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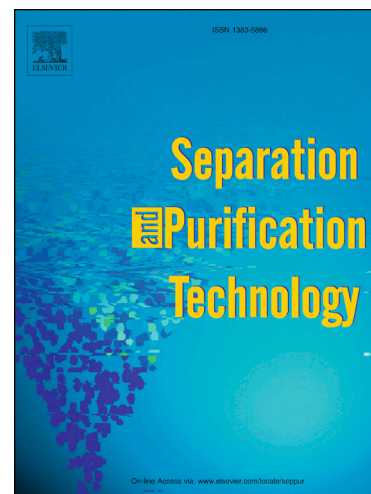
Extraction of Scandium (III) from acidic solutions using organo-phosphoric acid reagents: A comparative study

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Abstract

Comparative and synergistic solvent extraction of Sc(III) using two phosphoric acidic reagents such as di-(2-ethyhexyl) phosphoric acid and 2,4,4,tri-methyl,pentyl-phosphinic acid was investigated. Slope analysis method suggests a cation exchange reaction of Sc(III) with both extractants at a molar ratio of extractant: Sc(III) = 2.5:1 at equilibrium pH< 1.5. The plot of log D vs. log [Extractant] yield the slope (n) value as low as 1.2-1.3 and as high as n=7 at low and high extrcatant concentration level, respectively. Extraction isotherm study predicted the need of 2 stages at A: O=1:4 and A: O=1:3 using 0.1 M D_2EHPA and 0.1 M Cyanex 272, respectively. Stripping of Sc (III) was carried out at varied NaOH concentration to ascertain the optimum stripping condition for effective enrichment of metal. The predicted stripping condition (2-stages with A: O=1:3 and 1:4 for D_2EHPA and Cyanex 272, respectively) obtained from Mc-Cabe Thiele plot was further validated by 6-cycles CCS study. An actual leach solution of Mg-Sc alloy bearing 1.0 g/L of Sc (III), 2.5 g/L of Mg and 0.2 M HCl was subjected for selective separation of Sc at the optimum condition. The counter current simulation (CCS) study for both extraction and stripping of actual solution resulted quantitative separation of Sc with ~12 fold enrichment. The organic phase before and after loading of Sc (III) along with the diluents was characterized by FTIR to ascertain the phase transportation of Sc (III).

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1. Introduction

Scandium is generally classified as a rare earth element along with yttrium and lanthanides because of its limited availability in the Earth's crust and its stable oxidation state (Sc^{3+}) in aqueous solution and similar chemical properties with rare earth elements (REEs). There is a growing demand of scandium metal because of its extensive usages in several electronic/alloying materials such as optical, aeronautical, automotive and transportation industries, Mg-scandium alloy, aluminum–scandium alloys, high-intensity metal halide lamps, electronic components, fuel cells, oil well tracer and lasers [1-4]. Moreover, scandium metal is included as a major component in solid oxide fuel cells (SOFC) owing to its extraordinarily salient features like high oxygen-ion conductivity property in the form of Sc_2O_3-stabilized ZrO_2 materials [3].

Scandium exists in many minerals in trace quantities [4-6]. There is a growing interest to recover the scandium metal from low grade mineral or other secondary sources through suitable technology. Secondary sources like red mud from alumina industry contain ~100 g/t (100 ppm) Sc along with several unwarranted impurities. Red mud is an unwarranted burden to the environment globally because of the liberation of toxic gases and hazardous metals when dumped into soil level without any primary treatment. On the other hand, the presence of considerable amount of Sc in Mg-Sc and Al-Sc scrap lured the metallurgists for its economic value [4]. Therefore, recycling of this industrial waste by recovering the valuable metals such as scandium and gallium while removing other toxic metal impurities through suitable process technology resulting zero waste would resolve environment issues [7-10]. It is often a

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challenging task for the researchers to produce pure scandium metal from low grade ores, secondary or red mud with an overall Sc concentration of ~100 g/t along with other impurities [6-8]. Accordingly, hydrometallurgical unit operations like leaching and separation appear to be promising for dissolving the scandium content with said impurities to the aqueous phase. Scandium has been recovered from residues, tailings and waste liquors during the production of other metals such as RE, U, Ti, W, Al, Ni, Tl and Nb and dusts in chlorinating magnetovanailmenite, tungsten refinery residues and red mud [3, 6, 11].

Ample amount work has been devoted by the researchers over the last few decades, on purification of leach liquor to separate scandium [7-11]. The liquid-liquid extraction (solvent extraction), ion exchange (IX), liquid membrane, adsorption, precipitation and co-precipitation are being applied to purify the leach liquors. Solvent extraction is one of the most effective methods for the separation and purification of target metal ions because of the high extraction capacity, high selectivity, effective separation, high enrichment and operating at a large scale for recovery of trace rare metals like scandium from numerous aqueous solutions [10-13].

It has been found that a large number of commercially available organophosphorus extractants [3-6, 14-17] being used for the separation of Sc(III) from aqueous solutions. They are excellent in context of extraction efficiency, selectivity and enrichment aspect of reagents. The solvent extraction (SSE) process has proven more beneficial due to enhanced extraction efficiency by mixed reagents leading to enrich the trace metal ion concentrations (e.g. rare earth metal ions) to a high concentration range. Moreover, the alteration of equilibrium pH in SSE system may yield a high selectivity towards the targeted rare metal ions leading to the removal of impurities. Previous SSE studies on Sc(III) using different reagents are summarized in Table 1.

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The comparative study of extraction of Sc(III) using phosphoric acid reagents (D2EHPA, Cyanex 272) has not been reported.   Therefore, the present study aims to describe a detailed study on extraction of Sc(III) from aqueous solution using D2EHPA and Cyanex 272 as the extractants. The extraction was investigated as a function of parameters such as: pH, diluents, and concentration of extractant/stripping reagent to ascertain extraction efficiency of Sc(III). Extraction and stripping isotherms behavior of both reagents was studied and reported. In addition, an actual industrial liquor of Mg-Sc scrap was processed under the optimum experimental condition and simulation data was compared with either of the extractants. The selected samples were characterized to examine the bonding interactions between the Sc (III) ion and extractant.

2. Experimental

2.1. Chemicals and Reagents

The stock aqueous solution of Sc(III) was prepared by dissolving its oxide (Sc_2O_3, 99.9%, AR, Sigma) in a small volume of concentrated HCl followed by diluting with distilled water to obtain the desired concentration. The concentration of stock Sc(III) solution was 1 g/L (0. 022 M) and the total HCl concentration used for dissolving scandium oxide was 0.05 M. The extractants D2EHPA was procured from Dihalichi (Japan) and Cyanex 272 was supplied from CYTEC Canada. Both extractants were used without further purification. Different concentrations of extractant were prepared by diluting the above reagents with distilled kerosene (180-240°C). Small amounts of TBP (99.99 % purity) (5% v/v) procured from CYTEC was used as a modifier for both extractants especially while preparing stock organic extractant solution to ensure the phase separation with least co-extraction of metal ions. Moreover, the addition of TBP was avoided in subsequent dilution for changing extractant concentration, as TBP also extract

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Sc(III) which may interfere during synergistic behaviour of either of the extractant in this study. All other reagents used were of analytical reagent grade. The effect of diluents was tested using benzene, hexane, toluene or o-xylene instead of kerosene.

2.2. Apparatus

The concentration of aqueous samples bearing Sc(III) was determined after making dilution with 1 M HCl by MP-AES (Agilent, USA). The pH of the aqueous samples was measured with a digital Systronics pH meter provided with a combined glass electrode. The characteristic pattern of respective functional groups that are present in extractant phases before and after extraction was ensured using FTIR analysis (IR Afinity FTIR-1S Simazu, Japan).

2.3. General solvent extraction procedure

Equal volumes (5 ml each of aqueous and organic) of aqueous and organic phases taken in a separatory funnel were equilibrated for a period of 5 min. After the disengagement of phases, the raffinate phase was separated out and equilibrium pH of the respective samples was measured. The resulted raffinates were diluted using 1 M HCl prior to analysis of metal ion concentration. The loaded organic samples were filtered using phase separator (1PS) and then were stripped with 1 M HCl and diluted to desired concentration range for analysis by MP-AES. In addition, the concentration of Sc(III) in the organic phase was further verified using mass balance of metal ions in the aqueous phase before and after extraction. During scandium solvent extraction study the temperature (25°C) of the solution (s) was kept constant.

