of Cyanex 572 are incorporated in the extraction of one-mole metal from aqueous solution. The values of thermodynamic parameters were calculated for this mixture. The extraction was an endothermic process, and the thermodynamic functions, \( \Delta H \) and \( \Delta S \) were found to be 14.350 kJ/mol and 9.507 j/mol K, respectively for the system under study. The type of diluent influences the extraction efficiency of Nd(III). It can be found that non-polar diluents were suitable solvents for the extraction of neodymium(III).

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References


