

Separation and Recovery of Rare Metals by Solvent Impregnated Resin

(抽出剤含浸樹脂によるレアメタルの分離回収)

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Preface

This dissertation work was conducted under the supervision of Professor Dr. Kazuharu Yoshizuka and Professor Dr. Syouhei Nishihama at Department of Chemical and Environmental Engineering, the Graduate school of Environmental Systems, The University of Kitakyushu from 2016 to 2020.

The objective is to develop solvent impregnated resin for separation and purification of rare metals. Solvent impregnated resins were prepared and those were employed to both batch and column chromatography adsorption system after extractants were surveyed to confirm selectivity and extraction equilibrium.

The author hopes that the results in this thesis could be developed for the separation of rare metals on the industrial scale.



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Chapter 1

Introduction

1.1. Background

1.1.1. Rare Metals

Rare metals are defined as a rare metal on the earth, a metal that is difficult to extract due to technical and economic reasons, and is currently in industrial demand and is expected to be in high demand in the future, or a new industrial demand is expected due to technological innovation. Rare metals currently target 31 mineral species as Figure 1.1, but based on the definition, mineral species may be reviewed depending on the situation. Rare metals are essential materials for the production of high value products such as mobile phones, solar panels and motor of hybrid cars. Rare metals are generally localized and scarce in the earth's crust, thus it could be affected by the export policy of production country. Thus, stable supply is required to be guaranteed to be competitive in the worldwide industry [1].

Periodic Table of the Elements

The periodic table shows 118 elements. The following 31 elements are highlighted in red boxes, representing rare metals as defined by the Japan Government:

- Li (3), Be (4), Na (11), Mg (12), B (5), C (6), N (7), O (8), F (9), Ne (10)
- Al (13), Si (14), P (15), S (16), Cl (17), Ar (18)
- K (19), Ca (20), Sc (21), Ti (22), V (23), Cr (24), Mn (25), Fe (26), Co (27), Ni (28), Cu (29), Zn (30), Ga (31), Ge (32), As (33), Se (34), Br (35), Kr (36)
- Rb (37), Sr (38), Y (39), Zr (40), Nb (41), Mo (42), Tc (43), Ru (44), Rh (45), Pd (46), Ag (47), Cd (48), In (49), Sn (50), Sb (51), Te (52), I (53), Xe (54)
- Cs (55), Ba (56), La (57-71), Hf (72), Ta (73), W (74), Re (75), Os (76), Ir (77), Pt (78), Au (79), Hg (80), Tl (81), Pb (82), Bi (83), Po (84), At (85), Rn (86)
- Fr (87), Ra (88), Ac (89-103), Th (90), Pa (91), U (92), Np (93), Pu (94), Am (95), Cm (96), Bk (97), Cf (98), Es (99), Fm (100), Md (101), No (102), Lr (103)

Figure 1.1. 31 Metals defined as rare metals by Japan Government [1]

1.1.1.1. Platinum Group Metals

Platinum group metals – platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir), and osmium (Os) are six metallic elements clustered together in the periodic table, which have similar physical and chemical characteristics. The properties of PGM, such as high melting points, corrosion resistance, and catalytic qualities as shown in Table 1.1, make them indispensable to many industrial applications [2-3].

Platinum is probably the best known of this group of metals, due in large part to its use in jewelry making. It is dense, stable, and rare, and widely used in medical and

electronic devices and applications. Palladium is a soft, silvery-white metal valued for its catalytic properties. It has a high melting point, but the lowest melting point of all the PGMs. Both platinum and palladium are often used as catalysts, meaning they speed up chemical reactions without themselves being chemically involved in the process. Iridium considered the most corrosion-resistant pure metal, can resist salts, oxides, and mineral acids, but is affected by sodium chloride and sodium cyanide. It has a high melting point and is resistant to deformation, making it an excellent alloy strengthener. Rhodium and iridium are harder and more difficult to work with, although chemical compounds of these two metals are valued in a number of alloy applications. Rhodium is valued as a catalyst material and has high reflectance. It also has a low electrical resistance and a low and stable contact resistance. Ruthenium and osmium are hard and brittle, and have poor resistance to oxidation, but are valuable alloy additives and catalysts.

Table 1.1. Platinum group metals [2]

	Platinum	Palladium	Rhodium	Iridium	Ruthenium	Osmium
Chemical Symbol	Pt	Pd	Rh	Ir	Ru	Os
Atomic weight	195.08	106.42	102.91	192.22	101.07	190.23
Atomic number	78	46	45	77	44	76
Density (g/cm ³)	21.45	12.02	12.41	22.65	12.45	22.61
Melting point (°C)	1,769	1,554	1,960	2,443	2,310	3,050
Electrical resistivity (μΩ·cm at 0°C)	9.85	9.93	4.33	4.71	6.80	8.12
Hardness (Mohs)	4 - 4.5	4.75	5.5	6.5	6.5	7

PGMS are important materials for many countries, because they do not have appropriate substitute for industrial applications. PGMs are used to chemical industry as alloys, to petrochemical industry as catalysts, to electronic industry for electronic devices, to glass industry for liquid crystal displays and jewelry. In addition, PGMs are employed as the essential ingredients for lots of kinds of catalysts as shown in Table 1.2 From total demand of Pt in 2018, 40.1% of platinum was acquired for auto catalysts, 27% for jewelry, 7.9% for chemical, 2.9% for electronics, 6.1% for glass, 2.2% for petroleum. In the case of Pd demand in 2018, 80.1% was required for auto catalysts, 7.6% for electronics, 4.7% for chemical, 3.6% for dental, and 2.5% for jewelry. Total demand amounts of Pt and Pd was 223 tons, and 305.1 tons, respectively which were increased 2% for both than 2017 [4].

Table 1.2. Various kinds of PGM applied catalysts [5]

Pt-Pd-Rh auto catalysts	Reduction of toxic gases of automobile
Spent Pt-Rh or Pt-Pd-Rh alloys	Catalytic oxidation of ammonia to nitrogen oxide by air
Pt gauze catalyst	Oxidation of ammonia to produce nitric acid
Pt/Rh bimetallic catalyst	Catalytic reforming to upgrade the low octane naphtha to higher octane aromatic hydrocarbons
Pt-Zn-Hy catalyst	Hydro-isomerization of n-heptane
Pt-alumina catalyst promoted by Fe-oxide	Oxidation of CO in H ₂
Pt and Ni catalyst	Acetophenone hydrogenation, steam reforming of n-butane to produce hydrogen, and aromatic nitro compounds of reduction
Bimetallic Pt-Cu catalyst	Nitrate reduction
Pt-C catalyst	Hydroxylamine sulfate manufacturing
Pt-base metals catalyst	Reforming and isomerization catalyst
Pt-cobalt based catalyst	Fischer-Tropsch (FT) process to produce hydrocarbon from synthesis gas
Pt-Al ₂ O ₃ catalyst	Catalytic reforming
Pt-Sn-In/Al ₂ O ₃ -Li catalyst	n-Paraffin dehydrogenation to produce alpha-olefins

However, PGMs are scarce and limitedly distributed in the world. Only 0.5 ppb platinum exists in the upper parts of the earth's crust. From the research in 2018, more than 90% of PGMs are reserved in South Africa, and 5.65% in Russia, 1.74% in Zimbabwe. 72.5% of the mine production was in South Africa, 11.7% in Russia and 5.8% in North America. However, the total supply of Pt achieved by mine production was only 74.2%, and that of Pd was achieved by only 74.7%. The other 25 % for both metals to meet demand was supplied by recycling from secondary sources. Secondary resource of PGMs are mainly jewelry and spent automobile catalyst. In 2018, Pt was recycled from auto catalyst scrap and jewelry as the amount of 16.5% and 9.3% of total supply, respectively. Pd was also recovered from auto catalyst scrap as the amount of 24.7% of total supply [3, 6]. Thus, in view of resource sustainability, recycling of PGMs are inevitable. Then, these waste materials are required to be separated to obtain concentrated metals by pyro/hydrometallurgical process.

1.1.1.2. Rare Earth Elements

Rare earth elements (REEs) are 17 elements in periodic table including 15 lanthanides with scandium and yttrium. REEs can be divided into two groups: heavy rare earth or light rare earths. The heavy rare earths includes lanthanide elements from terbium (atomic number 65) to lutetium (atomic number 71), including yttrium (Y), while the light rare earths includes from lanthanum to gadolinium (atomic number from 57 to 64), and scandium (Sc), as shown in Figure 1.2 [7]. The light rare earth elements are more incompatible and more concentrated in the earth's crust than heavy rare earth elements.

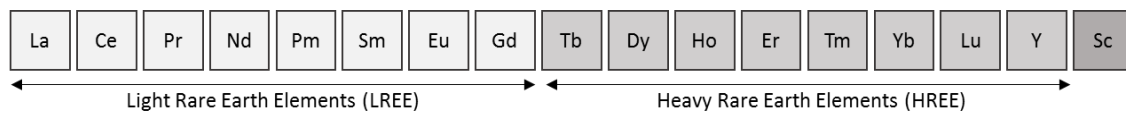


Figure 1.2. Rare earth elements

REEs are relatively abundant in the Earth's crusts not as their name [8,9]. However, they are produced only as a by-product during processing of various ores at low concentrations, or in combination with a variety of minerals, not only as a pure metal because of similarity among them. High-technology and environmental applications of the rare earth elements have grown dramatically in diversity and importance over the past four decades.

Figure 1.3 shows the supply and demand from 1975 to 2015. Both supply and demand are increasing. In the 1980s, REEs chemicals were used as carbonates and chlorides. From 1990s, REE oxides and metals were in demand, and it was started to be applied to REE magnets, phosphors, and polishing powders. And in the 2000s, REEs have gained attention as components of magnets, computer hard drive, electronic motors and liquid crystal displays. The annual growth of REE consumption is expected to increase more than 5% through 2020 globally.

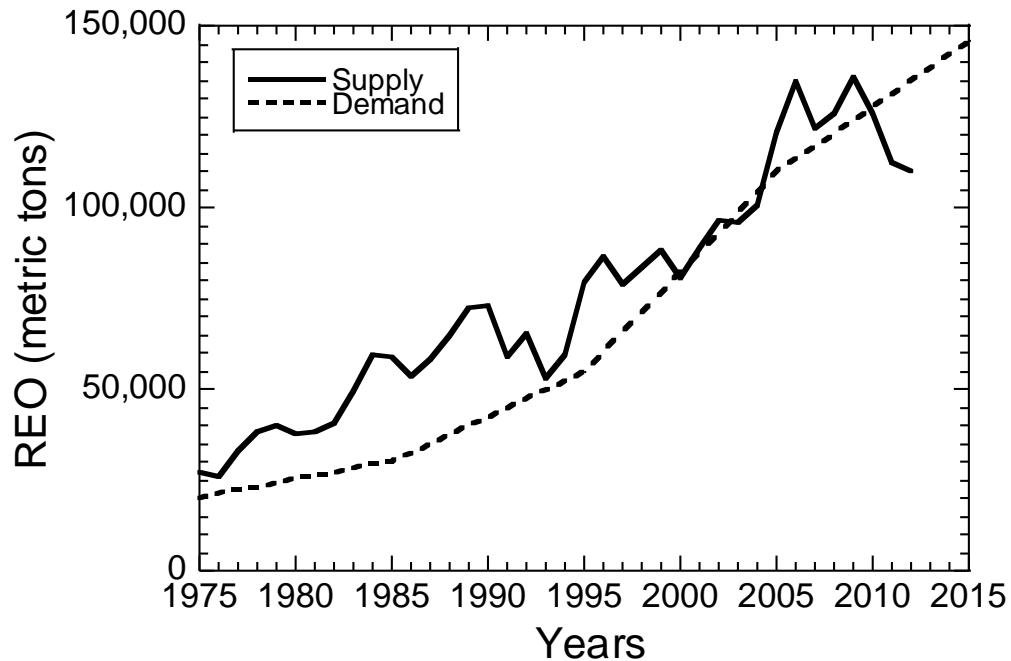


Figure 1.3. Supply and demand of REEs from 1975 to 2015 [7, 10]

Recently, about 19% of REEs are used for catalyst, since REEs are imperatively essential in automobile catalysts to convert the pollutants into non-toxic exhaust gas as in Figure 1.4. Also, REEs are critical in permanent magnets. From 1960s until now, although the main rare earth elements adopted for magnets were changed from samarium-cobalt magnets to neodymium which are significant for hybrid cars, 21% of REEs production is still necessary for permanent magnets because of the potential to increase the energy efficiency. The other 18% was for metallurgical alloys in ignition device, gas turbine engines, and electric generators. 7% was for phosphors for computer screens and liquid crystal display. REE in phosphors were used to display colors, and energy efficient lighting. The resultant share of REEs was also used for polishing, glass, ceramics, and others. As many of these applications are highly specific, in that substitutes for the REE are inferior or unknown, the REE have acquired a level of technological significance much greater than expected from their relative obscurity.

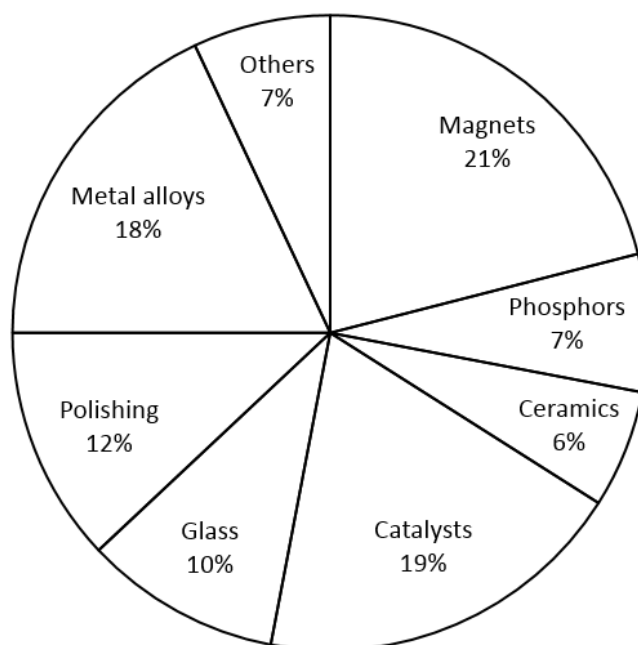


Figure 1.4. REEs applications [7]

As shown in Figure 1.3, demand is increasing and there is a necessary to secure supply from resources. Those resources of rare earths are primarily in four geological environments: carbonatites, alkaline igneous systems, ion-adsorption clay deposits, and monazite-xenotime-bearing placer deposits. Ion adsorption clays are the leading source of production of heavy rare-earth elements, while carbonatites and placer deposits are the leading sources of production of light rare earth elements. However, primary resources of REEs are limitedly distributed. More than 30% of REEs are reserved in China, and around 18% of REEs are also reserved in Brazil and Vietnam. In 2016, 84% of REEs were produced in China, 11% from Australia, 2% from Russia, 1% from India, Brazil, and others, respectively [8]. In those countries, REEs are extracted from four minerals: bastnaesite, monazite, xenotime, and loparite. Relatively abundant LREEs are composed of most of those minerals, while HREEs are concentrated in ion adsorption clay in southern China. In history, world REO production was increasing for all these years, but slightly fluctuated due to world's situation. For example, in 2006, China started to tighten rare earth export and production, production of rare earth was decreased sharply. Further, the limited distribution of rare earth resources concentrated in China suggests the possibility of the weaponization of rare earths. Thus, in view of resource sustainability, recovery and separation of REE are inevitable.

Among REEs, in specific, scandium is a soft, light, and silvery metal which looks similar as aluminum. Sc is known as an extremely rare and expensive element because of difficulty in metallurgical processes. Although its occurrence in Earth's crust is more than that of lead, deposits of minerals with high concentration scandium is rare. Sc is

mainly obtained as a by-product of uranium and tungsten production and by-products from apatite and titanomagnetite mining with the problem of radioactivity. However, Sc extraction from uranium waste involves a high level of radioactivity, and there are concerns about problems such as radioactive release into the environment. In nature such as from red mud, Sc is mainly found with Y and other heavy rare earth elements due to similarity in chemical and physical properties. For scandium, the principal use of Sc is aluminum - scandium alloys and solid oxide fuel cells (SOFCs). Other uses for scandium includes ceramics, electronics, lasers, lightning, and radioactive isotopes. In SOFCs, electricity is generated directly from oxidizing a fuel. Aluminum - scandium alloys are produced for sporting goods, aerospace, and other high-performance applications. Scandium is used in small quantities in a number of electronic applications. As demand for SOFCs grows, the recovery and recovery of scandium is essential [11].

1.1.2. Separation methods

1.1.2.1. Solvent extraction

Solvent extraction is one of hydrometallurgical methods to separate and recover the solutes. Two immiscible solvents are brought into contact with each other to transfer solutes (in this case, metal) from one phase to the other. This method is widely used because it is simple, easy to operate, can be rapidly performed and has high selectivity although it has high environmental load.

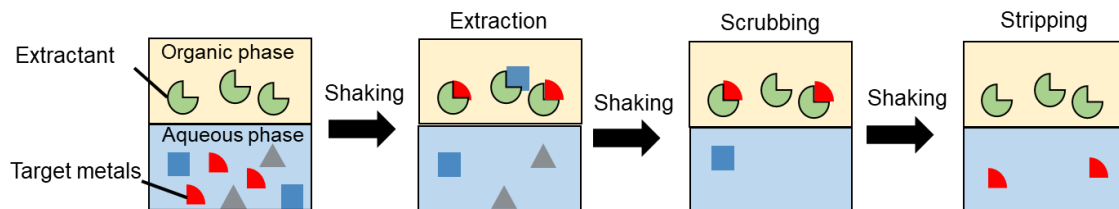


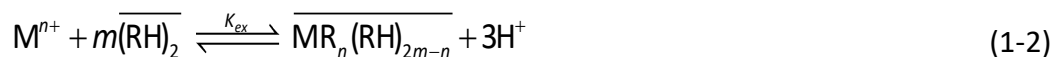
Figure 1.5. Solvent extraction processes

Solvent extraction process is basically composed of three steps as Figure 1.5: extraction, scrubbing, and stripping. In extraction, target metal is extracted selectively by organic solvent, then co-extracted metals are removed by scrubbing solution. Stripping is conducted to take the metals loaded in organic phase into aqueous phase. To describe extracted amount by solvent extraction, we use distribution ratio. The distribution ratio (D) was defined as:

$$D = \frac{[\bar{M}]}{[M]} \quad (1-1)$$

where $\overline{[M]}$ and $[M]$ are concentrations of metals in the organic phase and aqueous phase, respectively.

Slope analysis method is generally applied to verify extraction mechanism by determining the number of protons and extractants involved in solvent extraction [12, 13]. When M^{n+} is a metal cation and RH is acidic extractant that forms dimer in the organic phase, the extraction could be described as follows:



The equilibrium constant K_{ex} and distribution ratio D can be represented as Eq. (1-3) and (1-4).

$$K_{ex} = \frac{[\overline{MR_n(RH)_{2m-n}}][H^+]^n}{[M^{n+}][\overline{(RH)_2}]^m} \quad (1-3)$$

$$D = \frac{[\overline{MR_n(RH)_{2m-n}}]}{[M^{n+}]} \quad (1-4)$$

By substituting (1-4) into (1-3), (1-3) can be written as (1-5).

$$K_{ex} = \frac{D[H^+]^n}{[\overline{(RH)_2}]^m} \quad (1-5)$$

By taking the log on both sides, (1-5) will can be rewritten as (1-6)

$$\log K_{ex} = \log D + n\log[H^+] - m\log[\overline{(RH)_2}] \quad (1-6)$$

Since $\text{pH} = -\log[H^+]$, (1-6) can be converted as (1-7).

$$\log D = \log K_{ex} + m\log[\overline{(RH)_2}] + n\text{pH} \quad (1-7)$$

At constant concentration of $[\overline{(RH)_2}]$, this equation represents the equation of a line with $\log D$ as y-axis, pH as x-axis and $\log K_{ex}$ as of y intercept of this line. At constant

pH, the plot of $\log[\overline{(RH)}_2]$ vs $\log D[H^+]^3$ will give a straight line, having slope equal to total number of extractant molecules participating in the complex formation.