2.4. General equations

As per the reported investigations the Sc(III) extraction with either of the phosphoric acid derivatives is governed by cation exchange mechanism at low acidity and solvation mechanism

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at high acidity [18-21]. Thus, Sc(III) extraction onto organic phase by D2EHPA/ Cyanex 272 is considered as cation exchange reaction at low acid concentrations.

Omelchuk et al. (2017) [22] derived Eq. 2 for the extraction of divalent metal ions by organophosphorus cationic exchangers according to Eq. 1:

$$M_{(aq)}^{2+} + 2\{HL_2\}_{org} = \{ML_2\}_{org} + 2H_{(aq)}^+ \tag{1}$$
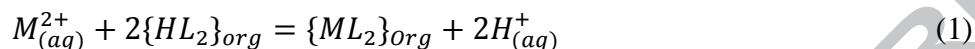
$$Log\ D = Log\ K_{D,ML_2} + Log\ \beta - 2pK_a + 2Log[\{HL\}_{org}] + 2pH \tag{2}$$

Where, D is the distribution coefficient given by the concentration ratio $[\{ML_2\}_{org}]/[\{M^{2+}\}_{aq}]$. Thus, for Sc^{3+} extraction given by Eq. 3, the distribution coefficient can be expressed by Eq. 4, where, the different terms are related to the chemical equilibria in Eqs. (5)-(10) and HL represents D_2EHPA or Cyanex 272, in solution equilibrated at pH values less than pK_a of the two reagents (2.75 and 3.73, respectively in Table 2). The extraction percentage is given by Eq. 11. These equations are useful in explaining the effect of change of initial and equilibrium pH and the concentration of extractants on equilibrium distribution coefficients extraction percentages listed in Table 3. If the uncomplexed of Sc^{+3} is involved in the extraction equilibrium the slope of the linear variation of logD as the function of pH should be 3.

$$Sc_{(aq)}^{3+} + 3\{HL\}_{org} = \{ScL_3\}_{org} + 3H_{(aq)}^+ \tag{3}$$
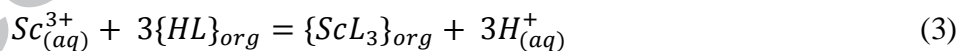
$$Log\ D = Log\ K_{D,ML_3} + Log\ \beta - 3pK_a + 3Log[\{HL\}_{org}] + 3pH \tag{4}$$

$$K_{ex} = [\{ScL_3\}_{org}][H^+]^3/[Sc^{3+}][\{HL\}_{org}]^3 \tag{5}$$

$$\{ScL_{3(aq)}\} = \{ScL_{3(org)}\}; K = [\{ScL_3\}_{(aq)}]/[\{ScL_{3(aq)}\}] \tag{6}$$

$$2\{HL_{(org)}\} = \{(HL)_{2(org)}\}; K_{Dimer} = [\{(HL)_{2(org)}\}]/[\{HL_{(org)}\}]^2 \quad (7)$$

$$\{HL_{(aq)}\} = H^+_{(aq)} + L^-_{(aq)}; K_a = [H^+_{(aq)}][L^-_{(aq)}]/[\{HL\}_{(aq)}] \quad (8)$$

$$Sc^{3+}_{(aq)} + mCl^-_{(aq)} = \{ScCl_{m(aq)}\}; \beta = [\{ScCl_{m(aq)}\}]/[Sc^{3+}_{(aq)}][Cl^-_{(aq)}]^m \quad (9)$$

$$pK_a = -logK_a \quad (10)$$

$$\%E = 100(D/(D+1)) \quad (11)$$

3. Results and discussions

3.1. Effect of equilibrium pH

The effect of pH on Sc(III) extraction was tested at an initial pH range of 0.5-4.5. Corresponding equilibrium pH (pH_e) was in the range 0.46 to 3.52 for D2EHPA and 0.49 to 3.59 for Cyanex-272) (Table 2) where other parameters such as phase ratio (A:O=1:1), extractant concentration (0.1 M), temperature (25^oC), were kept constant. The limit of the highest initial pH was 4.5 due to the precipitation of Sc(III) from aqueous solutions at pH > 4.5 [1, 10, 23].

The variation of Sc(III) extraction efficiency (%) with equilibrium pH for either of the two extractants is shown in Fig.1. There was a progressive increase of Sc(III) extraction from 0.2 to 54.1% and 0. 5 to 70.6% for Cyanex 272 and D2EHPA, respectively, with the latter giving a higher extraction. However, at higher pH values, percentage of Sc(III) extraction reached plateaus. The increase in the percentage of extraction of Sc(III) for both extractants at higher pH (initial pH 4 and 4.5) is consistent with Eq. 3. The slope of the plot of log D as a function of equilibrium pH (Fig.2) for extraction of Sc(III) is close to 3 at pH<1.5 for both D2EHPA and cyanex 272, indicating the release of 3 moles of H^+ ions for complexion of one mole of scandium(III), according to Eqs. (3) & (4). However, as Sc^{+3} forms the chloro-complexes $ScCl_m$
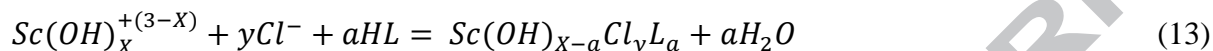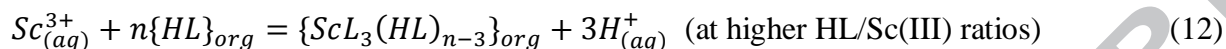
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species (Table 2) it need to be considered as in Eq.9, which would lead to a slope less than 3, as shown in Fig.2.

3.2. Effect of extractant concentration

The initial concentration of extractant, was changed in the range 0.0025-0.1 M at 1:1 phase ratio, pH 4.0, temp. 25^oC and the results are listed in Table 2 and plotted in Fig. 3. In general, the percentage extraction of Sc(III) increased with the increase in extractant concentration for both extractants and the trend was found to remain same at higher extractant concentration range of 0.08 M and 0.1 M (Fig. 3). It was observed that almost all Sc(III) content (more than 99%) was extracted using 0.08 M for D2EHPA and 0.1 M for Cyanex 272, due to higher molar ratios of [extractant]/[Sc(III)]. From the results it was ascertained that D2EHPA was very effective than Cyanex-272 even at the lower concentration range. The observation was further ensured from the resulted values of equilibrium pH data obtained at varied extractant concentrations as given in Table 2. To assure quantitative extraction of Sc(III) using both reagents 0.1M was kept fixed for extraction isotherm study.

The plot of log D as a function of log [Extractant] in Fig. 4 shows slopes in the range 1.2-1.3 for D2EHPA and Cyanex-272 at lower initial concentrations of extractants. The slope is as high as 7 for higher concentrations of extractants which is generally supported by the stoichiometry of the reaction proposed in Eq. 12, with n=1-2 or n~7 at lower or higher concentrations, respectively. The observations from this study agree with the previous findings on the extraction of rare earth metal ions by phosphoric acid derivative [13, 24-26]. The lower slope of 1.2-1.3 in Fig. 4 also indicates the coordination of the anion of the extractant HL to Sc(III) ion at a molar ratio of Sc(III):HL = 1:1 or 2:3. This implies that, instead of the uncomplexed species Sc^{3+}, Sc(III) is likely to be in the form of a range of complex ion species

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such as $Sc(OH)^{2+}$, $Sc(OH)_2^+$, $ScCl^{2+}$ and $ScCl_2^+$ with the stability constants reported in Table 2 leading to extraction given by the reaction in Eq. 13. Based on Sc^{3+} charge balance, if the value of a in Eq. 13 is in the 1.2-1.3 (Fig. 4), the value of y should be $y = 0.7$-0.8 and x = 1).

$$Sc_{(aq)}^{3+} + n\{HL\}_{org} = \{ScL_3(HL)_{n-3}\}_{org} + 3H_{(aq)}^+ \text{ (at higher HL/Sc(III) ratios)} \qquad (12)$$

$$Sc(OH)_X^{+(3-X)} + yCl^- + aHL = Sc(OH)_{X-a}Cl_yL_a + aH_2O \qquad (13)$$

3.3. Effect of diluents

Various diluents such as xylene, toluene, kerosene, n-hexane and benzene were used for Sc(III) extraction (Table 2), in order to examine the extraction behavior of Sc(III) with organophosphorous reagents. The effect of the diluents for extraction of Sc(III) using D2EHPA and Cyanex 272 is compared in Fig. 5(a) and 5(b) respectively. It is of interest to note that benzene and o-Xylene showed the lowest extraction of Sc(III) even at higher molar ratios of [Extractant]/[Sc(III)]. However, in other cases, the extraction was over 99% at molar ratios of [Extractant]/[Sc(III)] greater than 3.5. This supports the stoichiometry close to 3 which is also supported by the linear relationships close to 3 in Fig. 2 at low values of pH_e. The extraction efficiency of both extractants appears to be quantitative using toluene, hexane or kerosene as the diluents, at the higher molar ratios of [Extractant]/[Sc(III)] though overall change in efficiency was within 2-3%, due to changes pH_e, as shown in Table 3. However, there is a significant decrease in Sc(III) extractions when xylene and benzene were used as diluents as a result of the high pH_e values in these solutions. These pH values in the range 3.4-3.6 are generally closer to the pK_a values of HL (2.75-3.5) listed in Table 2. An equilibrium pH less than pK_a discourage the dissociation of HL and the formation of complex species between Sc^{3+} and L^- ions.

As shown in Table 3 and Fig. 5(a) and 5(b), D$_2$EHPA in the three diluents n-hexane, toluene and kerosene phases at a molar ratio of [Extractant]/[Sc(III)] > 3.5 showed comparatively better extraction efficiency than Cyanex 272 phase. However, K_{ex} for Eq. 3 for Cyanex 272 is larger compared to that of D2EHPA, listed in Table 2. This difference is, therefore, a result of relatively higher values of pH_e of 1.86-2.08 in the case of D2EHPA extraction equilibria, compared to lower pH of 1.67-1.72 in the case of Cyanex 272, listed in Table 2. From this study, it is apparent that the kerosene can replace n-Hexane/Toluene for commercial purposes as extraction efficiency is almost similar. This result is an important outcome of this investigation.

3.4. Extraction isotherm and counter-current simulation for Sc (III) extraction

The extraction isotherm was studied at an initial solution pH of 4.0 using 0.1 M solutions of the extractants (D2EHPA/ Cyanex 272) in order to know the number of stages needed for quantitative extraction of Sc (III) at a chosen phase ratio. In this investigation both aqueous and organic phases (A: O) were contacted at volume ratio varying from 1:5 to 5:1, keeping the total volume of the solution constant. The McCabe-Thiele plot (Fig.6) show quantitative extraction of Sc (III) in two stages, at 1:1 phase ratio using D2EHPA and at 1:4 phase ratio. As can be seen from the above results, D2EHPA appears to be effective extractant than Cyanex 272 while attaining maximum extraction of Sc (III) with high enrichment factor.

To confirm the above predictions of extraction isotherm, a two-stage countercurrent simulation study using 0.2 M D2EHPA and Cyanex 272 at 1:1 phase ratio was carried out. The raffinates and loaded organic samples were collected and analysed for metal ion concentration. The raffinate samples were analyzed to confirm the presence of <1.0 mg/L and <2.0 mg/L Sc (III) indicating 99.99% extraction using D2EHPA/ Cyanex 272. Sufficient quantity of Sc (III) loaded organic phase was generated to carry out the stripping studies.

3.5. Stripping of Sc(III) from loaded organic

The adoption of NaOH in this investigation would lead to allow the possibility of recovering the ScO_2 through the precipitation route [4]. In this investigation, the effect of NaOH concentration on stripping of scandium ion from loaded-D2EHPA and loaded-Cyanex 272 was examined in the concentration range of 0.1-5.0 M NaOH with a phase contact time of 5 min. The stripping efficiency of Sc(III) was increased from 22.2 to 99.95 % and 13.15 to 96.59 % from loaded D2EHPA and loaded-Cyanex 272, respectively with the increase in NaOH concentration from 0.1 to 2.5 M at 1:1 phase ratio. From the results it was found that the stripping efficiency of Sc(III) from loaded-D2EHPA was lower than that of Cyanex 272 at the studied concentration level. The required amount (3.0 M) of NaOH was relatively higher for the quantitative stripping of Sc(III) in case of loaded D_2EHPA than loaded-Cyanex 272 as can be seen from the results depicted in Fig. 7. The stripping efficiency of Sc (III) from both the loaded extractants remains unaltered at ~99.99% beyond 3.0 M NaOH. However, to enrich the scandium concentration into the strip solution, the concentration of NaOH was kept at 3.0M to strip Sc(III) from loaded-D2EHPA/ loaded-Cyanex 272, respectively, in subsequent stripping isotherm studies. The results of stripping behavior from loaded organic phase are compared and reported as described in the following section.

3.6. Stripping isotherm and counter current simulation (CCS)

To determine the number of stages required for stripping at a chosen phase ratio (A: O) stripping isotherm plot of Sc(III) from the loaded organic was constructed. Different phase ratio varying in the range of A: O=1:5 to 5:1 was investigated. As shown in the Mc-Cabe Thiele plot (Fig. 8), a quantitative stripping of Sc(III) was achieved, in 2-counter-current stages at A:O ratio of 1:3 from loaded D2EHPA and at A:O ratio of 1:4 from loaded Cyanex 272, respectively.

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Thus, the isotherm results suggested a high stripping efficiency with greater enrichment of Sc (III) from loaded organic using 3.0 M NaOH.

To confirm the above prediction, a 2-stage counter current simulation (CCS) study for stripping of Sc(III) from both loaded organic phase was performed up to 6 cycles. The spent organic contained < 0.5 mg/L Sc(III) suggesting more than 99.9% stripping efficiency of Sc(III) from loaded-D2EHPA and loaded-Cyanex 272. The final Sc(III) loaded acid solution bears ~12.0 g/L each of Sc(III) in the two cases shown in Fig. 8 indicating an enrichment of Sc(III) up to 3 and 4 times while stripping from loaded-D2EHPA and Cyanex 272, respectively, in comparison to its concentration in the loaded organic phase. In addition, overall scandium enrichment was of 12 folds with D$_2$EHPA/ Cyanex-272 as the extractant followed by stripping with NaOH in this process.

3.7. FTIR analysis of scandium (III) complex

The interactions by both of the extracatants; alkyl- phosphoric acid and phosphinic acid with Sc (III) were also evident from the FTIR results of both the extractant (in kerosene phase) before and after extraction. As shown in Fig. 9 both extractant and their corresponding loaded Sc(III) exhibits the characteristics peaks at 2970–2860 cm^{-1} and 1460 cm^{-1} for C–H stretching and bending vibrations of –CH$_3$ moiety, respectively[3]. The absence of low intensity characteristic peaks for P–(OH) in the region 2750–2550 cm^{-1} indicated the formation of Sc(III) complexes. The shift of –OH deformation bands (~30 cm^{-1}) with reduced intensity with Sc(III)–extractant complexes provided further evidence in favor of complex formation through phosphorous-hydroxyl group. The comparison of both the spectra revealed that the IR peak of P=O stretching observed at 1251 cm^{-1} of both D2EHPA and Cyanex-272 shifted to 1229 cm^{-1} when both extaractants were loaded with Sc(III). In addition, marginal shift of characteristic

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band for P= O, appeared in the range 1140–1200 cm^{-1} towards higher frequency which also indicated the strong interaction of P=O bonds in complex formation through co-ordination with Sc(III). The remaining peaks due to other hydrocarbon moieties found in the extractants before and after extraction were appeared to be merely same.