1.1.2.2. Solvent Impregnated Resins (SIRs)

Solvent extraction and ion exchange are well known two hydrometallurgical methods to recover metals. Solvent extraction has lots of merits as shown in 1.1.2.1. However, the main drawback of solvent extraction is the use of large amount of organic solvent and loss of organic solvents which could be environmentally unfriendly. Ion exchange has high adsorption ability from diluted solution with low environmental load and easy to handle, however it has lower selectivity, slower adsorption kinetics, and synthesis of ion exchange resin is time consuming and complex. Thus, solvent impregnated resin (SIR) is getting attention recently, which basically combines advantages of solvent extraction and ion exchange in polymeric adsorbent material [14, 15]. By impregnation, SIR has obtained the straightforward mechanism of metal ions by solvent extraction with selectivity of extractants without third phase, the possibility of employing continuous separation and relative simplicity in preparation. SIRs have been prepared to separate various metals using different support resins and extractants. Schematic image of extraction of metal by SIRs are shown in Figure 1.6 [16]. The organic extractant (E) is impregnated inside of the porous particles. On the one hand, solute S initially dissolved in the aqueous phase is moved in the organic extractant phase by forming complex ES during the extraction process.

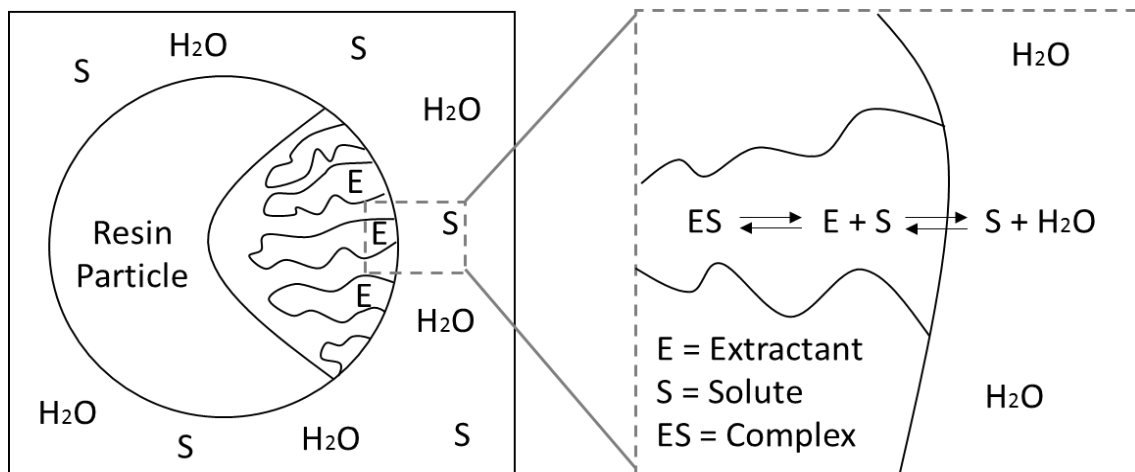


Figure 1.6. Solvent impregnated resin adsorption process [16]

Unfortunately, the main disadvantage of SIRs is the leakage of solvent in the aqueous phase. The leakage of solvent results in loss of adsorption capacity and environmental hazard. Coating of SIRs of solvent has been conducted to prevent leakage

using different kinds of polymers such as poly(sulfone) [17, 18], co-polymer of glycidyl methacrylate and N,N-methylene-bis(acrylamide) [19], and crosslinked polyvinyl alcohol (PVA) [14]. The first two has disadvantages of complex coating procedure and the usage of organic solvent, respectively. Thus, in this work, SIR is prepared and coated by crosslinked PVA as shown in Figure 1.7. At first, resin was washed with methanol to remove monomer, then washed resin was immersed in diluted extractant. SIR is then coated by thin polymeric film, employing 3wt% polyvinyl alcohol. Coated SIR was crosslinked using glutaraldehyde (GA) under acidic conditions, then coated SIR which is possible to suppress leakage of the extractant is obtained. In previous papers concerning SIR coated with crosslinked PVA, the thickness of the layer of the PVA on the SIRs were reported to be 10–15 μm [14] and 3–5 μm [20]. Figure 1.10 shows the SEM images of HP2MG, SIR, and SIR-GA by observing a scanning electron microscope (SEM, Keyence VE-8800) without spatter coating.

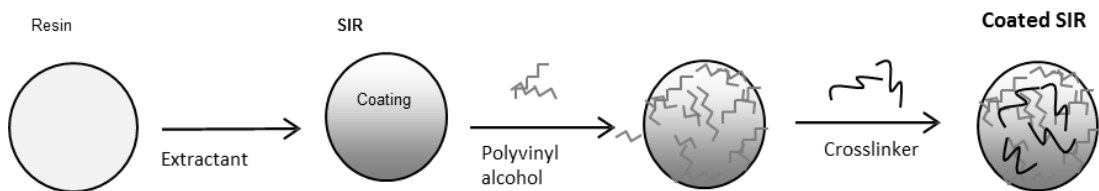


Figure 1.7. Preparation of coated SIR.

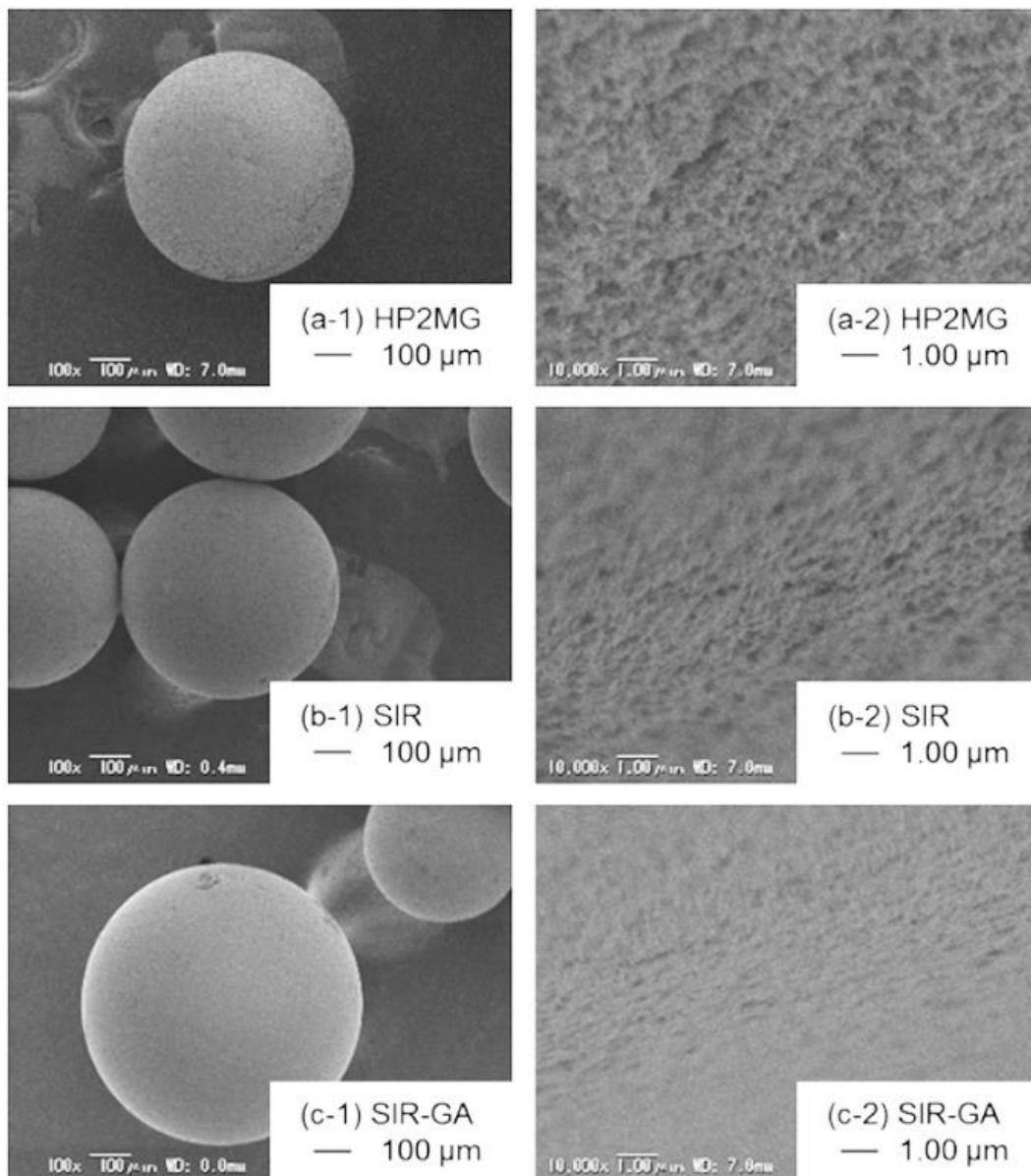


Figure 1.8. Scanning electron micrographs of (a) HP2MG, (b) SIR, and (c) SIR-GA.[21]

1.1.2.3. Principle of analyzer: ICP-AES

Inductively coupled plasma atomic emission spectroscopy (ICP-AES), is an analytical technique that uses a plasma as a source and relies on optical emission for analysis. In this instrument, excited electrons by a high temperature argon plasma emit energy at a specified wavelength when they return to ground state. Since their energy transfer varies from element to element depending on the electron composition of the orbit, so the wavelength of emitted light is unique. Each element emits energy at different wavelengths, and the intensity of the energy emitted at the selected wavelength is proportional to the amount (concentration) of the elements in the given feed solution under analysis. Thus, by determining the wavelength emitted from a

sample and determining its intensity, the elements of a given sample could be determined qualitatively and quantitatively. In this work, the concentration of metals in aqueous solution was determined using ICP-AES.

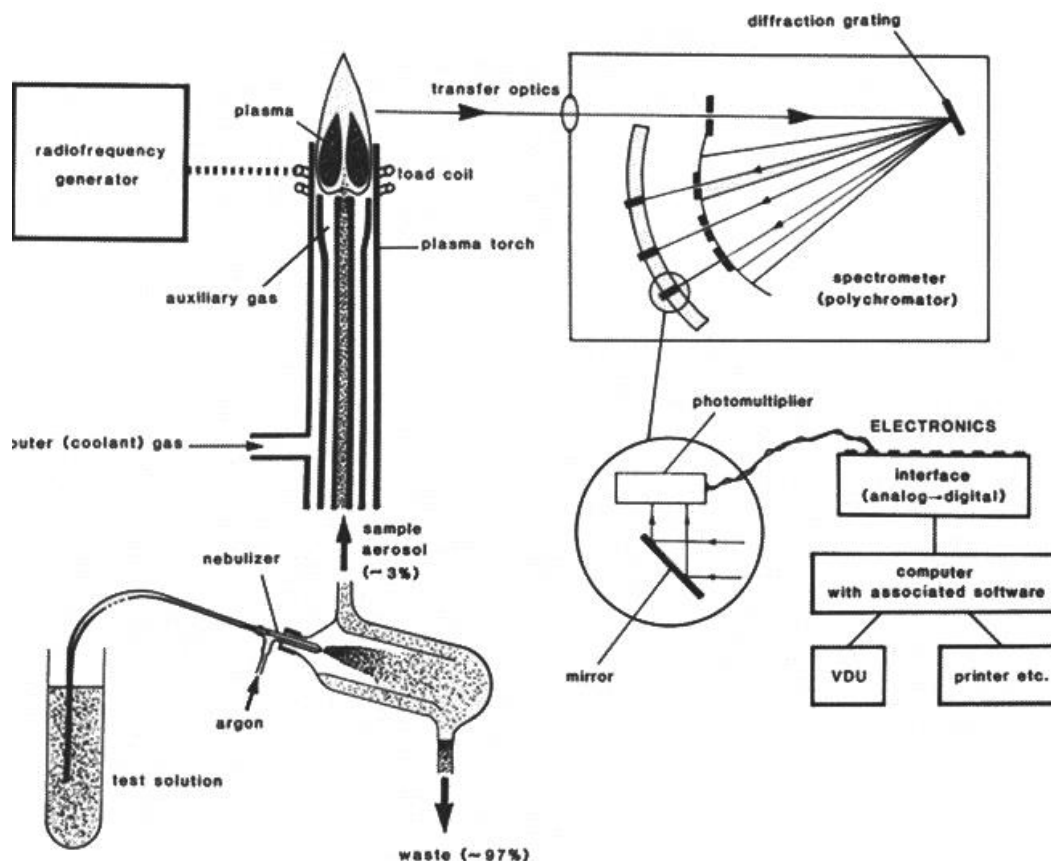


Figure 1.9. Schematic diagram of ICP system [22]

1.1.3. Previous works of separation metals

1.1.3.1. Separation of platinum group metals

Platinum group metals are getting attention due to their admirable characteristics, thus demand is skyrocketing. 25% of total demand of those was satisfied by recycling spent automobile catalyst and old jewelry since spent automobile catalysts contain high content of platinum group metals, and composed simply with impurities of Al_2O_3 or activated carbon. Thus, recovering PGMs from spent automobile catalysts have been widely examined [19-23]. In hydrometallurgical processing, metals are leached directly or after pretreatment using suitable solution such as hydrochloric acid, sulfuric acid and nitric acid, etc. By dissolving spent automobile catalysts in hydrochloric acids, platinum group metals usually present as anionic complexes. Thus, in the case of employing solvent extraction, PGMs are extracted by anion exchange applying various extractants in hydrochloride solutions. Separation by anion exchange of PGMs are

conducted based on the differences in anion charge/size, or stability of their chloro-complexes.

In the leaching solution of spent automobile catalysts, PGMs have to be separated from each other and from base metals. Barakat *et al* [28] discovered that Pt can be obtained by solvent extraction over Rh and Fe with high purify in 0.01 mol/L HCl using tri-octylamine diluted in kerosene. Jaree and Khunphakdee [29] also used tri-octylamine which is diluted in toluene, and they selectively extracted Pt and Rh and stripped by 8 mol/L nitric acid while Barakat *et al.* obtained Pt by precipitation. Marinho *et al.* [30] demonstrate that Pt can be extracted from leaching solution of spent automobile catalysts, using kerosene diluted Aliquat 336 (methyltrioctylammonium chloride), and can be stripped using sodium thiosulfate. Sun and Lee [31] compared various extractants to recover Pt from Rh which would be expected to exist in the leaching solution of spent automobile catalysts. However, separation of Pt from Rh was proceeded by amine based extractants (tri-n-dodecyl amine, tri-iso-octyl amine, and Trioctylmethylammonium chloride) except tri-octyl/decyl amine only in 9 mol/L HCl while neutral extractants, tri-butylphosphate and trioctylphosphine oxide, extract Pt from Rh with lower extraction yield or lower stripping yield. Although lots of researches were conducted, reported previous works had limitations such as low extraction, lower separation, use of phase modifiers, and limited use of metals.

In the case of ion exchange, Sun and Lee [32] used PC-88A Resin to recover Fe(II) and Al(III) from Pt which would be expected to exist in the leaching solution of spent automobile catalysts. However, in the column chromatography, simultaneous extraction of Fe(II) and Al(III) from Pt was found to be difficult. Purolite S985 and Lewatit MP 600 WS were used to separate Pt, and those excel among other anion exchangers [33]. It has been achieved to recover Pt by adsorption using weakly basic anion exchange resin WA30 and selective recovery of Pt by adsorption and elution with WA21J. However, the selective recovery of Pt by WA21J is disadvantageous in terms of selectivity due to the use of an ion exchange resin.

Platinum group metals were also separated by solvent impregnated resin. Rovira *et al.* [34] also applied Alamine 336 impregnated resin to separate Pd(II) and Pt(IV) from Rh(III) at low HCl concentrations, as well as partial separation between Pd(II) and Pt(IV) at high acid concentration. Tanaka *et al.* [35] prepared a SIR by impregnating di-hexyl sulfide (DHS) and employed DHS-SIR along with weak anion exchange resin, WA-21J, to separate and recover PGMs from leaching solution of spent automobile catalyst. However, the separation of Pt and Rh by WA 21J was incomplete, while Pd was selectively recovered by DHS-SIR from the other PGMs.

In the chapter 2 of this work, the selective recovery of Pt and Pd from the leaching solution of spent automobile catalyst using SIRs was explored. Amine based extractant impregnated resins which have secondary amine group similar to WA-21J and

di-hexyl sulfide impregnated resin were employed to separate of Pt and Pd leached from spent automobile catalyst.

1.1.3.2. Separation of rare earths

Rare earth elements are essential in various applications owing to their admirable physicochemical properties. Thus, separation and recovery of REEs have been investigated using various organic solvents and ion exchange resins. Solvent extraction is usually adopted for rare earths due to applicability for large scale and simplicity. Various kinds of organophosphorus compounds and carboxylic acids are used for rare earth's separation. Figure 1.10 shows three kinds of organophosphorus extractants. Although phosphoric acid, such as bis(2-ethylhexyl)phosphoric acids (D2EHPA) shows the highest extractability among organophosphorus extractants, stripping yield of the metals from loaded organic phase is the lowest [36]. Phosphonic acid esters, such as 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), was gained popularity, because the stripping was possible than lower acidities than phosphoric acid [37]. The use of PC-88A to recover REEs was also suggested from NiMnH Batteries [38]. Phosphinic acids have also been examined for REEs, such as dysprosium and terbium [39]. Cyanex 272 shows better stripping yield than phosphoric and phosphonic acids, but extractability was lower than that of those. Specifically, Sc was recovered using organophosphorus acids, D2EHPA and Cyanex 302, one of the organophosphorus acids, selectively extracted Sc from rare earth leach solution [35-38].

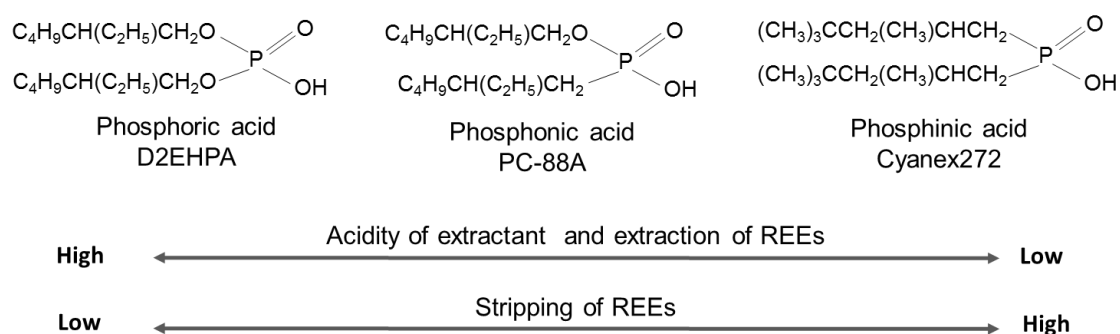


Figure 1.10. Organophosphorus Extractants

Also, the use of different carboxylic acids for extracting REEs were reported for the extraction of rare earths owing to their low costs and availability. The pK_a value of carboxylic acids is less than phosphinic acids, but higher than that of phosphonic acids, which means the extractability of carboxylic acid is lower than PC-88A but higher than Cyanex 272. It proposes the possibility of higher stripping yield of carboxylic acids than phosphonic acids and phosphoric acids. Extraction behavior of yttrium was verified by

Versatic acid 10 and naphthenic acid with different selectivity order. The changing order to the steric hindrance caused by the structure of the carboxylic acid and the atomic number of the REE was also verified [13].

Solvent extraction of REEs by carboxylic acids and phosphinic acids can be described as follows:



where $\overline{(\text{RH})}_2$ denotes dimeric form of extractants, and Ln^{3+} refers the elements of rare earth elements.

These organophosphorus acids and carboxylic acids were also applied for solvent impregnated resin. Nishihama *et al.* [21] applied PC-88A on methacrylic porous polymer to make SIR and recovered lanthanum and cerium and reusability of SIR was also confirmed.

Scandium, one of the rare earth elements which is indispensable and irreplaceable, is usually extracted with Y and heavy lanthanides while extracting REEs due to small ionic radius. It is well known that strip from organic phase is difficult.

Recovery of scandium in acidic sulfate solution solvent impregnated resin, TP272, which is commercially available [44]. TP272 reached equilibrium in 12 h and showed high separation factor for Sc(III) and Fe(II), and Sc(III) and Al(III). Ochsenkuhn-Prtropulu *et al.* [45] reported extraction separation of rare earth metal Sc including Sc using D2EHPA. Separation of Sc from rare earth metals at pH = 0 was easily achieved, but the stripping of Sc was carried out using 6 mol/L HCl. In addition, when the extraction of Sc proceeded below pH 1.0, stripping is difficult, it can be expected that a high concentration of acid is required. Di-(2-ethylhexyl) phosphoric acid (D2EHPA) was applied to separate Sc with tributyl phosphate as modifier, and successfully separate Sc from magnesium but failed to strip Sc with any concentration of HCl with co-extracting iron. [46] The stripping of Sc from Cyanex 272, Cyanex 302, and Cyanex 301 was much easier than from D2EHPA and HEHEHP. The stripping efficiencies of Sc(III) were 82%, 78%, and 75% with 1.5 mol/L, 3.5 mol/L and 5.8 mol/L H₂SO₄ solutions, respectively [43, 44].

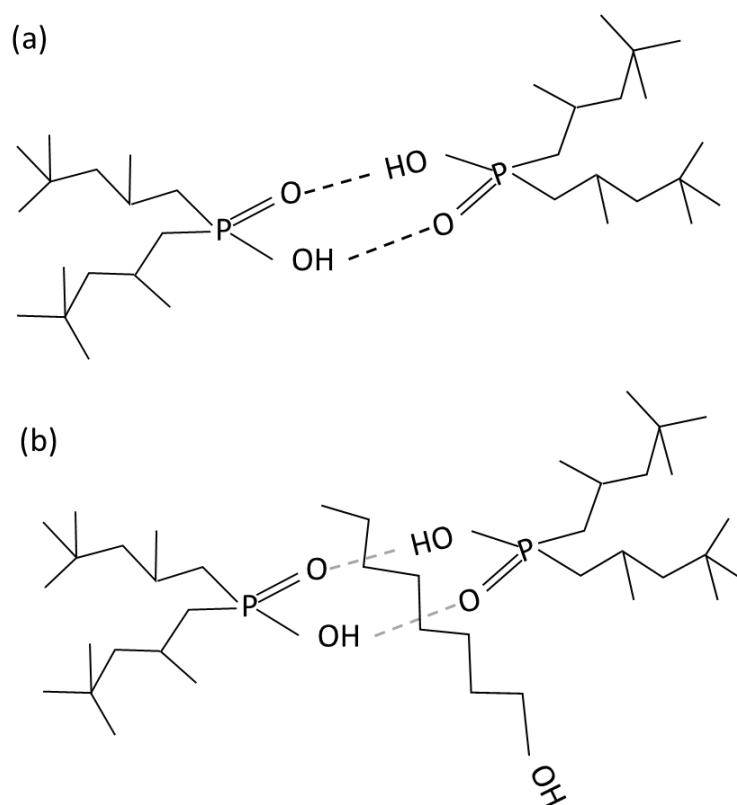


Figure 1.11. The effect of addition of 1-octanol to dimerized extractant

In the Sc stripping of the solvent extraction method, it was found that by adding 1-octanol to the organic phase, the distribution ratio in the Sc extraction can be decreased, and also the stripping of the multistage Sc is possible [49]. Dimerized extractant was separated by adding 1-octanol into the organic phase as shown in Figure 1.11.

This study, in the chapter 3 and 4, examined the extraction separation of Sc and Y using Cyanex272 which has higher acidity and Versatic acid 10, a kind of carboxylic acid which has lower extractability than phosphoric acid and phosphonic acid. In addition, the effect of adding 1-octanol, which has been reported to be effective in reducing the distribution ratio of Sc in the past study to achieve a full Sc stripping, was also explored.

1.2. Purpose of this study

In this study, the separation and recovery of rare metals was investigated using solvent impregnated resin. As elements for separation and recovery, Pt and Pd as platinum group metals, in the automobile waste catalyst, and Sc and Y as rare earth elements, were used. The contents and purpose of this study were as follows.

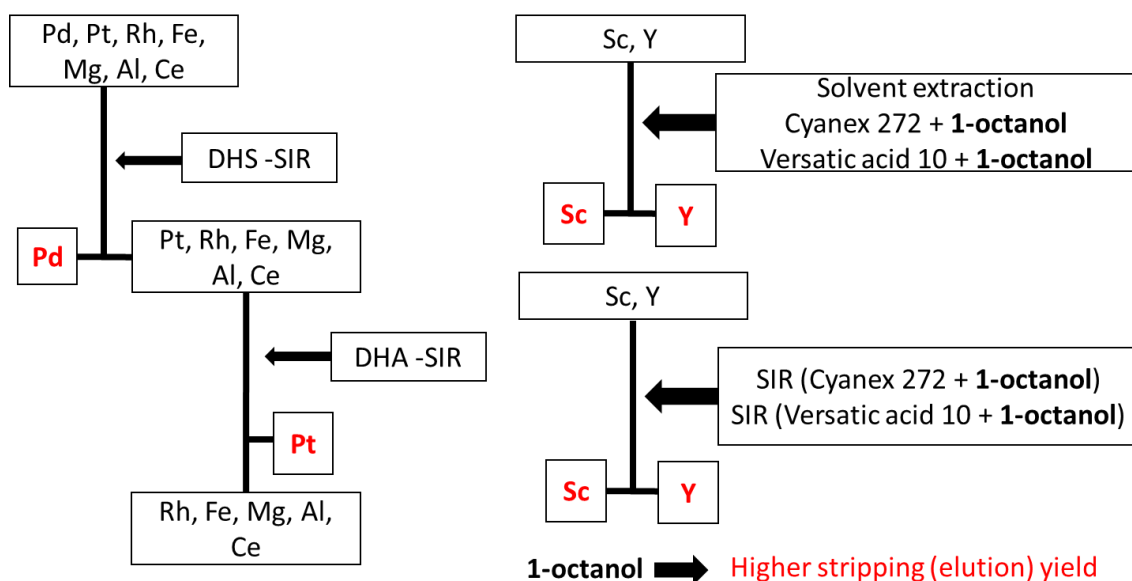


Figure 1.12. Structural scheme of this work

1. Separation and recovery of Pt and Pd from the leaching solution of automobile waste catalyst was carried out by coating SIR impregnated with di-n-hexylamine, an amine extractant, and SIR with di-hexyl sulfide, followed by elution process. The purity measurement of the obtained metal and the structural analysis by XRD are also parallel conducted. Targeted purity is more than 99.9%.
2. The separation coefficient is determined from the extraction equilibrium constant obtained by investigating the extraction equilibrium relationship between Sc and Y by solvent extraction using Cyanex272 as an extractant. In addition, to achieve Sc full stripping, the extraction and addition of 1-octanol are used to investigate the variation and optimum amount of extraction. Based on solvent extraction, the adsorptive separation of Sc and Y is carried out using the prepared coated SIR. Elution was also conducted using HCl, and the difference among SIRs depending on the added amount of 1-octanol was examined.
3. Separation coefficient is determined from the extraction equilibrium constant obtained by investigating the extraction equilibrium relationship between Sc and Y by solvent extraction using Versatic acid 10 as an extractant. The metal loaded organic phase is stripped by using HCl. In addition, to achieve Sc full stripping, the extraction and stripping were investigated using extractants added with 1-octanol. Based on the results obtained from solvent extraction, a coated SIR is prepared, and adsorptive separation of Sc and Y is carried out. Successive adsorption and elution processes were performed to confirm the availability of solvent-impregnated resins.

Chapter 2

Separation of Platinum Group Metals Using Solvent Impregnated Resin

2.1. Introduction

The separation of platinum and palladium using a solvent-impregnated resin coated with polyvinyl alcohol crosslinked by glutaraldehyde was investigated. Various extractants were impregnated to SIRs and those SIRs were compared to confirm selectivity of platinum from other base metals and platinum group metals existing in leaching solution of spent automobile catalysts. By comparative study, di-n-hexylamine impregnated resin was finally applied to the chromatographic recovery of Pt and di-hexyl sulfide impregnated resin which is selective for Pd verified from previous study [35] were applied to recovery of Pd, and quantitative adsorption-elution was performed via a frontal analysis mode for both metals. Finally, Pt was obtained from the eluent of the sequential chromatography system by simultaneously precipitating and reducing Pt with sodium borohydride. This chapter is partially overlapped with my master thesis, but it is more developed to achieve entire separation of platinum and palladium by applying sequential column chromatography system.

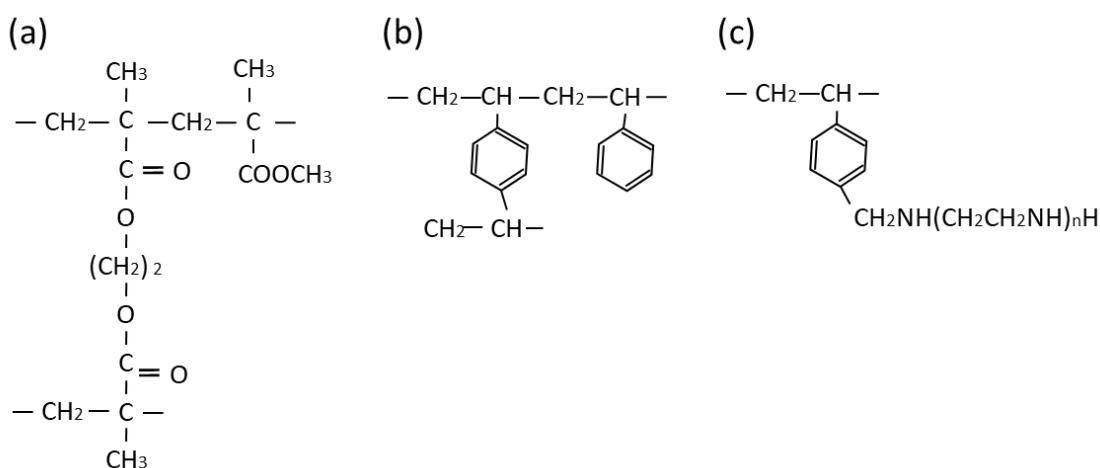


Figure 2.1 Three kinds of resin which was used in this work
 (a) DIAION HP2MG (b) DIAION HP20 (c) WA-21J

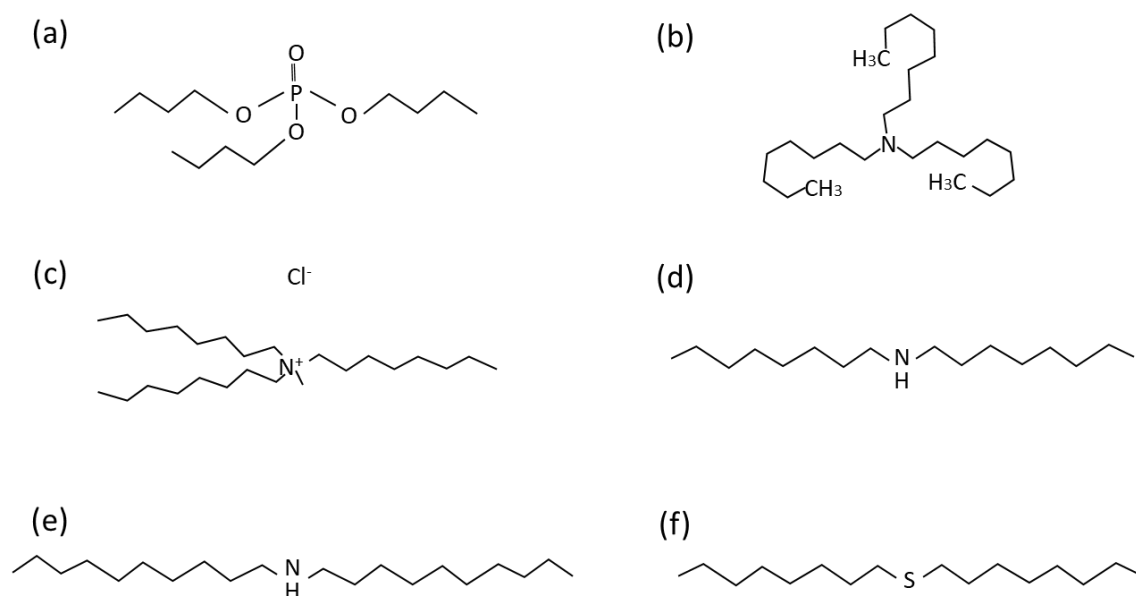


Figure 2.2 Structure of extractants used in this work

(a) Tributyl phosphate (b) Trioctylamine (c) Methyltrioctylammonium chloride
(d) Di-n-hexylamine (e) Di-octylamine (f) Di-hexylsulfide

2.2. Experiments

2.2.1. Reagents

Synthetic porous adsorbents DIAION HP20, HP2MG, and WA-21J which are shown in Figure 2.1 were supplied by Mitsubishi Chemical Corporation (Tokyo, Japan). DIAION HP20 is based on polystyrene/divinylbenzene matrix, DIAION HP2MG is non-ionic, highly porous synthetic adsorbent based on polymethacrylate matrix while WA-21J is polyamine type weakly basic anion exchange resin. The particle sizes of the adsorbents are, on average, 440 μm (250-600 μm) for HP20, 490 μm (355-850 μm) for HP2MG, and 610 μm for WA-21J, respectively as shown in Table 2.1. Tri-n-octylamine (TOA) was supplied by TCI Development Co., Ltd. (Shanghai, China). Secondary amines, Di-n-hexylamine (DHA) and Di-octylamine (DOA) were supplied by Tokyo Chemical Co., Ltd. (Tokyo, Japan) and Di-hexylsulfide (DHS) was supplied by Daihachi Chemical Industry Co., Ltd. (Osaka, Japan). Structure of extractants were shown in Figure 2.2. All other reagents were supplied by Wako Pure Chemical Industries, Ltd. (Osaka, Japan) as analytical-grade reagents.

Table 2.1. Detailed information about resins used for SIR and comparative studies

	DIAION HP20	DIAION HP2MG	WA-21J
Resin type	polystyrene/divinylbenzene	Polymethacrylate	Weak base anion
Particle Density	1.01 g/mL	1.09 g/mL	1.07 g/mL
Water content	55 – 65%	55-65 %	40 – 52%
Particle size distribution	250-600 μm	355-850 μm	610 μm

2.2.2. Preparation of coated SIR

Preparation SIR and successive coating of the SIR was carried out with the same method in a previous paper [14]. Support resin, HP20 or HP2MG, (40 g) was first washed by immersing in methanol (400 mL) and dried at 25 °C for 12 h. The washed HP20 (40 g) was immersed for 12 h in the solution (50 mL) of 0.2 mol/L DHA or 0.2 mol/L DOA in toluene, while the washed HP2MG (40 g) was immersed for 12 h in the solution (50 mL) of 0.1 mol/L DHS in acetone. 0.1 mol/L of TBP (tri-butyl phosphate), TOA, TOMAC were diluted in toluene and impregnated on HP2MG.

Diluent, toluene or acetone, was then evaporated thoroughly to produce the SIRs impregnated TBP (TBP-SIR), TOA (TOA-SIR), TOMAC (TOMAC-SIR), DHA (DHA-SIR), DOA (DOA-SIR), and DHS (DHS-SIR). The impregnation amounts of DHA, DOA, and DHS, determined by material balance, were 5.59 mmol/g, 4.60 mmol/g, and 1.48 mmol/g, respectively. Coating of SIRs were conducted using PVA, of polymerization degree ca. 2000, crosslinked by glutaraldehyde (GA). The prepared SIR (3 g) was immersed in an aqueous solution (50 mL) containing 3 wt% PVA and 1 wt% acetamide and the mixture was shaken for 17 h. The resultant suspension was then mixed with 1 mol/L KCl aqueous solution (10 mL) and the mixture was shaken for 24 h. The pretreated SIR was filtered and re-suspended in a 0.32 mol/L H₂SO₄ solution (10 mL) for 1 h. 0.32 mol/L GA aqueous solution (10 mL) was then added, followed by shaking the mixture for 24 h, to complete crosslinking. The coated SIR obtained was filtered, washed with deionized water, and then dried. Hereafter, prepared coated SIRs were used in the present study.

2.2.3. Batch Experiments

Aqueous feed solution was prepared by mixing chloride salts of Pt, Mg, and Fe in HCl solution for ternary solution. In the pH dependency experiments, the concentration of each metal ion was set to 50 mg/L ([Pt] = [Mg] = [Fe] = 50 mg/L) and the real leaching solution was also used ([Pt] = 99.5 mg/L, [Pd] = 50.6 mg/L, [Rh] = 15.3 mg/L, [Al] = 2215 mg/L, [Mg] = 4045 mg/L, [Fe] = 476 mg/L, and [Ce] = 4165 mg/L). HCl concentration was set to 5 mol/L for adsorption isotherm experiments. The SIR (20 mg) was added to 20 mL of aqueous solution, and the suspended mixture was shaken at 298 K for 24 h. The

concentrations of the metal ions were determined, after filtration of the resin, with an inductively coupled plasma atomic emission spectrophotometer (ICP-AES; Shimadzu ICP-9000). The amount of adsorbed metal ion, q (mmol/g), is defined as:

$$q = \frac{([M]_{ini} - [M]_{eq})V}{W} \quad (2-1)$$

where $[M]_{ini}$ and $[M]_{eq}$ are initial and equilibrium concentrations of metals in the solution (mmol/L), respectively, V is the volume of the solution (L), and W is the weight of the resin (g).