3.8. Separation study of Sc (III) from chloride medium Mg-Scrap leach liquor using D2EHPA and Cyanex 272

There is the issue on selective and quantitative separation of scandium from chloride media scrap leach solution after leaching of Mg-Sc alloy scrap as the base metal such as Mg content is relatively high. However, the selectivity for the extraction of Sc(III) can be improved by controlling the eq. pH of the solution while extracting the metals. In the present study, a typical synthetic solution equivalent to the Mg-Sc alloy scrap liquor bearing 1.0 g/L of Sc(III), 10.0 g/L of Mg and 0.2 M HCl [27] was subjected to investigate the separation behavior of the metals with either of the organo-phosphoric acid reagents (D$_2$EHPA and Cyanex 272) at the optimum extraction isotherm conditions (Initial pH 4.0, 0.1M D$_2$EHPA, A: O= 1:4 and 2. stages for D$_2$EHPA & initial pH 4.0, 0.1M Cyanex 272, A: O= 1:3 and 2 stages). At the above optimum condition 6-cycles counter current simulation studies (Fig.10.a) were carried out and the results are presented in Table 4. The resulted loaded organic was further simulated for 6 cycles (Fig.10.b) for quantitative stripping of scandium from the respective loaded organic phase using 3.0 M NaOH at the optimum stripping isotherm condition (2-stages, at A:O=1:3 for D2EHPA and 2-stages, at A:O=1:4 for Cyanex 272) and the results are as given in Table 4. From this investigation it was ascertained that Cyanex 272 has comparatively high selective extraction behavior at the optimum pH 4.0 than D2EHPA. The results of the study are in good agreement with the reported works, showing Cyanex 272 has poor extraction below pH 5.0 [28], thus

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ensuring its adoption for selective separation of Sc(III) from the scrap leach solution. On the other hand, at same concentration of either of the extractants, D2EHPA showed higher extraction ability than Cyanex 272 though, the co-extraction of Mg impurity in this case is high. Overall maximum co-extraction of Mg was only 1.67 % & 0.26 % with D2EHPA and Cyanex 272, respectively, as the eq. pH of the final raffinate are reported to be <2.0 (Table 3). This showed the selectivity and effective separation of Sc (III) with both organo-phosphorous reagents at the controlled pH from scrap leach liquor. The CCS results confirmed and overall enrichment of Sc content as ~12 fold higher as the final strip solution contained ~12 g/L of Sc(III) through extraction followed by stripping with either of the organ phosphorous reagents. The results of this study are promising while comparing the results of reported works where the impurity levels are different with regards to the types of feed samples used for separation study of scandium using numerous organic reagents.[3-6,28]

4. Summary and conclusions:

Liquid-liquid extraction of Sc(III) using organo-phosphorous reagents was investigated. The stoichiometry of the extraction by D2EHPA and Cyanex 272 are predicted by slope analyses method and reported along with their synergistic effect. Equilibrium studies showed the association of 2.5 mole of extractant with 1 mole of Sc(III) while releasing 2.5 mole of H^+. The loaded organic was stripped by NaOH. The Mc-Cabe Thiele diagram for the extraction of Sc(III) was constructed with 0.1 M D2EHPA and 0.1 M Cyanex 272 solutions at initial pH 4.0 indicating a quantitative extraction of Sc(III) in 2-stages at A: O = 1:4 and 1.3, respectively. Counter current simulation study at the same conditions showed 99.99% extraction of Sc(III) by both D2EHPA and Cyanex 272, respectively, indicating an effective extraction by the former extractant. The extracted species was further examined using FTIR analysis. Stripping isotherm

showed quantitative stripping using 3 M NaOH at A: O = 1:4 and 1:3 for loaded-Cyanex 272 and loaded D2EHPA, respectively, in 2-stages. The predicted condition was further confirmed by 6-cycles of CCS study. The final stripped solution bears ~12.0 g/L of Sc (III) indicating 12 fold enrichment of Sc(III) with both extractants as compared to Sc(III) content in the original aqueous solution. Actual liquor of Mg-Sc alloy scrap simulated at the optimum condition of extraction and stripping ensures effective and selective separation of Sc. The co-extraction of Mg was small (1.67 % with D2EHPA and 0.26% with Cyanex 272), though, it was comparatively high with D2EHPA than that of Cyanex 272. The results of this investigation are reasonably promising while applying in process liquor bearing Sc(III) with other base metal impurities.

Acknowledgements

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Figure 1. Effect of equilibrium pH in extraction of scandium

Figure 2. Effect of equilibrium pH on extraction of scandium (A:O=1:1, extractant (D2EHPA or Cyanex 272) concentration 0.1 M, temperature 25 ^{o}C)