2.2.4. Column experiments

Two kinds of operation modes, single column adsorption mode and sequential column adsorption mode, were used for the chromatographic separation of Pt. DHA-SIR (wet volume = 1.70 mL) was packed into a glass column of 100 mm in length and 8 mm in diameter, and then D.I. water was fed to the column to wash the adsorbent for 12 h. Aqueous feed solution of 5 mol/L HCl solution containing 50 mg/L of single Pt or actual leaching solution of automobile catalyst containing [Pt] = 99.5 mg/L, [Pd] = 50.6 mg/L, [Rh] = 15.3 mg/L, [Al] = 2215 mg/L, [Mg] = 4045 mg/L, [Fe] = 476 mg/L, and [Ce] = 4165 mg/L was fed upward to the column packed with DHA-SIR at flow rate of 0.17 mL/min {space velocity (S.V.) = 6 h⁻¹}, using a peristaltic pump (EYELA, SMP-21).

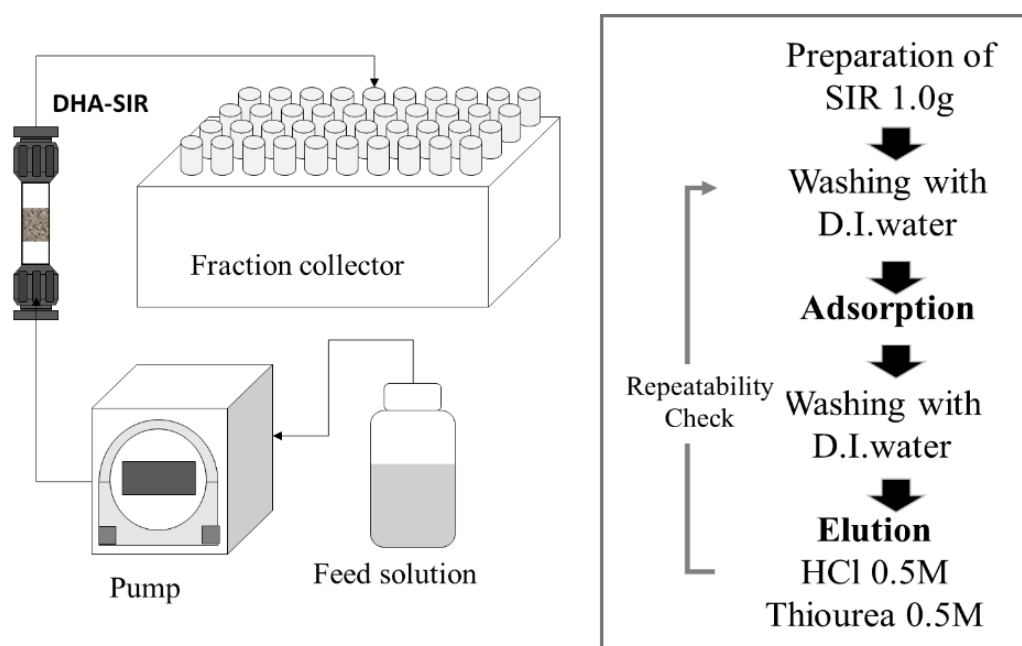


Figure 2.3. Column experimental setup

In the case of sequential chromatographic separation, DHS-SIR (wet volume = 1.6 mL) for Pd adsorption was used followed by DHA-SIR (wet volume = 1.7 mL) for Pt adsorption. The leaching solution was first fed to the column packed with DHS-SIR (S.V. = 6.2 h⁻¹), and this effluent was fed to the column packed with DHA-SIR (S.V. = 6.0 h⁻¹). The metal ions loaded into the columns were separately eluted with 1.5 mol/L ammonia solution in case of DHS-SIR, and with 0.1 mol/L thiourea – 0.5 mol/L HCl solution, and 0.5 mol/L thiourea solution in case of DHA-SIR, respectively. The eluents were determined by the preliminary study for optimizing eluents using various acids and bases. The effluents were collected with a fraction collector (EYELA DC-1500). The number of bed volumes of the effluent is defined as:

$$\text{Bedvolume} = v \cdot t / V \quad (2-2)$$

where v , t , and V are the volumetric flow rate of solution, the time for which the feed solution was applied, and the wet volume of the adsorbent, respectively.

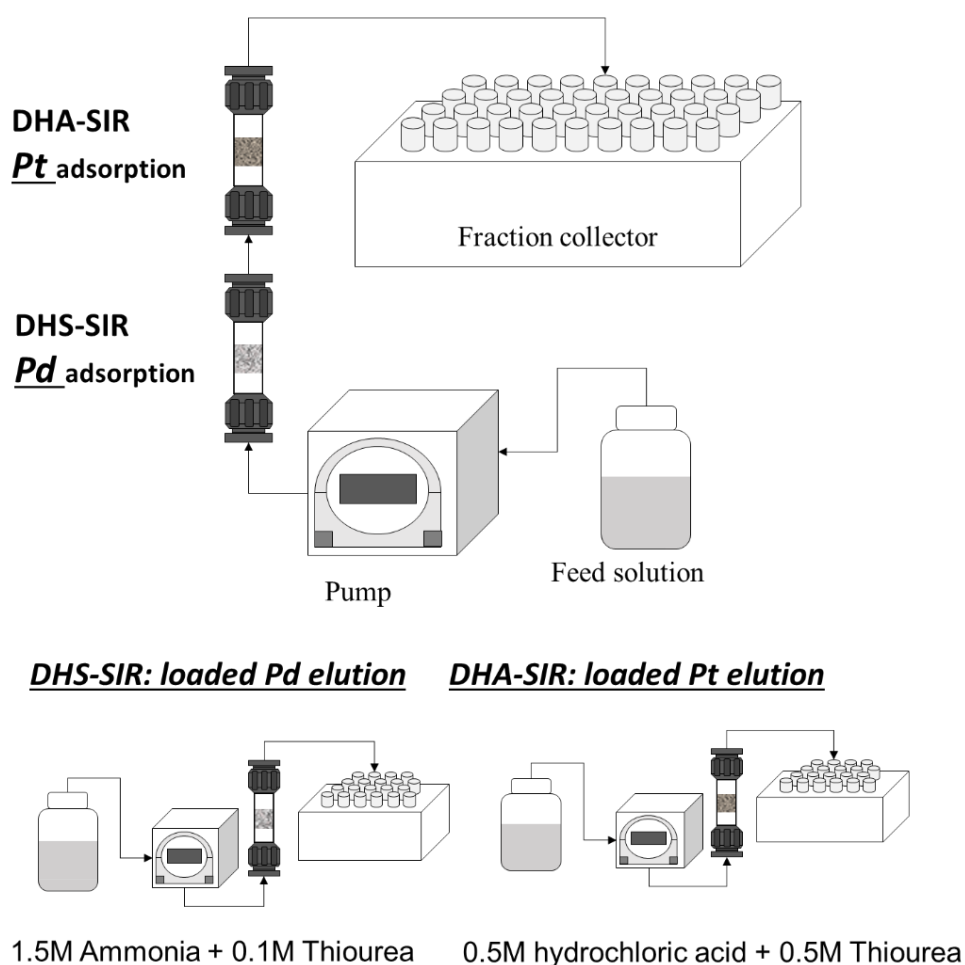


Figure 2.4. Sequential column experimental setup

2.2.5. Precipitation and reduction

Pt in the eluent from the column operation was recovered by reductive precipitation with sodium borohydride (NaBH_4). NaBH_4 (0.01 – 0.1 g) was added to 20 mL of eluent solution, containing 185 mg/L of Pt, and the mixture was stirred under 298 K for 1 h. The solution was then filtered, and pH of filtrated solution was measured with a pH meter. The concentrations of metals in the filtrated solution were determined by ICP-AES. The precipitates were dried in vacuo at 298 K for 24 h and were measured by an X-ray diffraction meter (XRD, 40 kV and 20 mA, $\text{CuK}\alpha$, Shimadzu XRD-6100). Purity of Pt in the precipitates was determined by dissolving the precipitates with 1 mol/L HCl, followed by measurement of the concentration of Pt by ICP-AES.

2.3. Results and Discussion

2.3.1. Batch experiments

Figures 2.5 – 2.7 show the effect of HCl concentration on the adsorption of Pt in leaching solution by TBP-SIR, TOA-SIR, and TOMAC-SIR. Those three solvent impregnated resins did not show any selectivity for Pt among base metals and other PGM metals. Since those resins did not show any selectivity, WA-21J was then adopted to separate Pt. As in Figure 2.8, WA-21J shows selectivity among base metals. WA-21J has polyamine functional group, thus di-n-hexylamine and di-octylamine were explored which possesses functional group as WA-21J as candidate solvents to recover Pt. Prepared DHA-SIR and DOA-SIR were applied in the experiment of effect of HCl concentration among base metal and in the leaching solution.

Figures 2.9 and 2.10 show the effect of HCl concentration on the adsorption of Pt, Mg, and Fe with DHA-SIR and DOA-SIR. Both of DHA-SIR and DOA-SIR possess the selectivity for Pt with high adsorption yield even in the range of 4 – 6 mol/L HCl, while other metals are scarcely adsorbed. This is because PGM complexes with amine extractants [48] are generally much more stable than the other metal complexes in the feed solution. Then those SIRs were employed to separate Pt in the leaching solution of spent automobile catalysts in Figure 2.11 and Figure 2.12. They showed selectivity for Pt from 4 mol/L HCl to 6 mol/L HCl suppressing the adsorption of other metals. Although both SIRs have selectivity to Pt, DHA-SIR is better than DOA-SIR in view of selectivity according to separation factor.

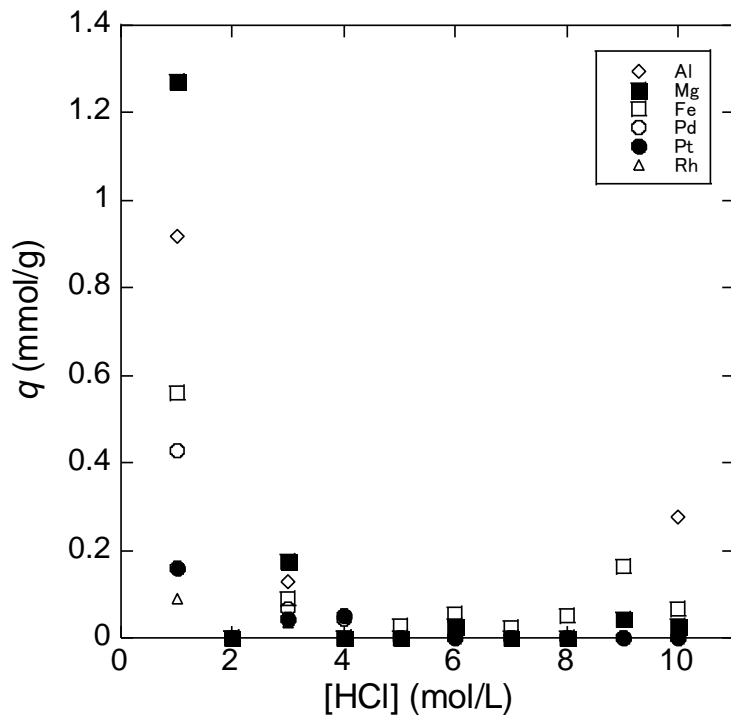


Figure 2.5. Effect of HCl on the adsorption of metals using TBP-SIR

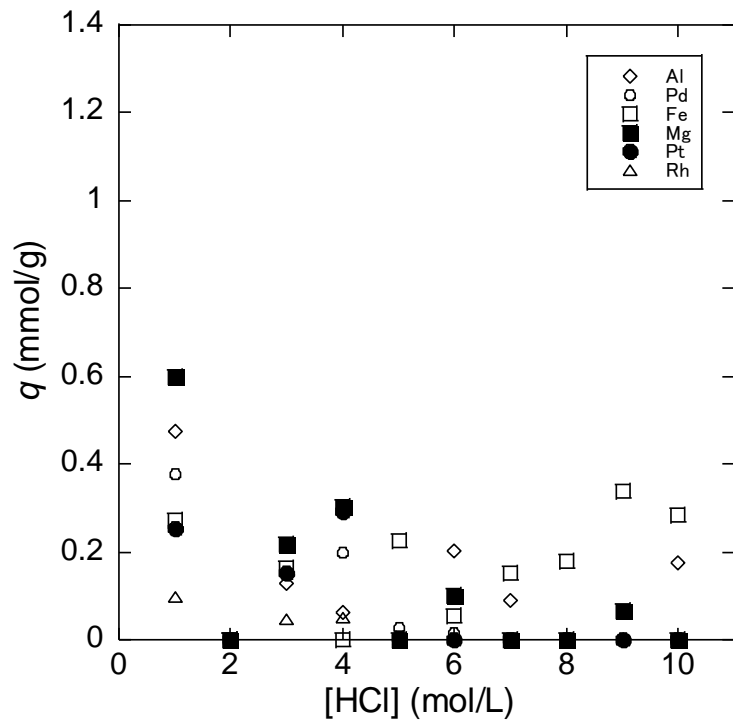


Figure 2.6. Effect of HCl on the adsorption of metals using TOA-SIR

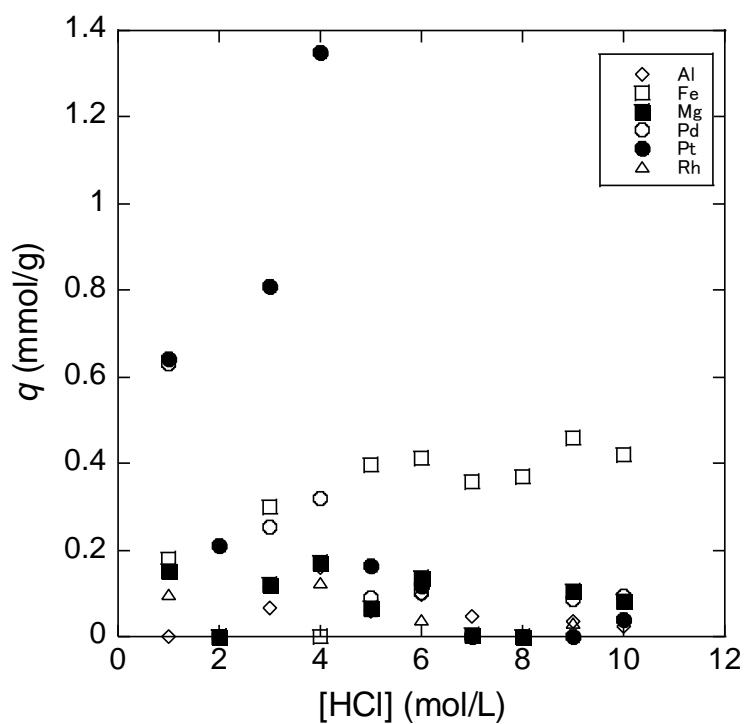


Figure 2.7. Effect of HCl on the adsorption of metals using TOMAC SIR

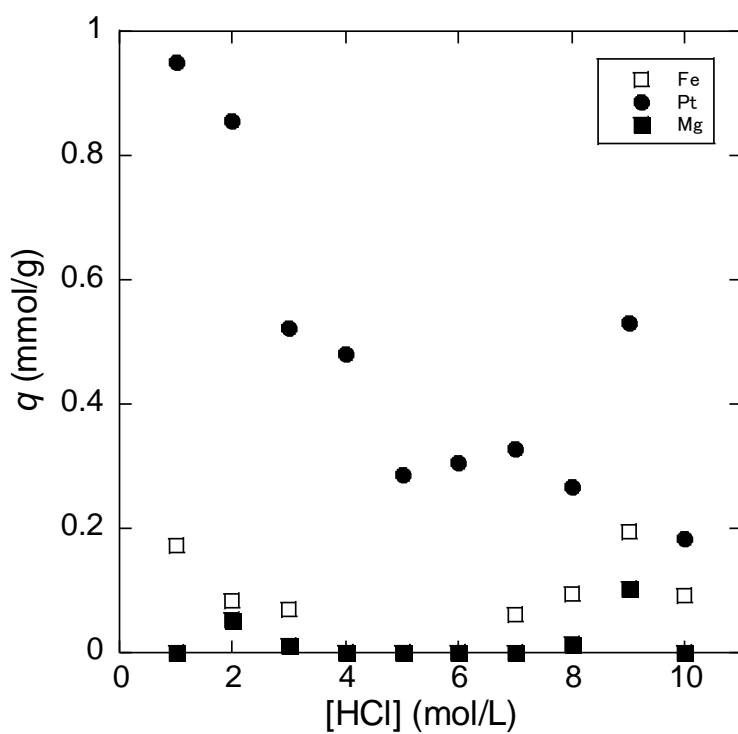


Figure 2.8. Effect of HCl on the adsorption of metals using WA-21J

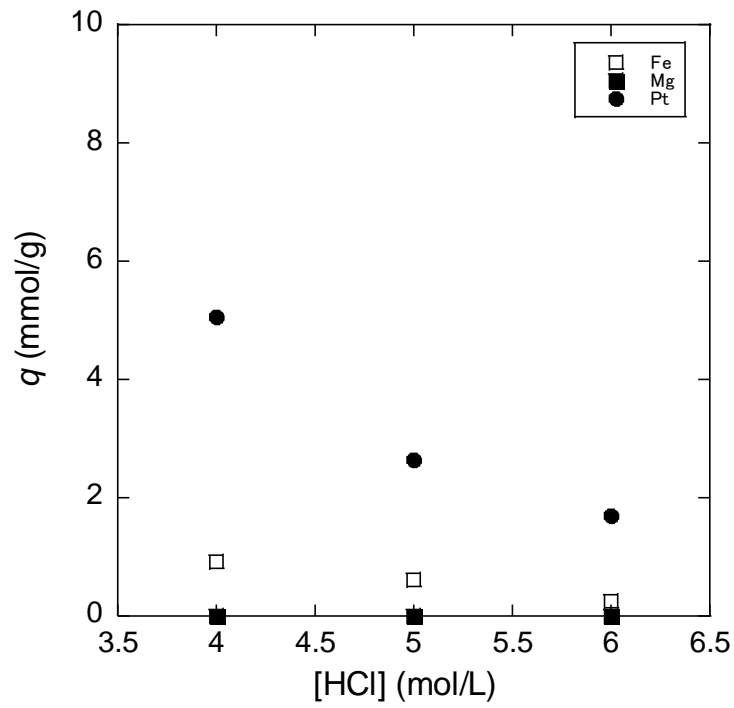


Figure 2.9. Effect of HCl on the adsorption of metals using DHA-SIR in simulated solution

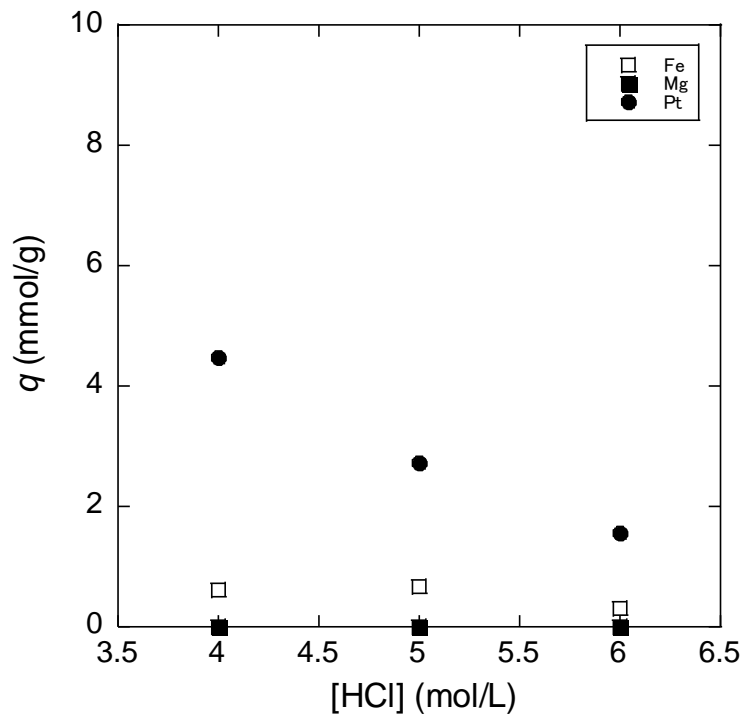


Figure 2.10. Effect of HCl on the adsorption of metals using DOA-SIR in simulated solution