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Figure 10. Two (2) Stage Counter Current Simulation (CCS) study for (a) Extraction and (b) Stripping, of Scandium (III) from scrap leach liquor
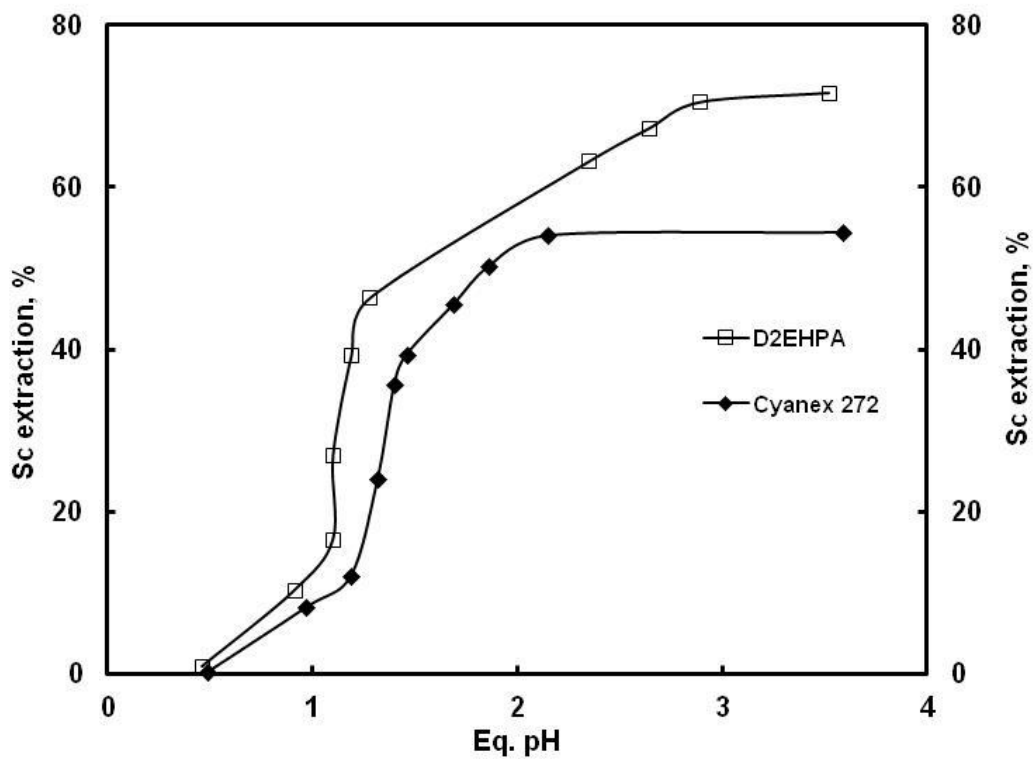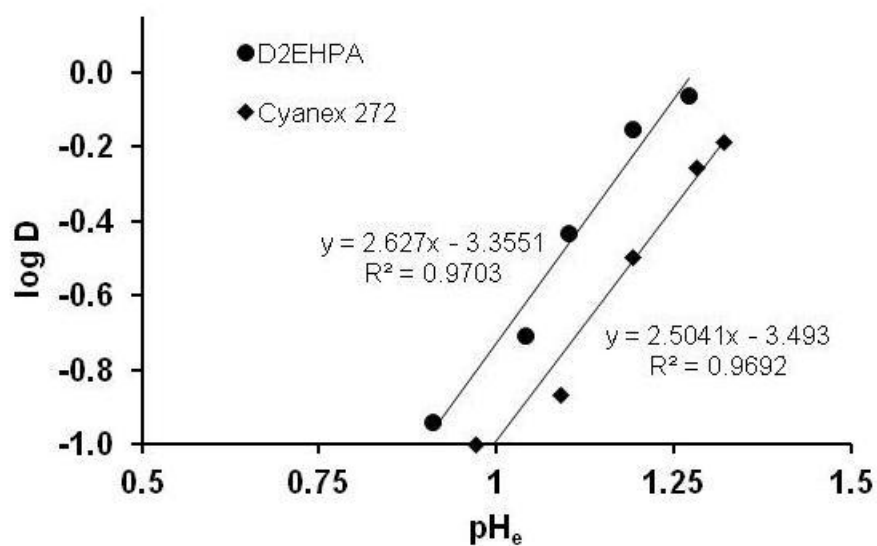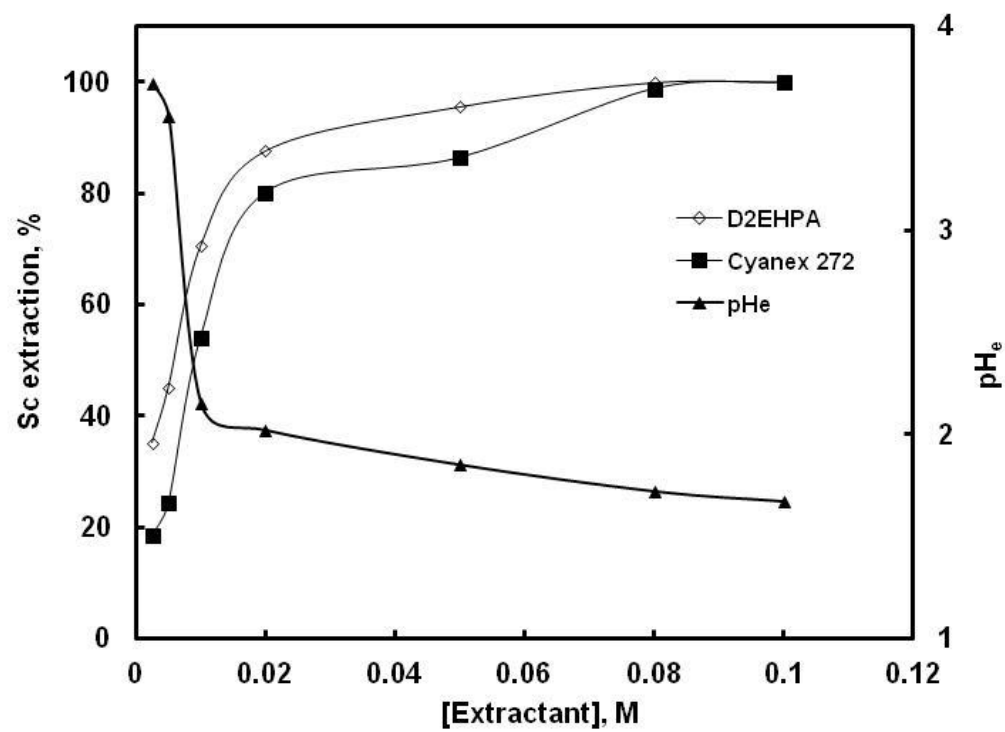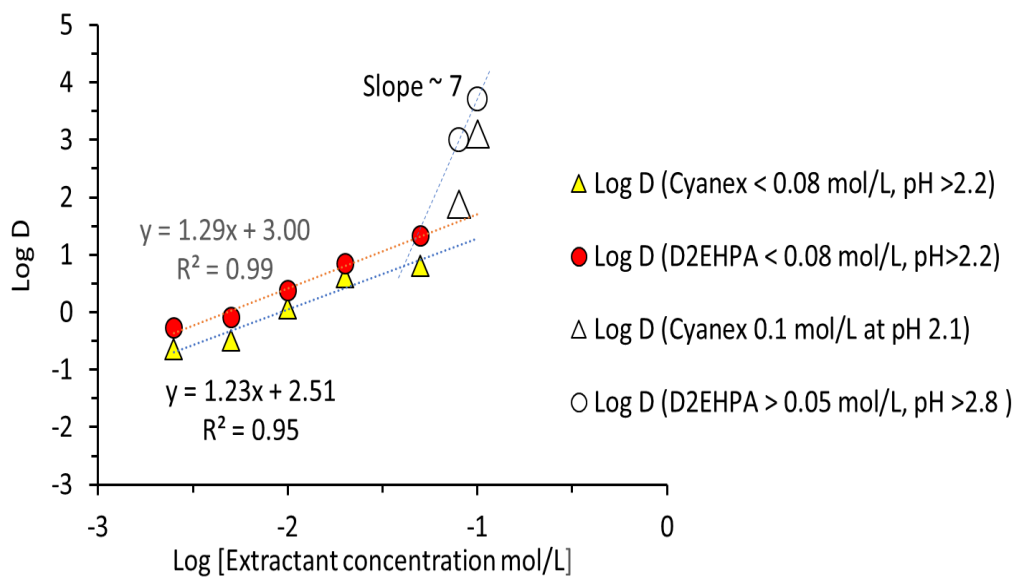
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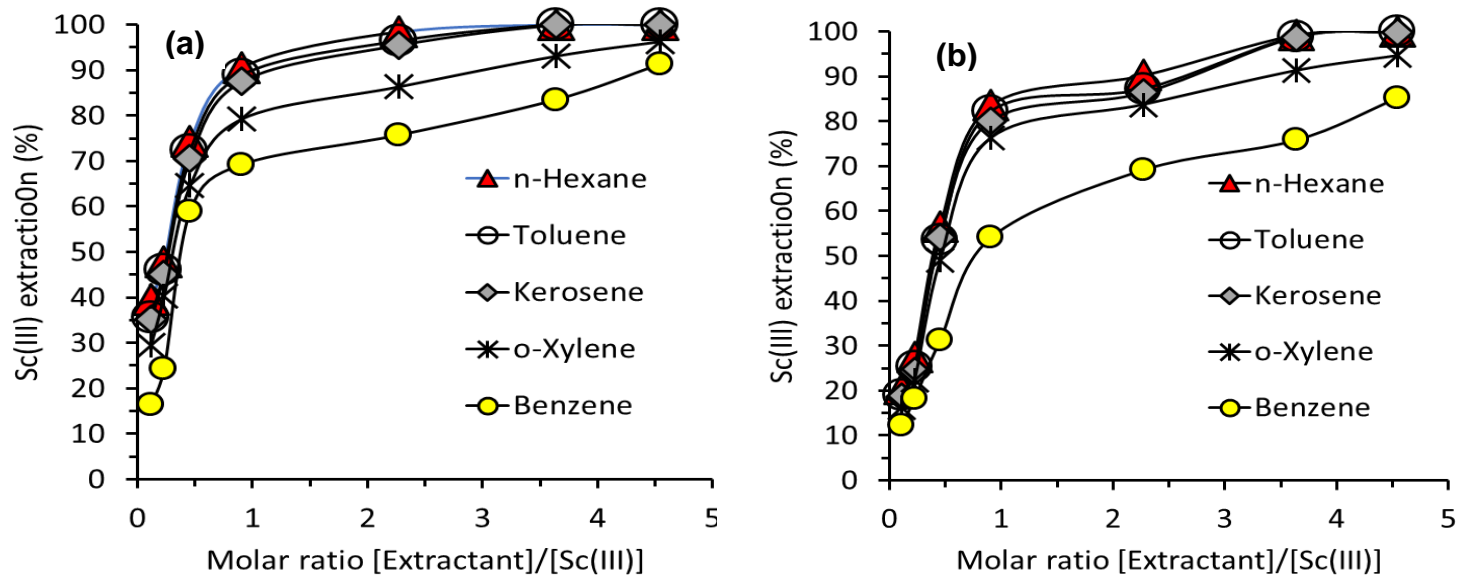
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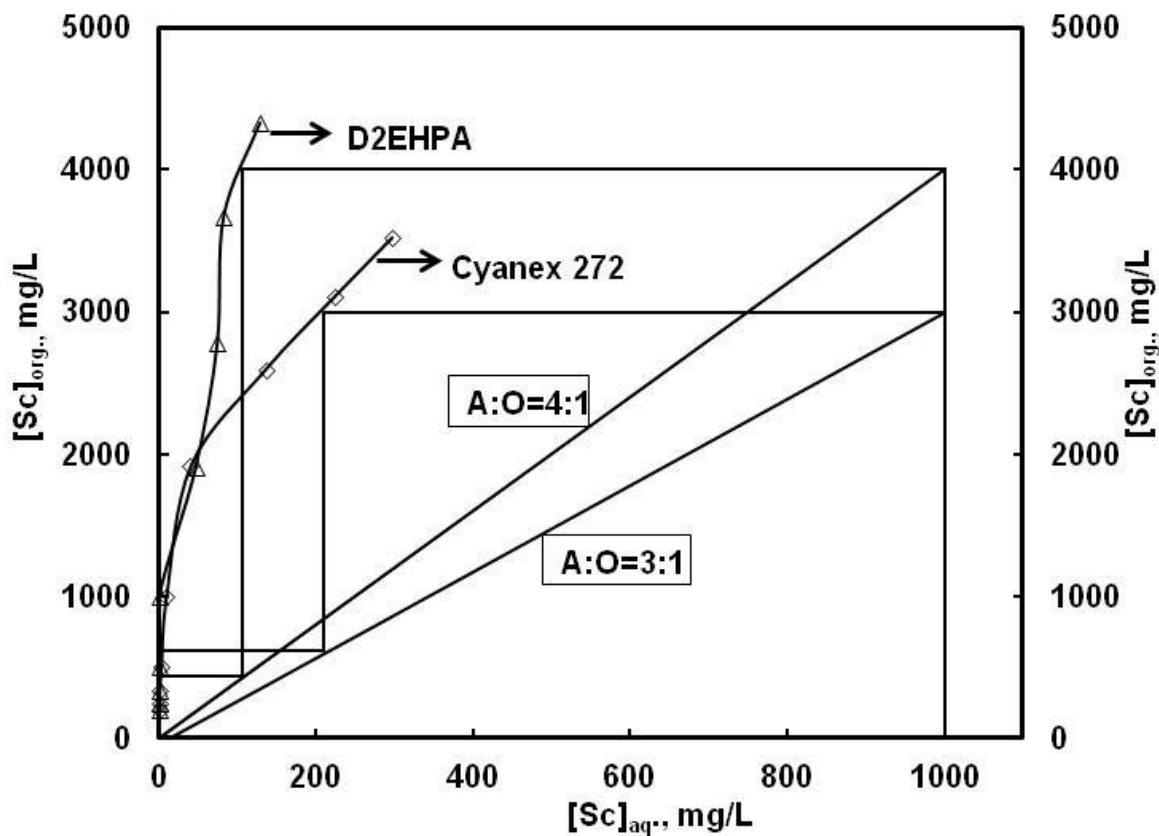
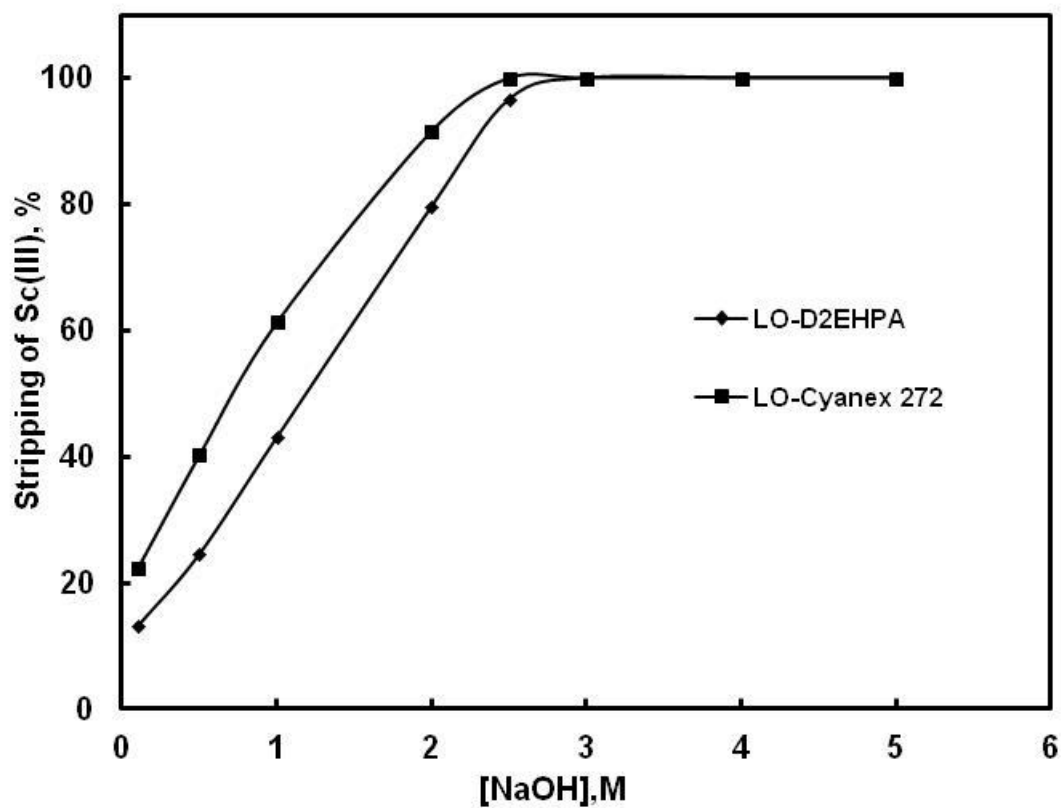Figure 6. Mc-Cabe Thiele plot for extraction of Sc(III) using 0.1M D_2EHPA / Cyanex-272