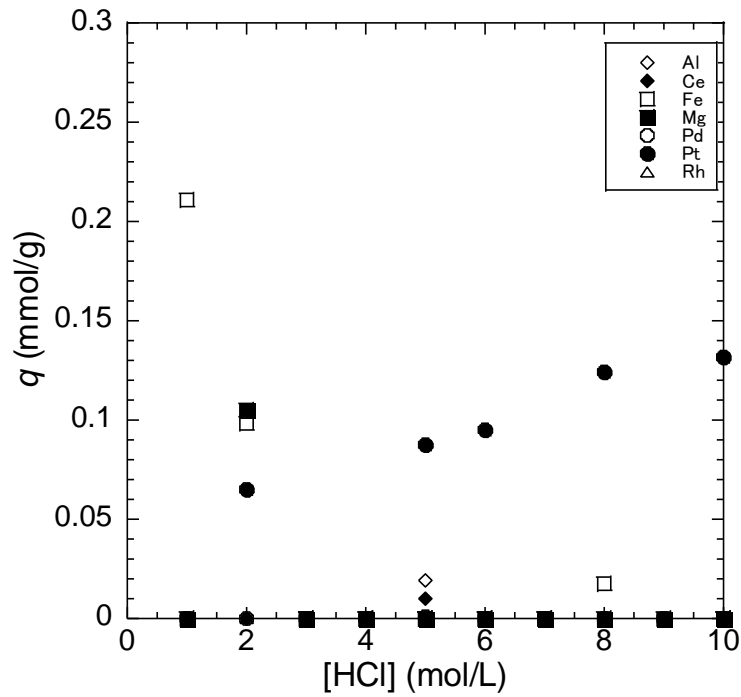


Figure 2.11. Effect of HCl on the adsorption of metals using DHA-SIR in leaching solution

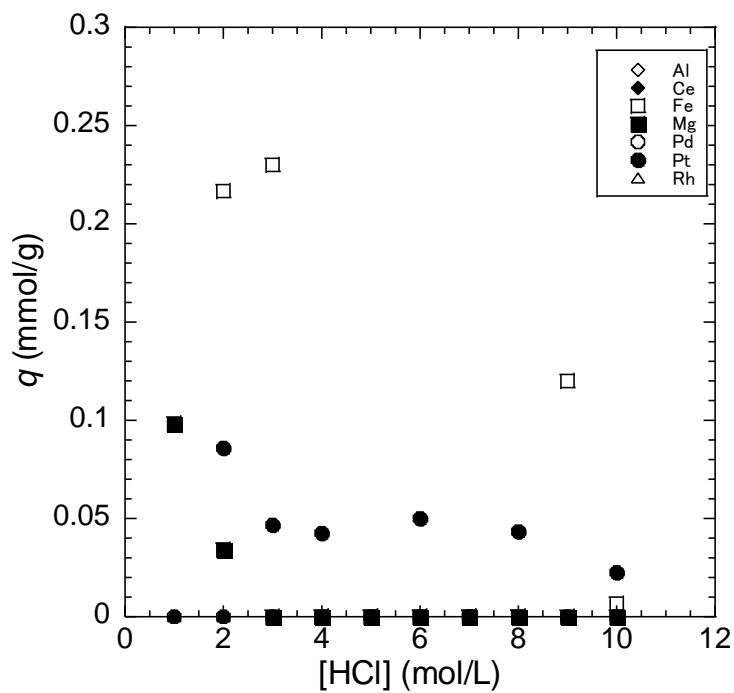


Figure 2.12. Effect of HCl on the adsorption of metals using DOA-SIR in leaching solution

Adsorption isotherm of Pt from 5 mol/L HCl solution with DHA-SIR is shown in Fig. 2.13 (a). Assuming that the adsorption is of Langmuir mechanism, as shown in Eq. (2-3),

$$q = \frac{q_0 \cdot K \cdot [M]}{1 + K \cdot [M]} \quad (2-3)$$

then linearized Langmuir equation can be obtained, as Eq. (2-4).

$$\frac{[M]}{q} = \frac{1}{q_0} [M] + \frac{1}{K \cdot q_0} \quad (2-4)$$

where q_0 is the maximum adsorption amount (mmol/g) and K is the adsorption equilibrium constant (L/mmol). From the linear relationship in Fig. 2.13 (b), the adsorption of Pt with the DHA-SIR is of Langmuir mechanism. The maximum adsorption amounts of Pt calculated was 5.434 mmol/g, and the adsorption equilibrium constant was 0.533 L/mmol, respectively.

These adsorptions using amine based extractants were progressed via Eq. (2-5)

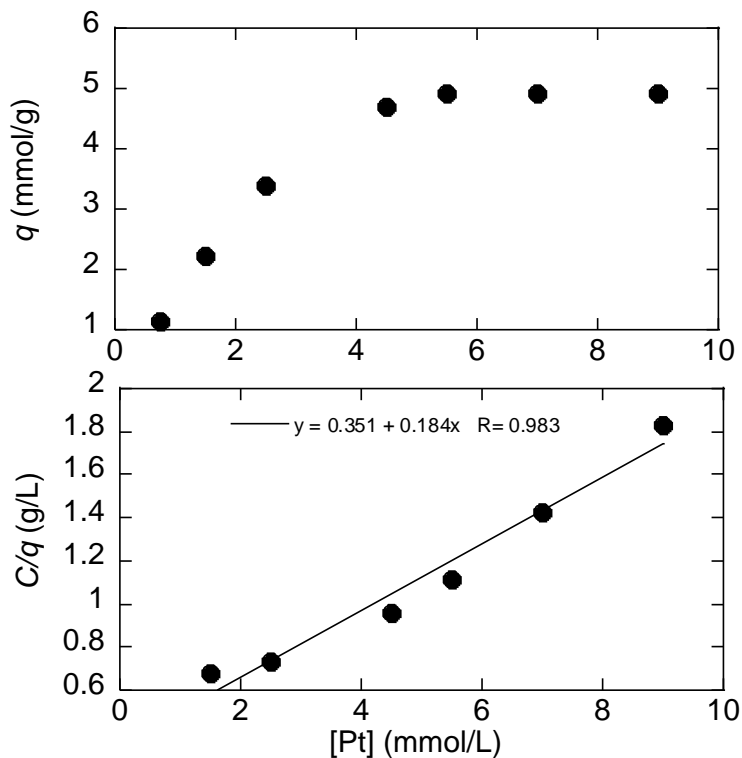
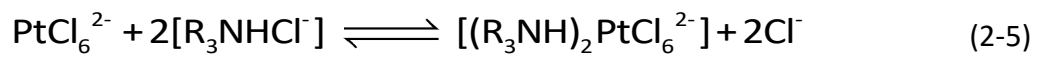


Figure 2.13. (a) Adsorption isotherm of Pt with DHA-SIR in 5 mol/L HCl, (b) Linearized Langmuir isotherm model of Pt with DHA-SIR in 5 mol/L HCl

2.3.2. Column experiments

The DHA-SIR was then applied to column chromatography. Figure 2.14 and 2.15 show the breakthrough and elution curves of Pt from single solution by packed column of 1 g of DHA-SIR. Pt in feed solution was successfully adsorbed until the number of bed volumes = 60 as expected by the batch adsorption. Thereafter, elution was progressed using the mixture of 0.5 mol/L thiourea and 0.5 mol/L HCl solution with the elution ratio of Pt was 95%.

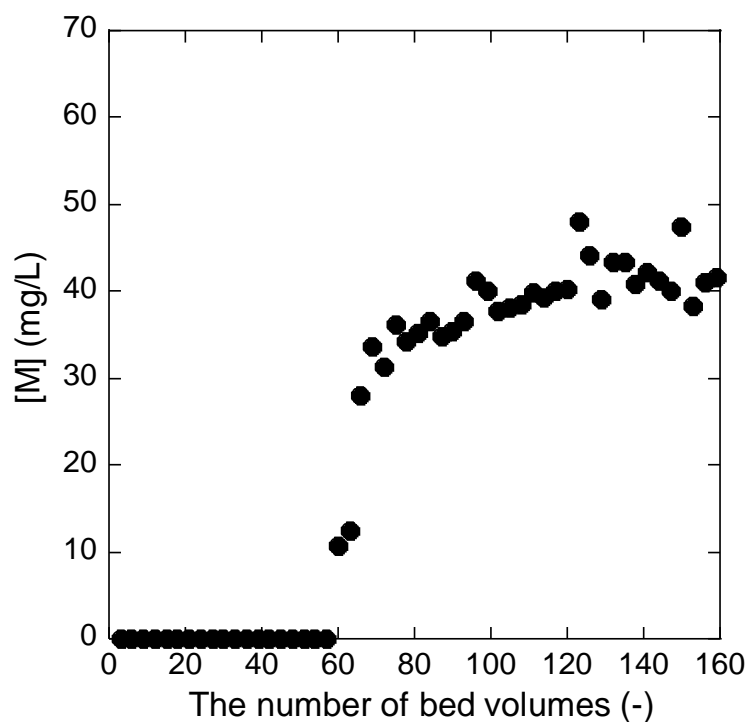


Figure 2.14. Breakthrough curve of single Pt solution

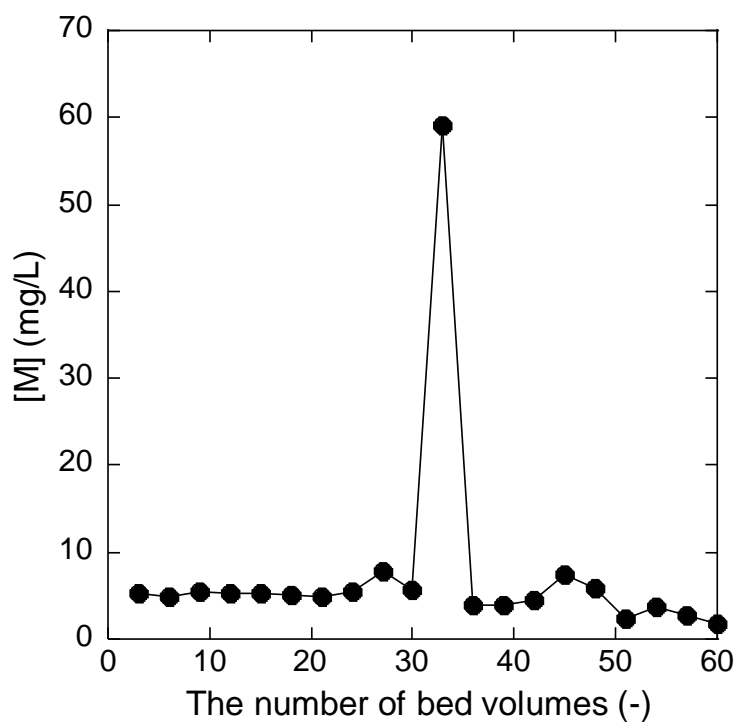


Figure 2.15. Elution curve of single Pt solution

Then, the DHA-SIR was applied for the actual leaching solution of spent automobile catalyst. Figures 2.16 and 2.17 also shows the breakthrough and elution curve of PGMs. Both quantitative adsorptions of Pt and Pd are achieved until the number of bed volumes = 50. However, as shown in elution curves, selective recovery of Pt could not be achieved since Pd was also eluted in the effluent due to its similar characteristics of Pt and Pd. In order to mutually separate Pd and Pt from the leaching solution, sequential chromatographic system of DHS-SIR column for Pd recovery and DHA-SIR column for Pt recovery was applied.

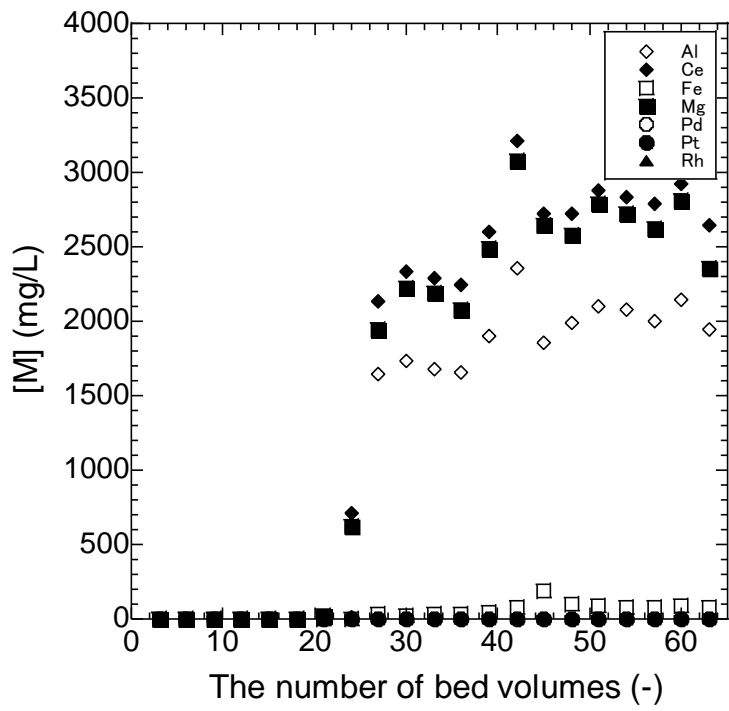


Figure 2.16. Adsorption curves of DHA-SIR in leaching solution

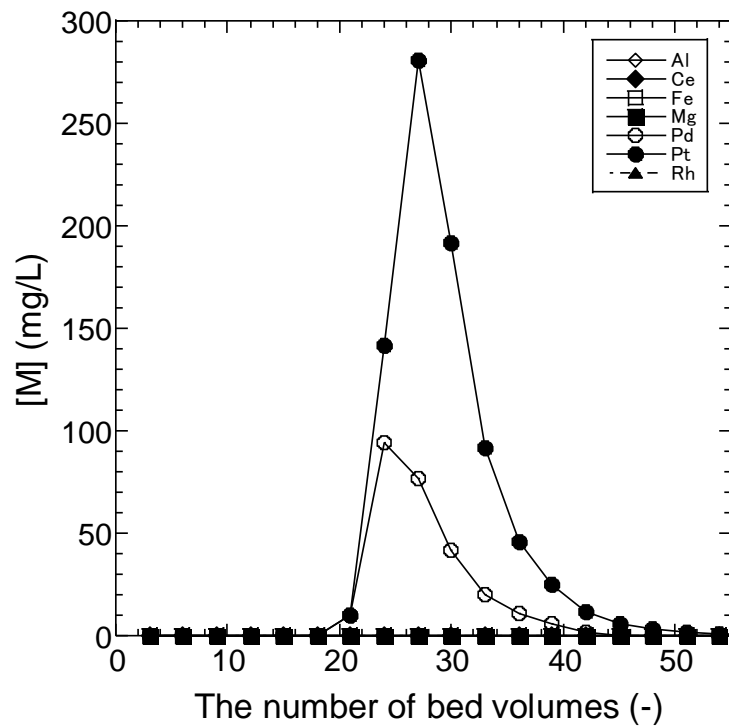


Figure 2.17. Elution curves of DHA-SIR in leaching solution

Figures 2.18 and 2.19 show the breakthrough curves and enlarged breakthrough curves obtained by sequentially feeding the actual leaching solution into DHS-SIR column and DHA-SIR column. Coexisted metal ions are confirmed not to affect adsorption of PGMs in both SIRs. Pt was adsorbed until the number of bed volumes = 50, while Pd was adsorbed until the number of bed volumes = 100. Pd and Pt could be successfully separated by eluting from the sequential column system. The maximum concentration of Pd in the elution stage reached to 3750 mg/L and the quantitative elution of Pd can be achieved. In case of DHA-SIR after removal of Pd in Figure 2.20, the selective adsorption of Pt in Figure 2.21 can be observed. The elution yields are 101% for Pt and 101% for Pd, respectively.

Figures 2.22–2.27 show the repeatability and reusability of DHA-SIR. Repeatability was assured through three adsorption experiment. Adsorption ability decreased as 96.7%, 95.8% of the first one, respectively. Resin is poisoned with Mg since it was not eluted fully, although it was adsorbed. It should be eluted with another eluent. Since in the repeatability experiment has only three metals, Fe, Pt, Mg, the adsorption of base metals was not suppressed by other metal ions effect. With only three metals, the adsorption of Fe has to be removed by scrubbing with another agent.