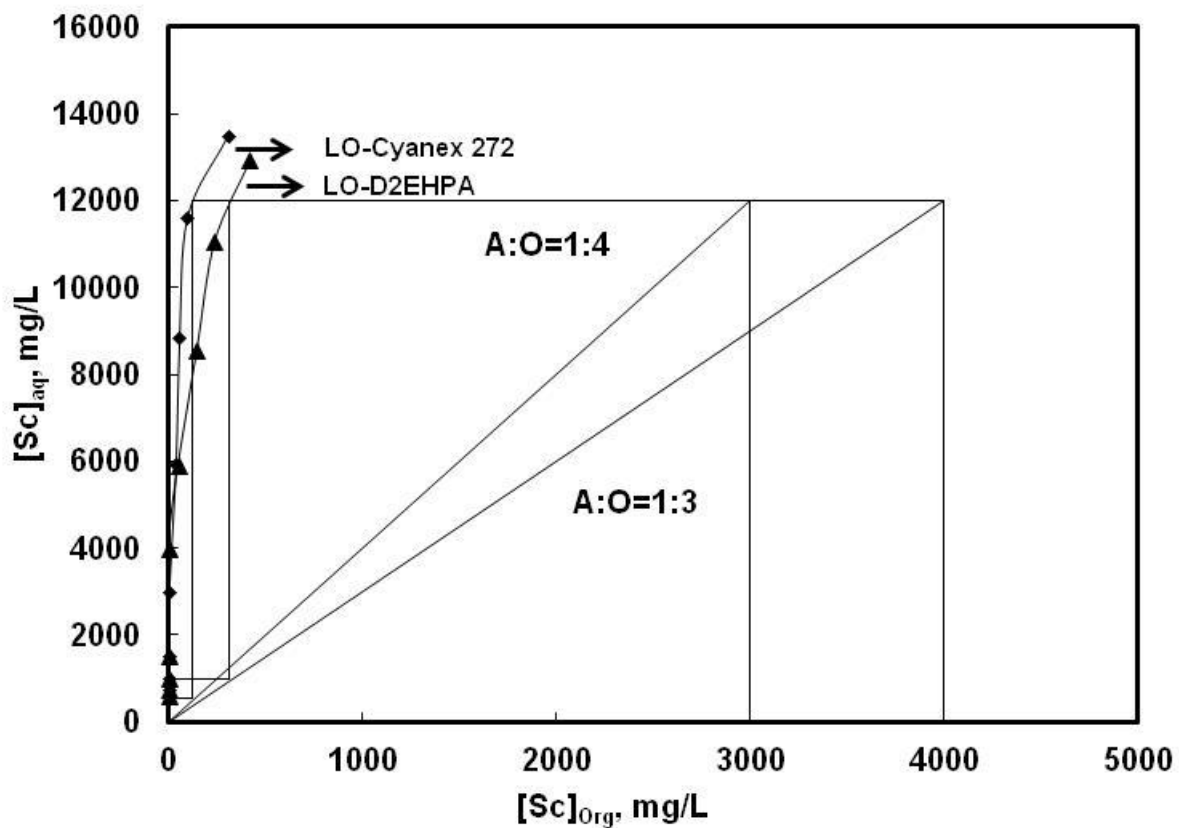Figure 7: Effect of NaOH concentration on stripping of Sc from loaded organic

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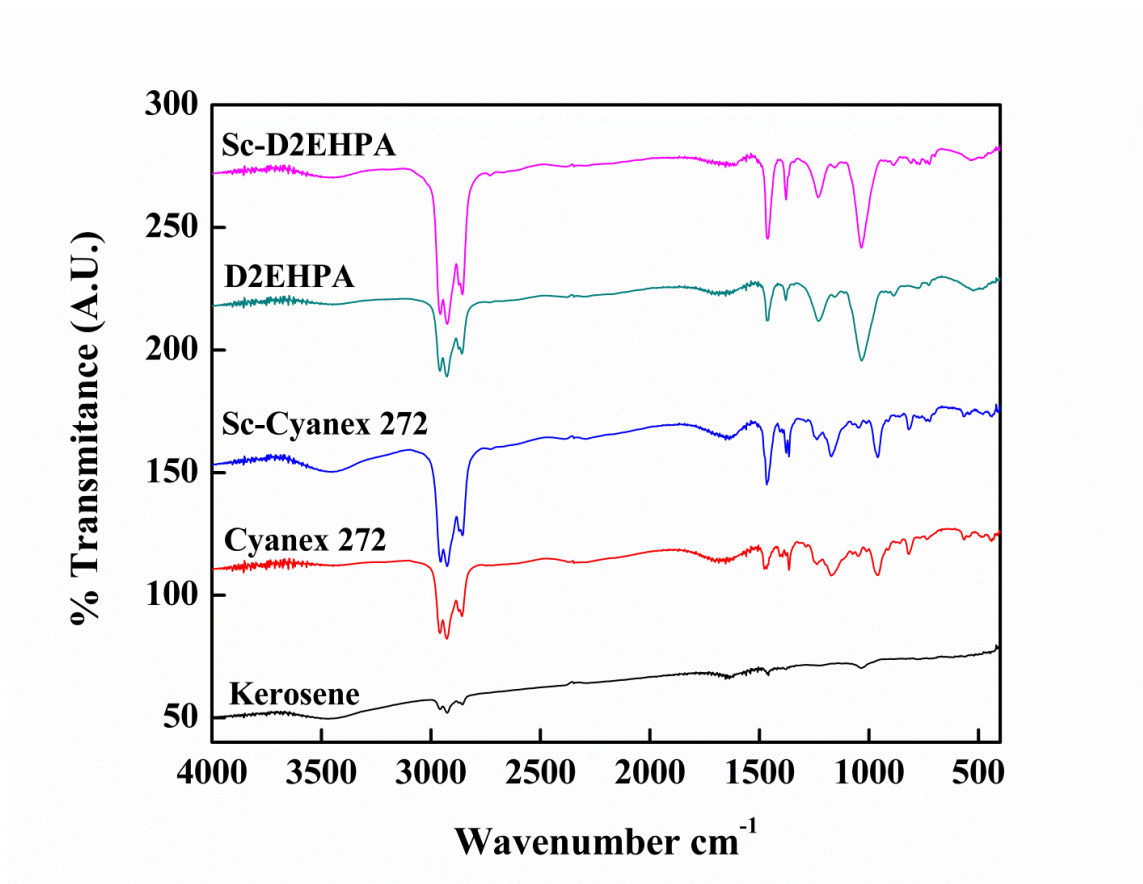
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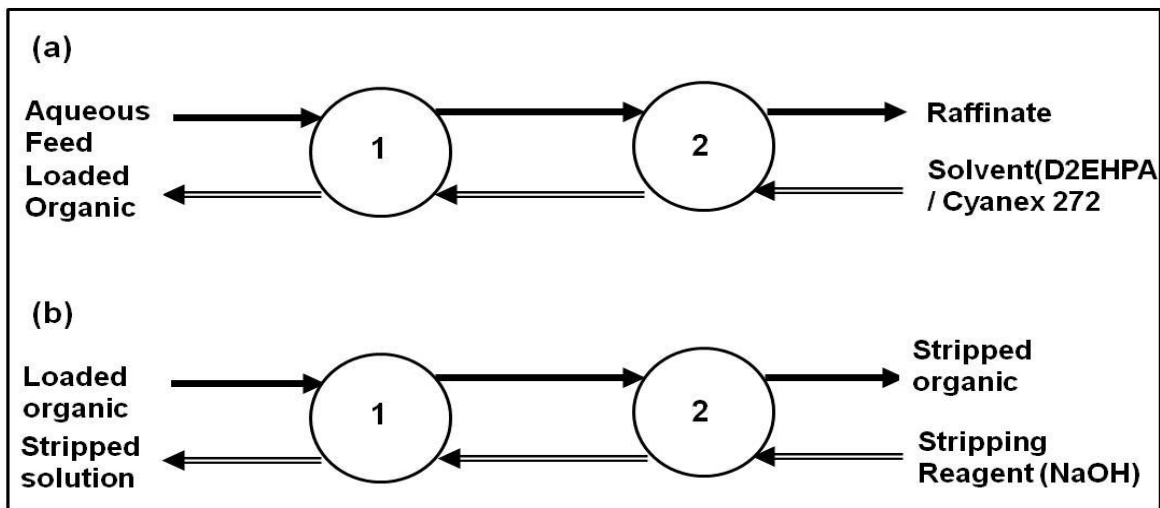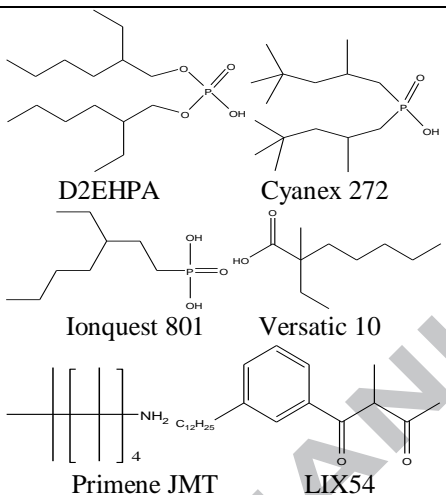
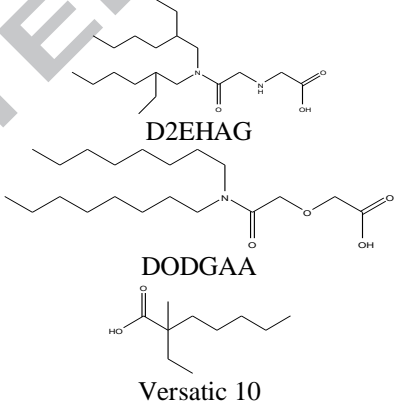**Fig.10. Two (2) Stage Counter Current Simulation (CCS) study for (a) Extraction and (b) Stripping, of Scandium (III) from scrap leach liquor**

Table 1. Summary of the literatures reported on extraction of Sc(III) studies based on solvent extraction (SX) process

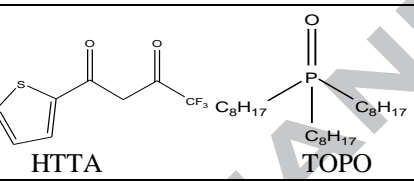| No.	Author(s) / Year	Extractant	Metal(s)	Remarks
1	Wang et al. (2013)	D2EHPA Cyanex 272 Ionquest 801 Versatic 10 Primene JMT LIX54	Sc, Ti, Fe, Zr and Ga	D$_2$EHPA appears to be selective than other reagents while extracting Sc (III) from the leach solution bearing Zr, Fe, Ti& Ga.
2	Onghena and Binnemans (2015)	Betainium Bis (trifluoromethylsulfonyl) Imide [Hbet][Tf2N]	Sc, Y, La, Ce, Nd, Dy, Fe, Al, Ti, Ca and Na	Sc(III) was selectively extracted using [Hbet][Tf2N] from red mud leachate solution.
3	Baba et al. (2014)	D2EHAG DODGAA Versatic 10	Sc,Y, La, Nd, Eu and Dy	Sc was selectively extracted by D2EHAG due to the chelating effect and the size recognition ability of D2EHAG.
4	Chen et al. (2017)	[(CH2)nCOOHmim][Tf2N] (n = 3, 5, 7)	Sc,Y, La	Sc extraction was quantitative (99.5%) by [(CH2)7COOHmim][Tf2N] dissolved in [C4mim][Tf2N].
5	Karve and Vaidya (2008)	Cyanex 302	Sc, Y, La, Ce, Pr, Nd, Gd, Dy and Yb	Selective separation of Sc(III) was achieved from mixed rare earth leach solution.