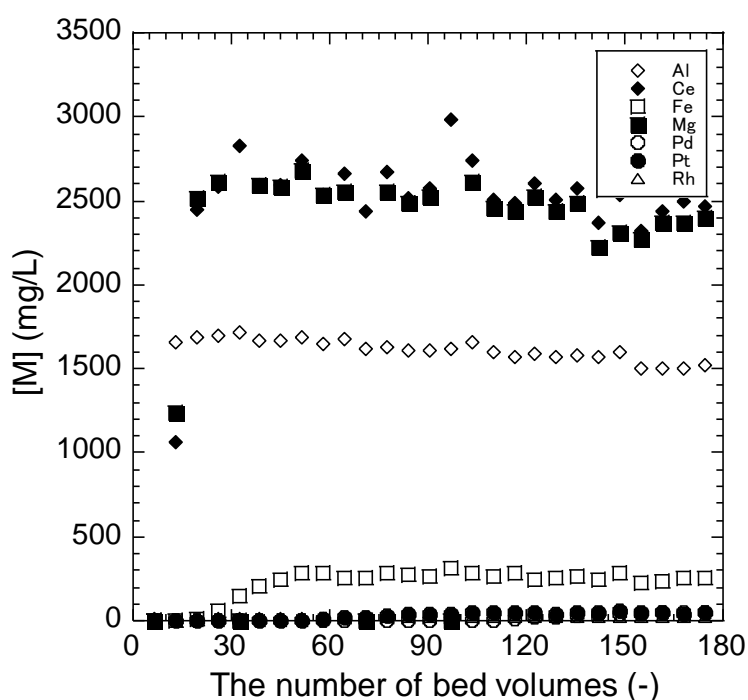


Figure 2.18. Adsorption curves of DHA-SIR in leaching solution with sequential adsorption system

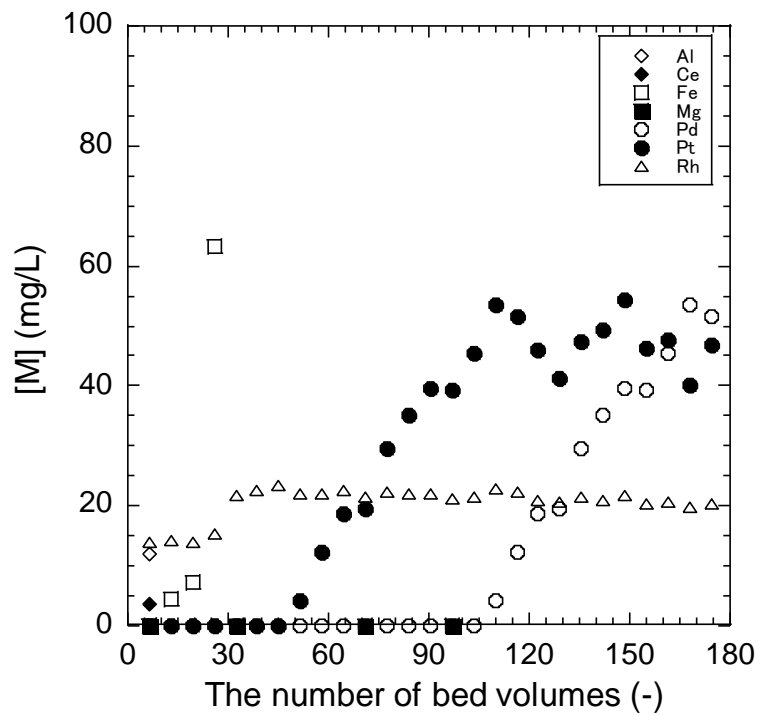


Figure 2.19. Enlarged adsorption curves of DHA-SIR in leaching solution with sequential adsorption system

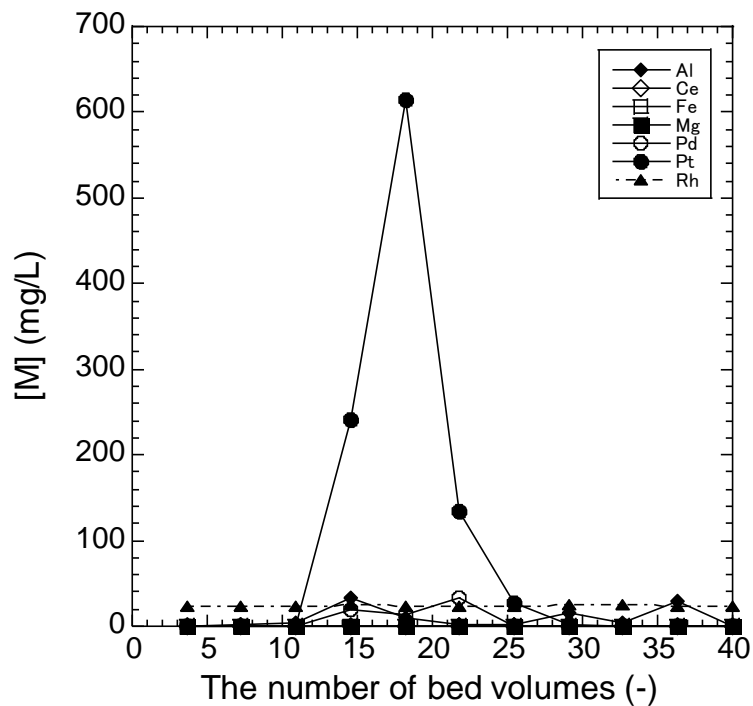


Figure 2.20. Elution curves of Pt with DHA-SIR in leaching solution with sequential adsorption system

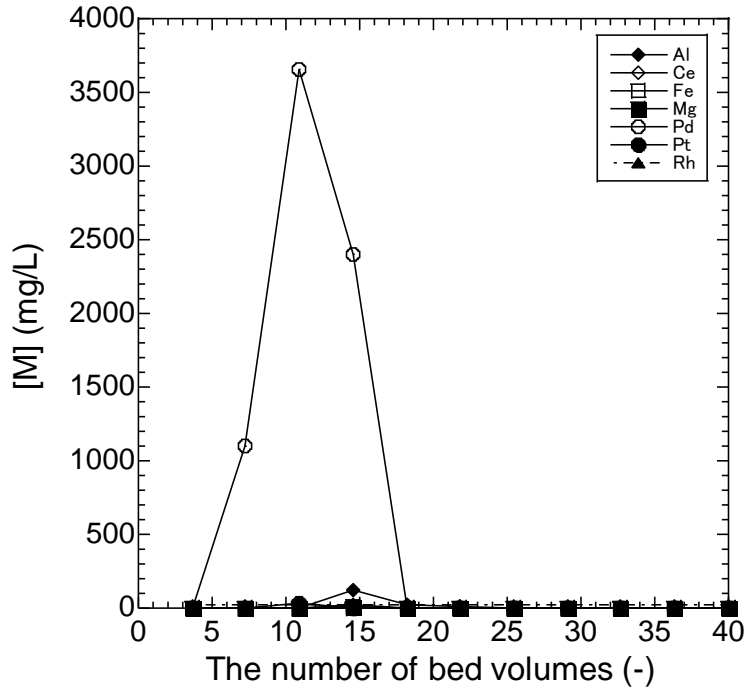


Figure 2.21. Adsorption curves of Pd with DHS-SIR in leaching solution with sequential adsorption system

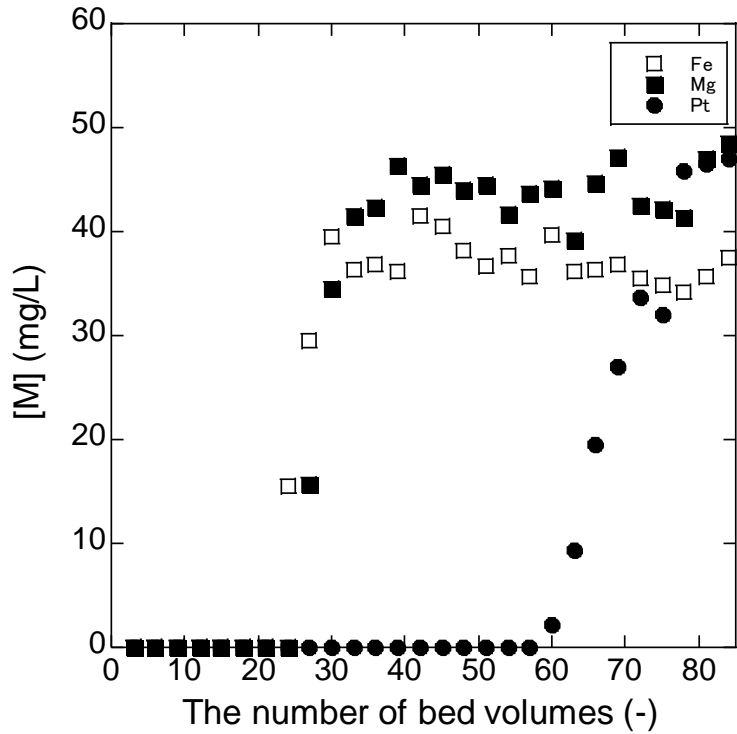


Figure 2.22. 1st breakthrough curves with DHA-SIR in simulated solution

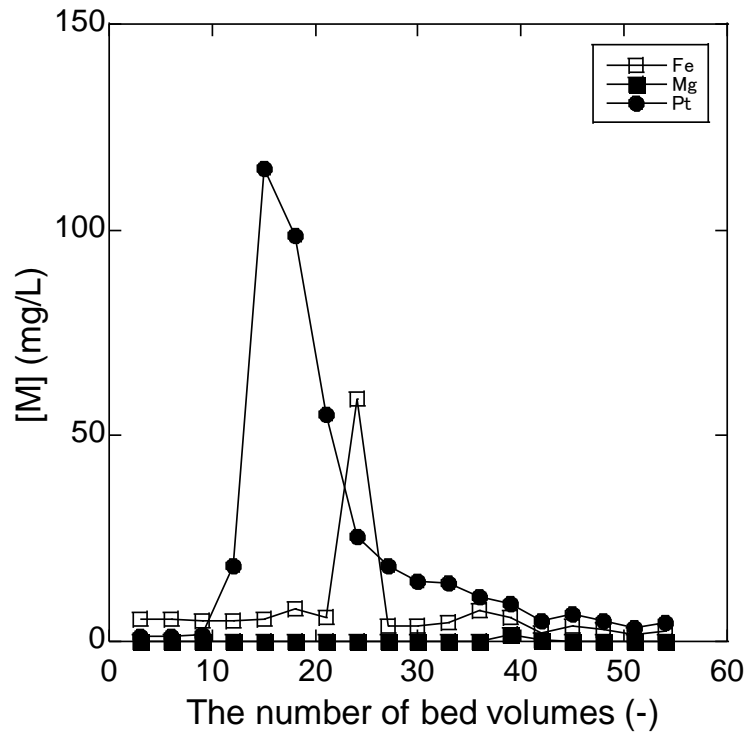


Figure 2.23. 1st elution curves with DHA-SIR in simulated solution

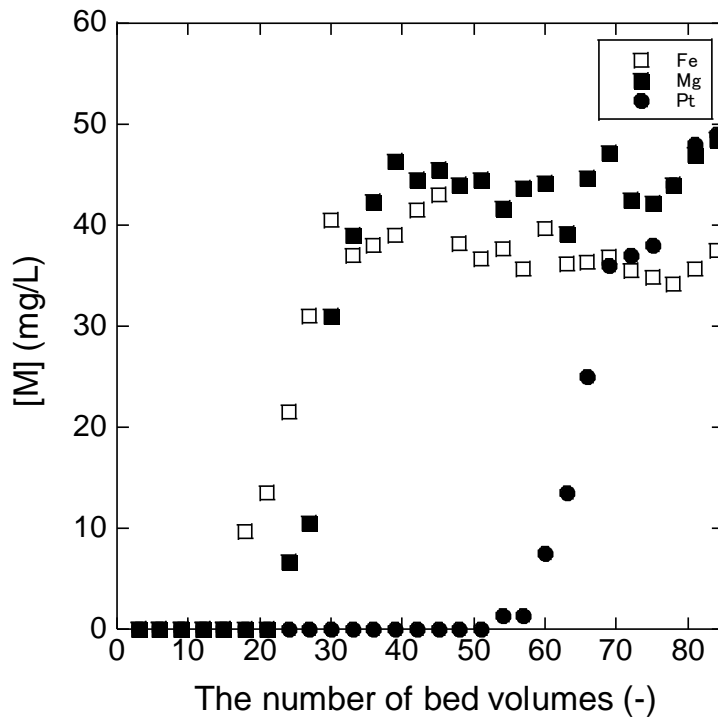


Figure 2.24. 2nd breakthrough curves with DHA-SIR in simulated solution

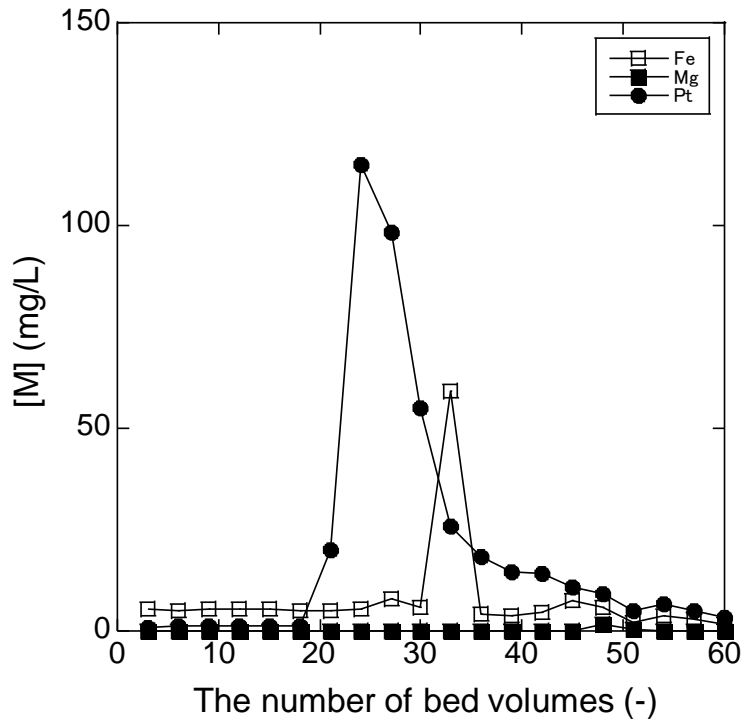


Figure 2.25. 2nd elution curves with DHA-SIR in simulated solution

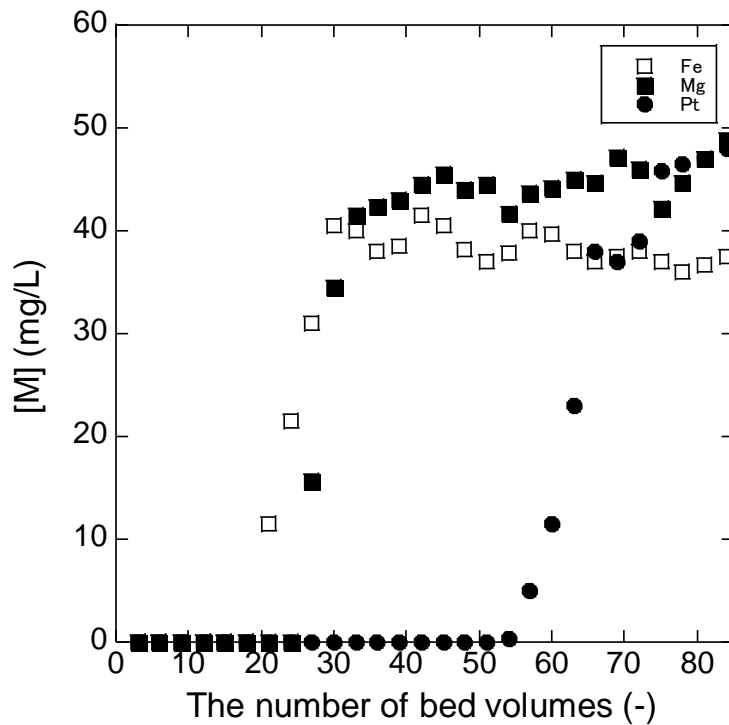


Figure 2.26. 3rd breakthrough curves with DHA-SIR in simulated solution

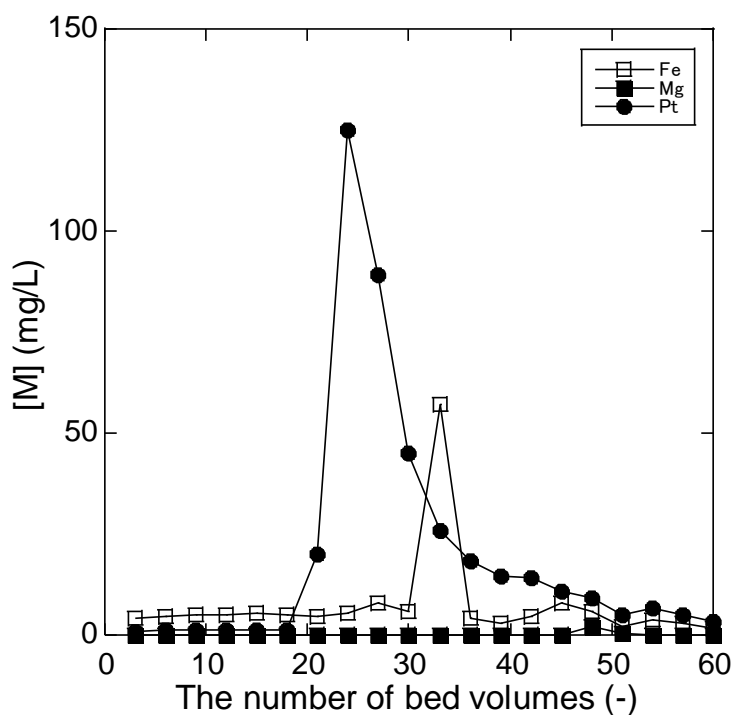


Figure 2.27. 3rd elution curves with DHA-SIR in simulated solution

2.3.3. Precipitation and reduction

Recovery of Pt from the eluent by reductive precipitation was finally investigated. The eluent from the DHA-SIR column ($[Al] = 8.9 \text{ mg/L}$, $[Pd] = 13.5 \text{ mg/L}$, $[Pt] = 198 \text{ mg/L}$, $[Rh] = 14.7 \text{ mg/L}$) was collected, and then NaBH_4 was added. Firstly, the amount of NaBH_4 added to the eluent was changed for elucidating the precipitation yield of Pt. Figure 2.28 shows the effect of pH on the precipitation yield of Pt, since pH of the solution was increased by increasing the amount of NaBH_4 added. Precipitation yield of Pt was increased with increase in pH, and 100% precipitation was obtained at $\text{pH} > 10$, Figure 2.29 shows the XRD patterns of the precipitates. Diffraction peaks at $2\theta = 40.0^\circ$, 46.5° , 67.9° and 81.5° identified with the elementary Pt were successfully obtained. The purity of precipitate was also confirmed to be 99.2%.

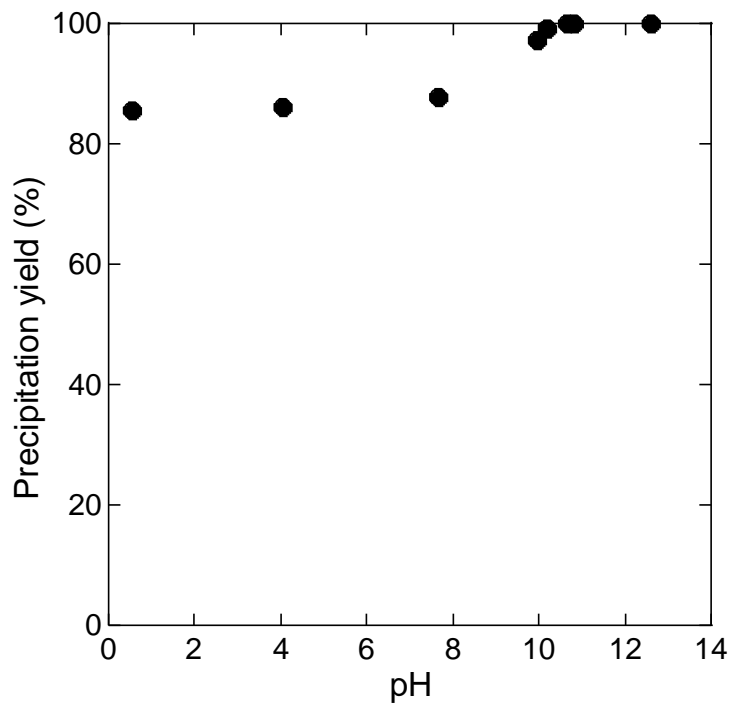


Figure 2.28. Effect of pH on the precipitation yield of Pt

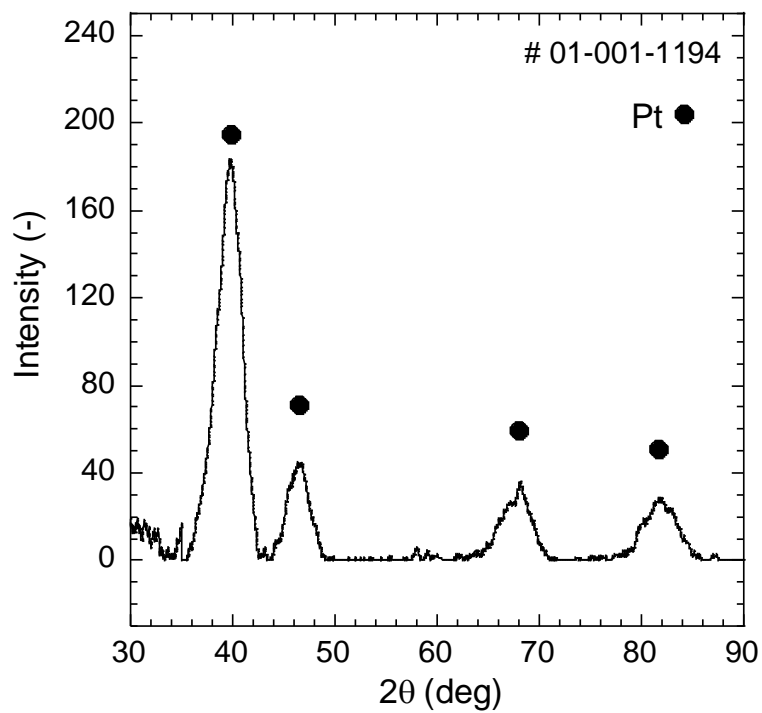


Figure 2.25. Precipitation yield of Pt depending on pH

2.4. Conclusion

DHA-SIR, DOA-SIR, and DHS SIR coated with crosslinked polyvinyl alcohol were employed to separate Pt and Pd from spent automobile catalyst. The important features of the system are as follows:

- (1) Both DHA-SIR and DOA-SIR possess the selective adsorption ability for Pt, while adsorption of other metals are suppressed in the batchwise adsorption system. DHA-SIR is better than DOA-SIR from the viewpoint of separation factor.
- (2) Adsorption of Pt by DHA-SIR follows the Langmuir adsorption model and the maximum adsorption amounts of Pt was 5.434 mmol/g, and the adsorption equilibrium constant K was 0.533 L/mmol, respectively.
- (3) Selective adsorption–elution of Pt and Pd using DHA-SIR and DHS-SIR can be achieved by sequential chromatographic system. Mutual separation of Pd and Pt can be achieved by DHS-SIR to separate Pd followed by DHA-SIR to separate Pt. The Pt adsorbed in DHA-SIR was quantitatively eluted by the mixture of 0.5 mol/L thiourea and 0.5 mol/L HCl, while Pd adsorbed in the DHS-SIR was eluted with the mixture of 1.5 mol/L ammonia solution with 0.1 mol/L thiourea.
- (4) Pt was reduced as precipitates by adding sodium borohydride into the collected eluent from column chromatography. The precipitation yield of Pt was increased with increase in pH, to reach 100% precipitation at $\text{pH} > 10$. Elementary Pt having the purity of 99.2% was obtained.