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6	Fujinaga et al. (2013)	 Kelex 100 PC88A Cyanex 302 Phoslex DT-8	Sc, ZrO, Ti, Y and Al	Extraction of Sc by Cyanex 302 was significantly higher than other extractants;Kelex 100, PC88A.
7	Zaho et al. (2016)	 HTTA TOPO	Sc, Al, Fe, Mn, Ni and Zn	Selective extraction of Sc(III) using HTTA synergism with TOPO
8	Sun et al. (2007)	 [C8mim][PF6]	Sc, Y, La and Yb	Sc was preferentially separated in presence of Y, La and Yb by the extranctant [C8mim][PF6]/Cyanex 925 at A:O=1:3.
9	Onghena et al. (2017)	 Betainiumbis(trifluoromethylsulfonyl)imide, [Hbet][Tf2N]	Sc, Al, Fe	Sulfation-roasting-leaching of Sc from bauxite residue (red mud) followed by selective extractin of Sc with [Hbet][Tf2N] was achieved.
10	Depuydt et al. (2015)	 [P$_{444}$C$_1$COOH]Cl	Sc	The IL-rich phase of the aqueous biphasic system has a very low viscosity, in comparison to the pure IL [P444C1COOH] Cl. This system has excellent extraction properties for scandium

2
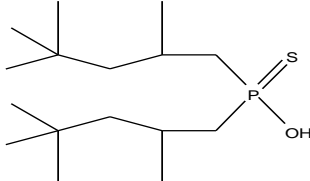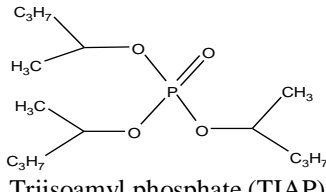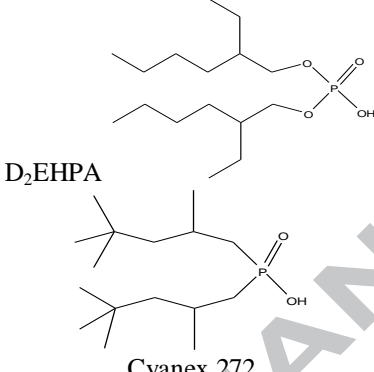
11	Wu et al. (2007)	Cyanex 302	Sc, Y, La and Gd	Extraction of metals follows the order as Sc>>Y>La>Gd with the extractant Cyanex 302 from their hydrochloride solution.
12	Kostikova et al. (2005)	Triisoamyl phosphate (TIAP)	Sc, Zr, Ce,Nd, Sm, Eu, Y, Lu	High-purity Sc can be prepared by multi-step counter current extractive treatment of Sc concentrate with TIAP.
13	Present investigation (2017)	D₂EHPA Cyanex 272	Sc(III)	Comparative and synergistic approach on quantitative extraction of Sc(III).

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Table 2. Equilibrium constants and pK_a values

Extractant	pK_a	K_a	K_{ex}	Stability constant (β)
Cyanex 272 (0.1M) in kerosene	3.73	1.68×10^{-4}	-	
D2EHPA (0.1 M) in kerosene	2.75	17.8×10^{-4}	-	
Scandium(III) + Cyanex 272 in kerosene	-	-	5.36	-
Scandium(III) + D2EHPA in kerosene	-	-	2.73	
$Sc^{3+} + Cl^- = ScCl^{2+}$				11.7[a]
$Sc^{3+} + 2Cl^- = ScCl_2^+$				10.9[a]
[Sc(III)-L-OH)]				12.8

(Data from Omelchuk et.al., 2017; Kerdjoudj et.al., 2016; Sc(III)-Cl data (a) from A.D. Paul, J. Phys. Chem., 66, 1248 (1962)

Table 3. Effect of parameter on extraction of scandium (III) using D2EHPA and Cyanex 272

Concentration (mol/L) and other conditions						Cyanex 272			D2EHPA		
Sc(III)	HCl	Diluent	Temp.,K	Extractant	pH (initial)	pH_e	D	%	pH_e	D	%
0.022	0.05	Kerosene	298	0.01	0.5	0.49	0.0015		0.46	0.0088	
					1	0.97	0.0929		0.91	0.114	
					1.25	1.09	0.124		1.04	0.1987	
					1.5	1.19	0.317		1.1	0.368	
					2	1.32	0.553		1.19	0.702	
					2.5	1.46	0.649		1.28	0.864	
					3	1.69	0.756		2.35	1.319	
					3.5	1.86	0.923		2.64	1.666	
					4	2.15	1.179		2.89	2.397	
					4.5	3.59	1.197		3.52	2.534	
0.022	0.05	Kerosene	298	0.0025	4	3.72	0.228		3.92	0.542	
				0.005	4	3.56	0.32		3.79	0.819	
				0.01	4	2.15	1.179		2.89	2.396	
				0.02	4	2.02	4.025		2.52	7.08	
				0.05	4	1.85	6.319		2.32	21.44	
				0.08	4	1.72	76.69		2.14	1009	
				0.1	4	1.67	1261		2.05	5049	
0.022	0.05	n-Hexane	298	0.0025	4	3.64		20.35	3.82		39.58
				0.005		3.49		27.56	3.67		47.88
				0.01		2.06		56.48	2.77		74.34
				0.02		1.94		83.56	2.44		90.61
				0.05		1.76		90.25	2.21		98.39
				0.08		1.68		99.26	2.02		99.99
				0.1		1.61		99.99	1.86		99.99
0.022	0.05	Toluene	298	0.0025	4	3.67		19.02	3.85		35.62
				0.005		3.52		25.26	3.72		46.01
				0.01		2.1		53.56	2.81		72.35
				0.02		1.99		82.25	2.48		88.95
				0.05		1.81		87.22	2.27		96.38
				0.08		1.7		98.88	2.08		99.93
				0.1		1.64		99.95	1.97		99.99
0.022	0.05	Kerosene	298	0.0025	4	3.72		18.61	3.92		35.14
				0.005		3.56		24.25	3.79		45.04
				0.01		2.15		54.1	2.89		70.56
				0.02		2.02		80.09	2.52		87.62
				0.05		1.85		86.33	2.32		95.54
				0.08		1.72		98.71	2.14		99.95
				0.1		1.67		99.92	2.05		99.99
0.022	0.05	o-Xylene	298	0.0025	4	3.92		16.25	3.98		29.36
				0.005		3.82		22.36	3.88		40.22
				0.01		3.72		48.94	3.77		64.59
				0.02		3.68		76.28	3.71		79.33
				0.05		3.62		83.69	3.68		86.39
				0.08		3.59		91.25	3.62		93.11
				0.1		3.52		94.59	3.54		96.33
0.022	0.05	Benzene	298	0.0025	4	3.84		12.35	3.95		16.39
				0.005		3.75		18.25	3.78		24.25
				0.01		3.61		31.2	3.67		58.95
				0.02		3.54		54.14	3.6		69.25
				0.05		3.51		69.25	3.55		75.69
				0.08		3.45		75.89	3.51		83.44
				0.1		3.42		85.29	3.48		91.25

Table.4: Results of counter current simulation (CCS) study for separation of Sc (III) from

the actual Mg-Sc alloy scrap leach solution

Sample Id	Extraction				Sample Id	Stripping				Remarks
	D2EHPA		Cyanex 272			D2EHPA		Cyanex 272		
	[Sc], mg/L	[Mg], mg/L	[Sc], mg/L	[Mg], mg/L		[Sc], mg/L	[Mg], mg/L	[Sc], mg/L	[Mg], mg/L	
LO_1	3635	65.29	2448	11.6	SO_1	285	165	125	25.4	Small quantity (1.67 % & 0.26%) co-extraction of Mg was observed with D2EHPA and Cyanex 272, respectively
LO_3	3997.6	58.35	2997.1	7.3	SO_3	5.54	166	2.26	24.8	
LO_5	3998	57.56	2997.8	7.1	SO_5	4.25	167	1.8	25.3	
LO_7	3998.4	56.48	2996.9	7.4	SO_7	4.21	165	1.7	25.2	
LO_9	3998	57.46	2996.8	7.3	SO_9	4.2	166	1.8	25.5	
LO_{11}	3998.3	56.59	2996.9	7.4	SO_{11}	4.2	166	1.8	25.4	
R_2	95.86	-	189.5	-	SS_2	11195	-	11488	-	Quantitative and selective separation of Sc(III) was achieved
R_4	0.72	-	0.92	-	SS_4	11977	-	11974	-	
R_6	0.64	-	0.71	-	SS_6	11981	-	11976	-	
R_8	0.62	-	0.68	-	SS_8	11982	-	11977	-	
R_{10}	0.61	-	0.7	-	SS_{10}	11982	-	11976	-	
R_{12}	0.63	-	0.7	-	SS_{12}	11981	-	11976	-	

Research Highlights

- ➢ Extraction of Sc(III) has been highly effective with D2EHPA than Cyanex 272
- ➢ Slope analysis method suggests cation exchange mechanism of Sc(III) with either of extractants
- ➢ Sc(III) enrichment was 12 fold in SX with both D2EHPA and Cyanex 272
- ➢ FTIR of the organic phase before and after Sc(III) extraction ensuring about complexation.
- ➢ Selective separation of Sc(III) from Sc-Mg-Scrap leach solution was resulted