Chapter 3

Separation of Scandium and Yttrium Using Organophosphorus Acid

3.1. Introduction

Separation and recovery of Sc and Y in aqueous media using organophosphorus compound, bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), was investigated. 1-octanol was added as modifier to enhance stripping efficiency for both solvent extraction and SIR, since stripping of heavy rare earths from the organic solution containing organophosphorus extractants is difficult. Solvent extraction was conducted to obtain extraction equilibrium, then SIR was applied to separation.

Separation of scandium (Sc) and yttrium (Y) using solvent-impregnated resin (SIR) containing Cyanex272 along with 1-octanol as a modifier was investigated. The coated SIR was applied to both batch and chromatographic recovery of Sc and Y. The adsorption of Sc followed Langmuir isotherm model. Separation of Sc from Y was achieved by employing chromatographic adsorption system together with the quantitative elution from SIR by 5 mol/L HCl.

3.2. Experiments

3.2.1. Reagents

Cyanex 272 was supplied by Cytec Solvay Japan Co., Ltd (Tokyo, Japan), and PC-88A was supplied by Daihachi Chemical Industry Co., Ltd (Osaka, Japan). Scandium oxide and yttrium oxide were supplied by Nippon Yttrium Co., Inc. (Fukuoka, Japan). IP Solvent 2835, synthetic isoparaffinic hydrocarbon having 99.8 vol % or more iso-paraffin, was supplied by Idemitsu Kosan Co., Ltd (Tokyo, Japan). DIAION HP2MG (macroporous methacrylate polymeric resin) was supplied by Mitsubishi Chemical Corporation (Tokyo, Japan). All other organic and inorganic reagents were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) as analytical-grade reagents.

3.2.2. Purity measurement of extractant

Purity of Cyanex272 was measured using an automatic potentiometric titrator (Kyoto Electronics Co., Ltd., AT-510). 0.2464 g of Cyanex272 was weighed into a 50 mL beaker and adjusted by ethanol to the appropriate volume. To facilitate electricity easily, a few drops of deionized water were added and titrated with 0.1 mol/L NaOH while stirring. The content of Cyanex 272 was determined from the obtained amount of loading using Eq. (3-1), and the purity was determined using Eq. (3-2).

$$\text{The content of solvent} = 0.1 \times f_{\text{NaOH}} \times I_{\text{NaOH}} \times M_{\text{Extractant}} \quad (3-1)$$

Here, f_{NaOH} is the factor of 0.1 mol/L NaOH obtained with amidosulfuric acid [Wako], which is a standard substance for volumetric analysis. I_{NaOH} is the amount of NaOH drop (L), and the $M_{\text{Extractant}}$ is the molecular weight of the extractant.

$$\text{Purity of extractant (wt\%)} = \frac{\text{content of extractant (g)}}{\text{amount of extractant measured (g)}} \times 100 \quad (3-2)$$

The purity of the extractant calculated from Eq. (3-1) and Eq. (3-2) was 87.1 wt% for Cyanex 272 and the purity of the extractant used in this study. The concentration of the extractant used in this study was determined by an automatic potentiometric titrator.

3.2.3. Solvent Extraction

3.2.3.1. Extraction

The aqueous rare earth chloride solutions were prepared by dissolving the oxides in 1 or 2 mol/L HCl solution, and then diluted with deionized water to obtain 1 mmol/L Sc or Y aqueous solution. The pH of the aqueous solution was adjusted by HCl or NaOH. Organic solution was prepared by diluting Cyanex 272, together with 1-octanol, in IP Solvent 2835. Concentrations of the extractant as a dimeric species base are shown in Figure captions. Extraction of Sc and Y was carried out by shaking the organic and aqueous solutions at volume ratios of 1 : 1 at 25°C for more than 3 h. Concentrations of the metals in the resultant aqueous solutions were determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu ICPE-9000) and those in the organic solutions were calculated based on material balance. The pH was measured by a pH meter (Horiba F-74). The distribution ratio (D) was defined as:

$$D = \frac{[\bar{M}]}{[M]} \quad (3-3)$$

3.2.3.2. Stripping

Stripping experiments were carried out using the metal loaded organic solution. In this case, extraction was carried out with same manner as described above, and the metal loaded organic solution was employed to the stripping experiments. Stripping was performed by contacting the loaded organic solution with different concentration of HCl (2 – 3 mol/L) at a volume ratio = 1 : 1, and the mixture was shaken at 25°C for more than 3 h. Concentrations of the metals in the resultant aqueous solutions were determined by ICP-AES and those in the organic solutions were calculated based on material balance.

3.2.4. Solvent impregnated resin

3.2.4.1. SIR preparation

Preparation of the SIR and the coating of the SIR were carried out by the same manner described in the previous work [14, 15, 41]. The support resin, HP2MG (40 g), was first washed by dipping in methanol (400 mL) and dried for overnight. Washed

HP2MG (40 g) was immersed in a solution of acetone containing different amounts of Cyanex 272 and 1-octanol (50 mL) for 24 h. Concentration of Cyanex 272 and 1-octanol used for the preparation of SIR in the present work is shown in Table 3.1. Acetone was then completely evaporated to produce an SIR impregnating Cyanex 272 and 1-octanol. Coating of SIR was then carried out using polyvinyl alcohol (PVA, average polymerization degree 2000) and glutaraldehyde (GA). The prepared SIR (3 g) was immersed in an aqueous solution (50 mL) containing 3 wt% PVA and 1 wt% acetamide and the mixture was shaken for 17 h. The resulting suspension was then mixed with 1 mol/L KCl aqueous solution (10 mL) and the mixture was shaken for 24 h. The pretreated SIR was filtered, followed by adding 0.32 mol/L H₂SO₄ solution (10 mL) and standing for 1 h. Then 0.32 mol/L GA solution (10 mL) was added and the mixture was shaken for 24 h to complete crosslinking. The coated SIR obtained was filtered, washed with deionized water, and then dried. SIR used in this study was all coated SIR.

3.2.4.2. Determination of impregnated amount of Cyanex 272

A piranha solution was prepared by mixing 15 mL of concentrated H₂SO₄ in 5 mL of 30% H₂O₂. SIR (20 mg), before coating, was added to 20 mL of the piranha solution, and the resin was completely dissolved by heating and stirring at 323 K using a hot stirrer. Concentration of P in the resultant solution was determined by ICP-AES (Shimadzu ICPE-9000). Since one Cyanex 272 molecule has one P molecule, the impregnation amount of Cyanex 272 was calculated by the following equation (3-4).

$$\text{Impregnated amount of Cyanex 272 (mmol / g)} = \frac{[P]}{w} \times \frac{20}{1000} \quad (3-4)$$

where [P] is the concentration of P measured by ICP-AES (mmol/L), w is the amount of SIR (g). The impregnation amount of 1-octanol was determined by the material balance after subtracting the impregnation amount of acetone.

$$\begin{aligned} &\text{Impregnated amount of 1 - octanol (mmol / g)} \\ &= \frac{w_{\text{eq}} - w_{\text{ini}} - w_{\text{sol}} - I_{\text{Cyanex272}} \times M_{\text{Cyanex272}} \times w}{w} / M_{\text{1-octanol}} \end{aligned} \quad (3-5)$$

where w_{eq} is the weight of resin after impregnation (g), w_{ini} is the weight of resin before impregnation (g), w_{sol} is the weight of acetone in the resin (g), $I_{\text{Cyanex272}}$ is the impregnated amount of Cyanex 272 (mmol/g), $M_{\text{Cyanex272}}$ is the molecular weight of Cyanex 272 (g/mol), and $M_{\text{1-octanol}}$ is the molecular weight of 1-octanol (g/mol). The impregnated amount of SIR determined is summarized in Table 3.1.

Table 3.1. Impregnated amount of Cyanex 272 and 1-octanol.

Organic solvent (Cyanex 272/1-octanol)	Impregnated amount of Cyanex 272 (mmol/g)	Impregnated amount of 1-octanol (mmol/g)
(a) 0.05 mol/L/0.00 mol/L	0.74	0
(b) 0.05 mol/L/0.01 mol/L	0.76	0.34
(c) 0.05 mol/L/0.03 mol/L	0.80	0.74

3.2.4.3. Batch Experiments

Aqueous solution of the rare earth metals of 1 mmol/L were prepared with HCl solution, and the pH was adjusted using HCl and NaOH. The SIR (20 mg) was added to 20 mL of aqueous solution in the 50 mL Erlenmeyer flask, and the suspended mixture was shaken at 298 K for 24 h. After filtering the resin, the concentrations of the metal ions were determined with ICP-AES. Equilibrium pH was measured by pH meter (Horiba F-74). The adsorption amount of the rare metals, q (mmol/g), is defined as:

$$q = \frac{([M]_{\text{ini}} - [M]_{\text{eq}}) \times L}{w} \quad (3-6)$$

where $[M]_{\text{ini}}$ and $[M]_{\text{eq}}$ are initial and equilibrium concentrations of metals in the solution (mmol/L), respectively, L is the volume of the solution (L), and w is the weight of the resin (g).

Elution experiment was performed by immersing 20 mg of metal loaded SIR from batch experiment to 20 mL of 1 – 3 mol/L HCl in 50 mL Erlenmeyer flask. The suspended mixture was shaken at 298 K for 24 h. After filtering the resin, the concentration of the metal ions was determined with ICP-AES. The elution yield was calculated by the equation (3-7).

$$\text{Elution yield (\%)} = \frac{[M] \times L}{q \times w} \times 100 \quad (3-7)$$

3.2.4.4. Column experiments

SIR (weight = 1.0 g, wet volume = 2.71 mL) was packed into a glass column of 100 mm in length and 8 mm in diameter, and then deionized water was fed to the column to wash the adsorbent for 12 h. Aqueous feed solution containing $[\text{Sc}^{3+}] = [\text{Y}^{3+}] = 1$ mmol/L at $\text{pH}_{\text{ini}} = 1.45$ was fed to the column at flow rate of 0.18 mL/min {space velocity (S.V.) = 6 h^{-1} }, using a peristaltic pump (EYELA, KP-11). The metal ions loaded into the

columns were eluted with 5 mol/L HCl, which is determined by the preliminary study by comparing various acids and bases. The effluents were collected with a fraction collector (EYELA DC-1500). The number of bed volumes of the effluent is defined as:

$$\text{Bed Volume} = \frac{v \times t}{V} \quad (3-8)$$

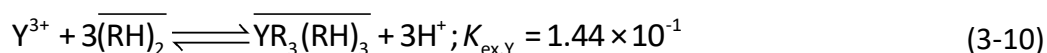
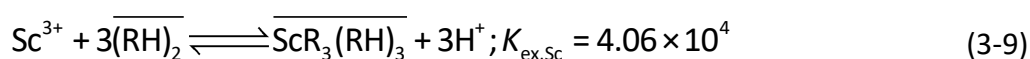
where v , t , and V are the flow rate of the solution (mL/min), time the solution was applied (min), and the wet volume of the adsorbent (mL).

3.3. Results and Discussions

3.3.1. Solvent extraction

3.3.1.1. Extraction of Sc and Y in the absence of 1-octanol

Figure 3.1 shows the effect of pH on the distribution ratio (D) of Sc and Y. Linear relationship between pH and $\log D$ was obtained for both metals with slope of 3, indicating the extraction is proceeded by cation exchange between the metal and three protons. Figure 3.2 shows the effect of the concentration of dimerized extractant on the distribution ratio. The relationship between $\log D[\text{H}^+]^3$ and $\log[(\overline{\text{RH}})_2]_{\text{feed}}$ of Sc and Y showed a dependency of slope 3, so that three dimeric extractants participate in extraction of one metal ion. Based on the results of the slope analysis, the extraction equilibrium of Sc and Y is formulated as Eq. (3-9) and (3-10).



The K_{ex} value for Sc is extremely high, and the stripping of Sc is thus expected to be quite difficult. The separation factor $S_{\text{Sc/Y}}$, defined as $K_{\text{ex,Sc}}/K_{\text{ex,Y}}$, is 2.82×10^5 , indicating separation of the two metals is easy to be achieved. Figure 3.3 shows effect of pH on the distribution ratio of Sc with 1-octanol/Cyanex 272 = 6. A linear relationship between pH and $\log D$ was obtained with a slope of 3 for Sc same as the relationship obtained from the experiment without 1-octanol. This shows that the extraction proceeds with the exchange of the metal and three protons, and that the mechanism does not change even when 1-octanol is added.

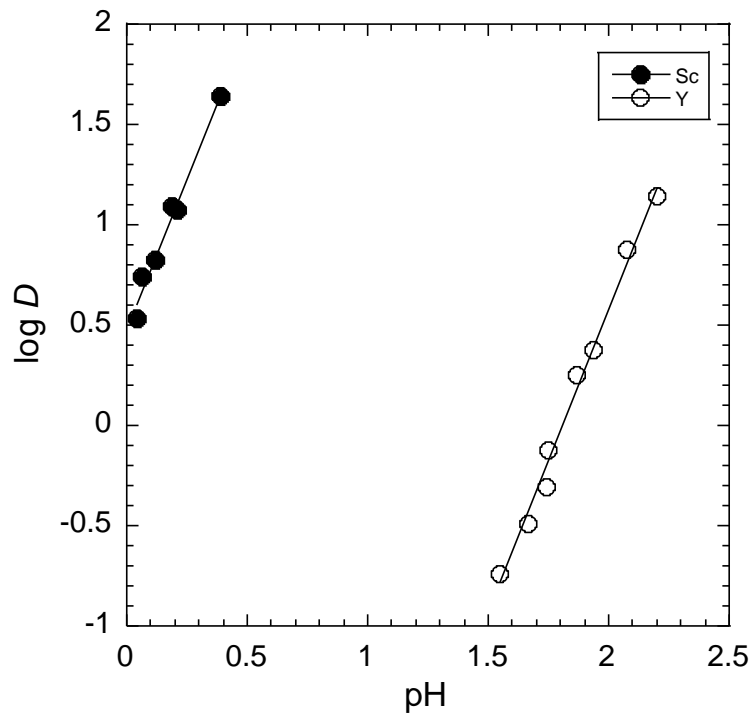


Figure 3.1. Effect of pH on distribution ratios of Sc and Y. $[(\overline{\text{RH}})_2]_{\text{feed}} = 0.0354 \text{ mol/L}$, $[\text{Sc}]_{\text{feed}} = 1.00 \text{ mmol/L}$, and $[\text{Y}]_{\text{feed}} = 1.00 \text{ mmol/L}$

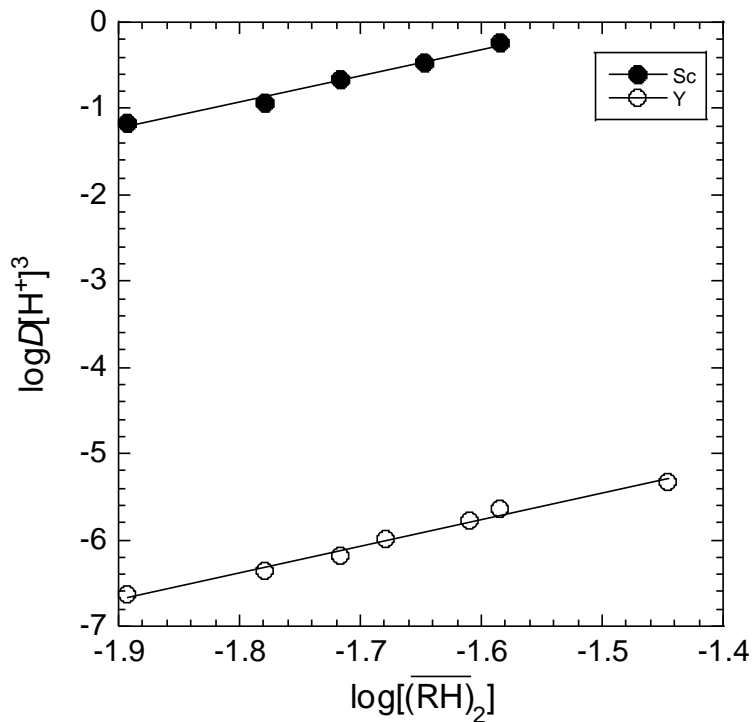


Figure 3.2. Effect of concentration of dimeric extractants on normalized distribution ratios of Sc and Y. $[(\overline{\text{RH}})_2]_{\text{feed}} = 0.0354 \text{ mol/L}$, $[\text{Sc}]_{\text{feed}} = 1.00 \text{ mmol/L}$, and $[\text{Y}]_{\text{feed}} = 1.00 \text{ mmol/L}$.

3.3.1.2. Stripping of Sc and Y in the absence of 1-octanol

Stripping of the loaded Sc and Y was then investigated. Table 3.2 lists the stripping yields of the metals from loaded organic solution containing Cyanex 272 alone with HCl of different concentrations. Stripping yield of Y was reasonably high and was hardly affected by the HCl concentration, while that of Sc was still low but was increased with increasing HCl concentration. Therefore, improvement of the stripping yield is required.

Table 3.2. Stripping yield of Sc and Y from loaded organic solution containing Cyanex 272 alone with HCl.

[HCl] (mol/L)	Sc	Y
1.0	18.6%	91.1%
2.0	39.1%	91.9%
3.0	50.5%	85.9%

3.3.1.3. Effect of addition of 1-octanol on extraction and stripping of Sc

Effect of addition of 1-octanol to the organic phase was finally investigated. Figure 3.3 shows the effect of pH on the distribution ratio of Sc, in Sc single metal system, with organic phase containing 1-octanol (molar ratio of $[1\text{-octanol}]/[\overline{(\text{RH})}_2] = 12$). The distribution ratio of Sc in the absence of 1-octanol, shown in Figure 3.1, is also plotted in Figure 3.3 for the comparison. The distribution ratio of Sc is dramatically decreased with addition of 1-octanol to the organic phase. In addition, the slope of $\log D$ against pH is 3 even in the case of 1-octanol/Cyanex 272 mixture, indicating the extraction of Sc is still occurred by a cation exchange mechanism. Effect of addition of 1-octanol to the organic phase was finally investigated to improve stripping of Sc. Figure 3.4 shows the effect of molar ratio of $[1\text{-octanol}]/[\overline{(\text{RH})}_2]$ on the distribution ratio of Sc from aqueous solution of $\text{pH}_{\text{feed}} = 0.41$.

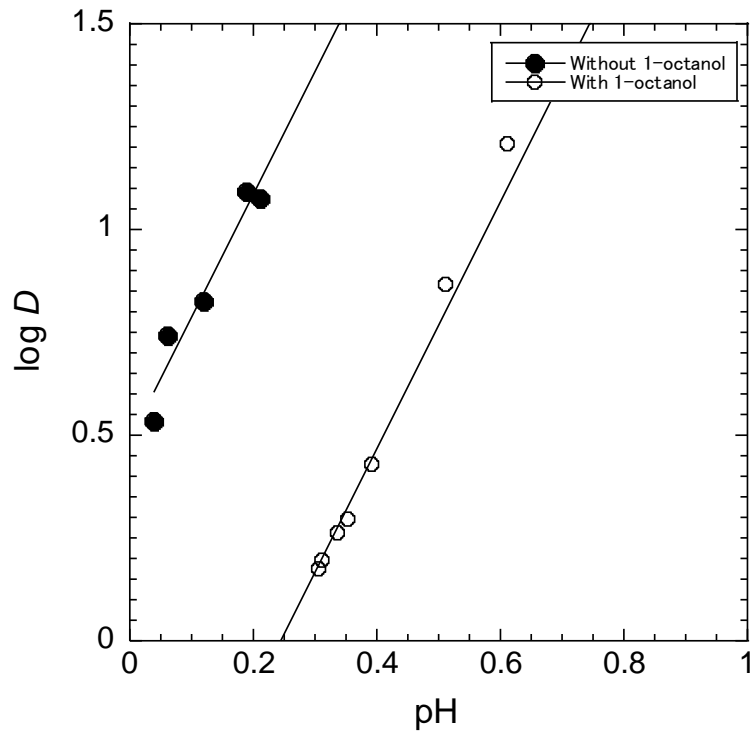


Figure 3.3. Effect of pH on distribution ratios of Sc

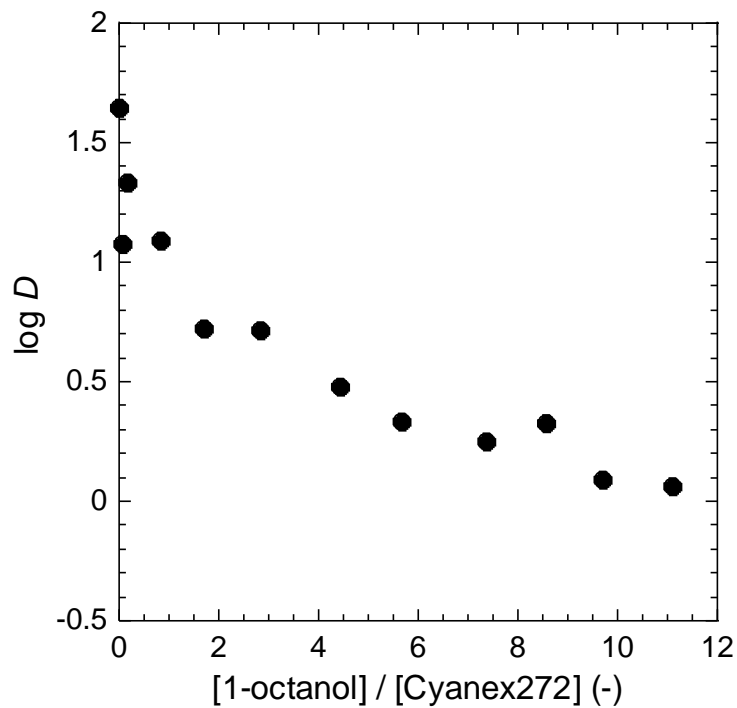


Figure 3.4. Effect of molar ratio of 1-octanol/Cyanex 272 on the distribution ratio of Sc.

$[(RH)_2] = 0.0340 \text{ mol/L}$, $[Sc]_{\text{feed}} = 0.97 \text{ mmol/L}$, $\text{pH}_{\text{feed}} = 0.41$.

As the amount of 1-octanol added to the organic solution was increased, the distribution ratio of Sc was decreased. This is likely because 1-octanol dissociate the dimeric species of the extractant in the organic phase due to its polar characteristics [49]. Effect of molar ratio of $[1\text{-octanol}]/\overline{[(RH)_2]}$ on the stripping yield of Sc was then investigated. In this case, the loaded organic solution was stripped with 2 mol/L HCl solution for 3 times. Figure 3.5 shows the stripping yield of Sc. In the case of 1-time stripping, the stripping yield was increased with $[1\text{-octanol}]/\overline{[(RH)_2]}$ molar ratio, as expected from the results of extraction shown in Figure 3.4. After 3-times stripping, almost complete stripping could be achieved at molar ratio of more than 12, and 99.8% stripping yield was obtained at molar ratio of 24. Therefore, addition of 1-octanol was revealed to suppress the extractability to improve the stripping ability of Sc.

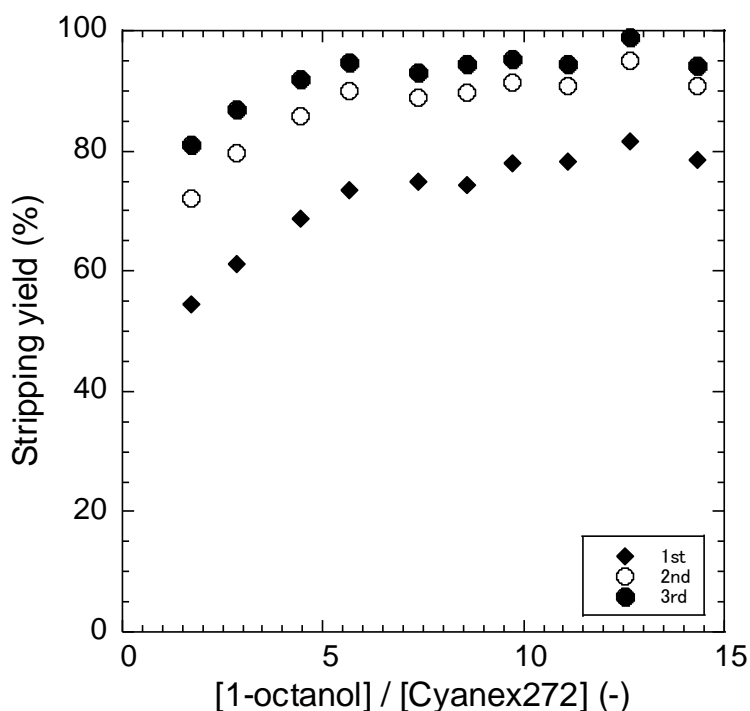


Figure 3.5. Effect of molar ratio of 1-octanol/Cyanex 272 on the stripping yield of Sc.

$\overline{[(RH)_2]}_{\text{feed}} = 0.0340 \text{ mol/L}$ and $[HCl] = 2.0 \text{ mol/L}$.

3.3.2. Batch experiments

The SIRs prepared in the present work were first applied for batchwise adsorption of Sc and Y. Figures 3.6 – 3.8 show effect of pH on the adsorption amount of Sc and Y. In all cases, almost no adsorption of Y was observed, while Sc was adsorbed with high adsorption amount in the pH range investigated. When comparing the adsorption amount of Sc with the different SIRs, the adsorption amount was slightly

decreased by increasing the amount of 1-octanol in the SIR. However, the effect of 1-octanol to decrease in the adsorption of Sc is decreased compared with that observed in the conventional solvent extraction system. The decrease in the adsorption/extraction ability for metals by adding 1-octanol is caused by the decrease in the dimerization of the extractant. In the SIR system, however, most of diluent is evaporated, leading the extractant exists as monomeric species in the support resin, and thus the effect of addition of 1-octanol was decreased.

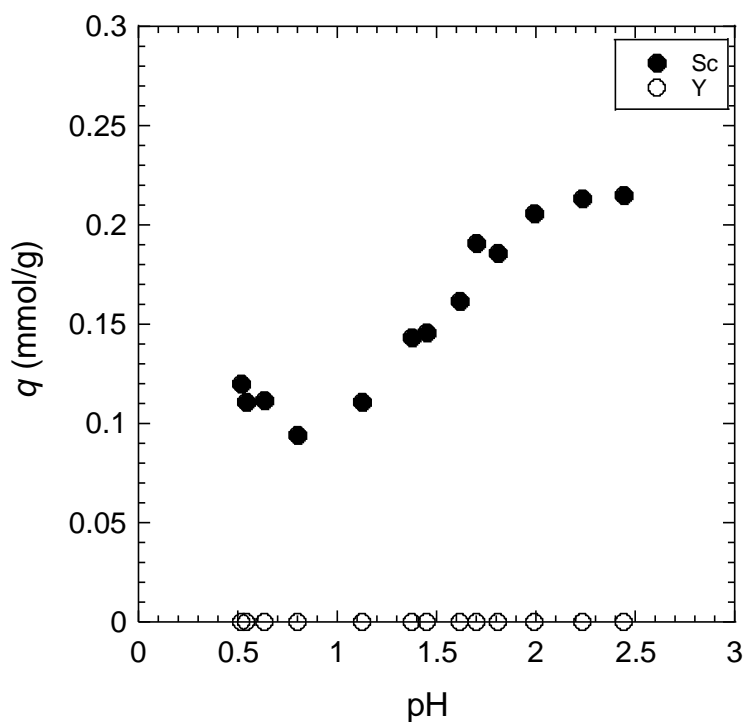


Figure 3.6. Effect of pH on adsorption of Sc and Y by SIRs with different concentration of organic solvent; (Cyanex 272/1-octanol) = 0.05 mol/L/0.00 mol/L

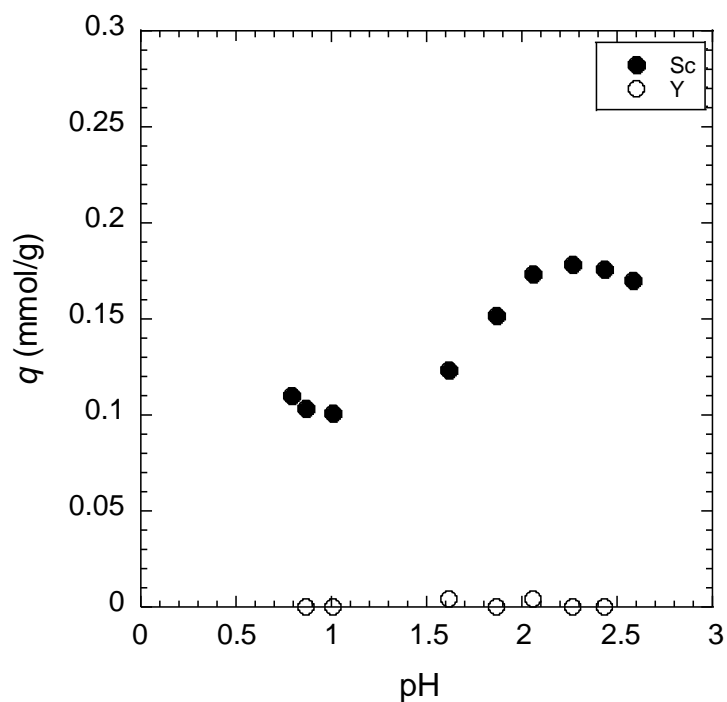


Figure 3.7. Effect of pH on adsorption of Sc and Y by SIRs with different concentration of organic solvent; (Cyanex 272/1-octanol) = 0.05 mol/L/0.01 mol/L

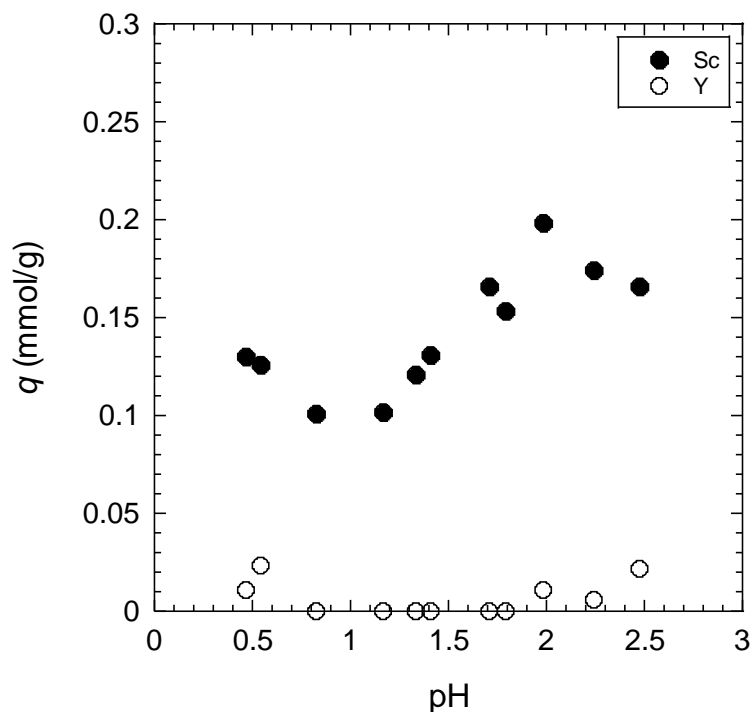


Figure 3.8. Effect of pH on adsorption of Sc and Y by SIRs with different concentration of organic solvent; (Cyanex 272/1-octanol) = 0.05 mol/L/0.03 mol/L

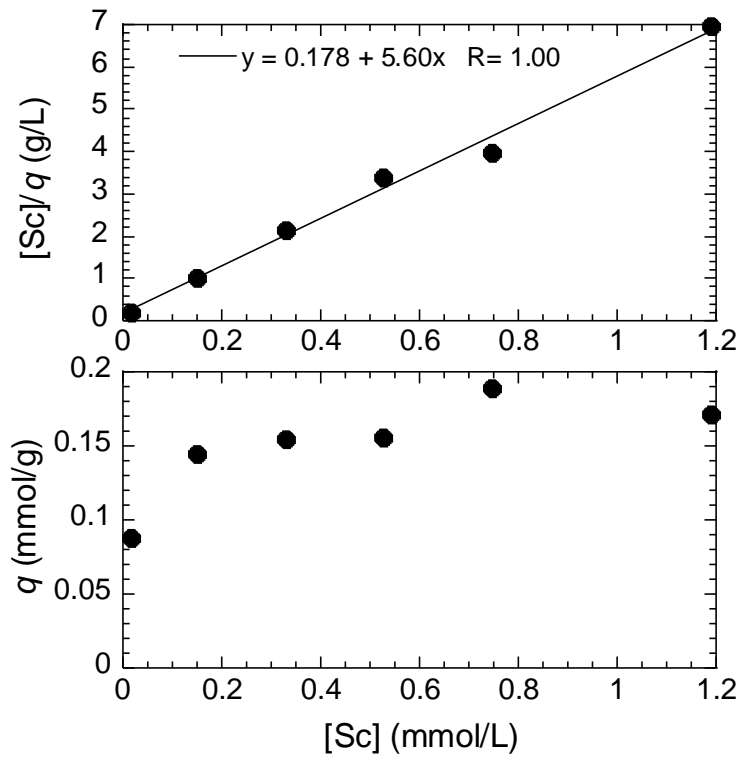


Figure 3.9. Langmuir isotherm model of SIRs with different concentration of organic solvent; (Cyanex 272/1-octanol) = 0.05 mol/L/0.00 mol/L

Adsorption isotherms of Sc with the SIRs were then investigated at equilibrium pH = 1.58 ± 0.07 , 1.54 ± 0.06 , 1.53 ± 0.06 , respectively. The isotherms obtained are shown in Figures 3.7 – 3.9. Assuming that the adsorption is of Langmuir mechanism, as shown in Eq. (3-11),

$$q = \frac{q_0 \times K \times [M]}{1 + K \times [M]} \quad (3-11)$$

then linearized Langmuir equation can be obtained, as Eq. (3-12).

$$\frac{[M]}{q} = \frac{1}{q_0} [M] + \frac{1}{q_0 \times K} \quad (3-12)$$

where q_0 is the maximum adsorption amount (mmol/g) and K is the adsorption equilibrium constant (L/mmol). The linearized relationship of the adsorption isotherm data was also shown in Figure 3.9 – 3.11, and the data was fitted well to the Langmuir adsorption model. The maximum adsorption amount and adsorption equilibrium constant are summarized in Table 3.3. Almost same maximum adsorption amount was

obtained with the SIR with no 1-octanol and SIR with 0.01 mol/L 1-octanol, while it is dramatically decreased in the case of SIR with 0.03 mol/L 1-octanol. Increase in the impregnated amount of 1-octanol to the SIR can therefore decrease in the adsorption amount.

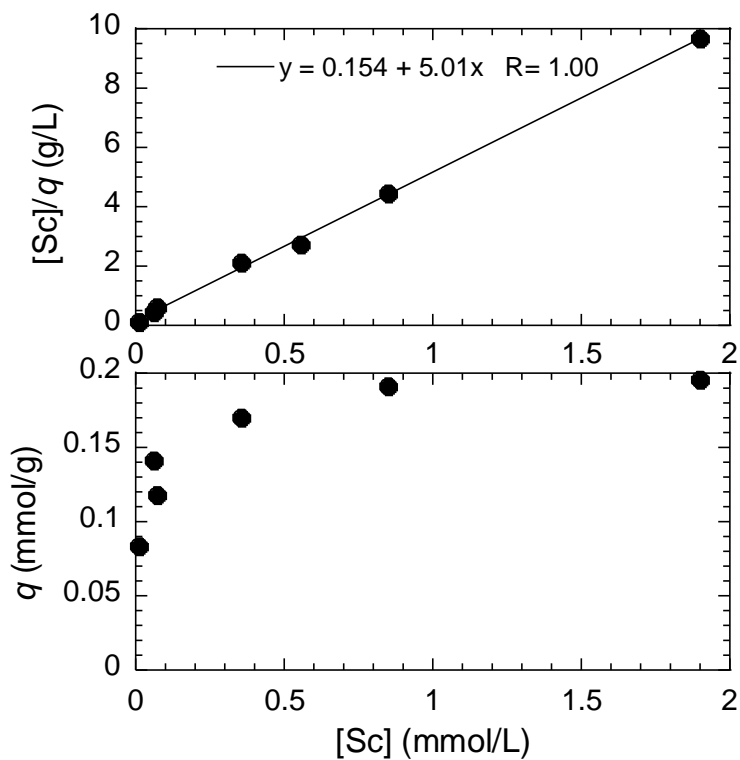


Figure 3.10. Langmuir isotherm model of SIRs with different concentration of organic solvent; (Cyanex 272/1-octanol) = 0.05 mol/L/0.01 mol/L

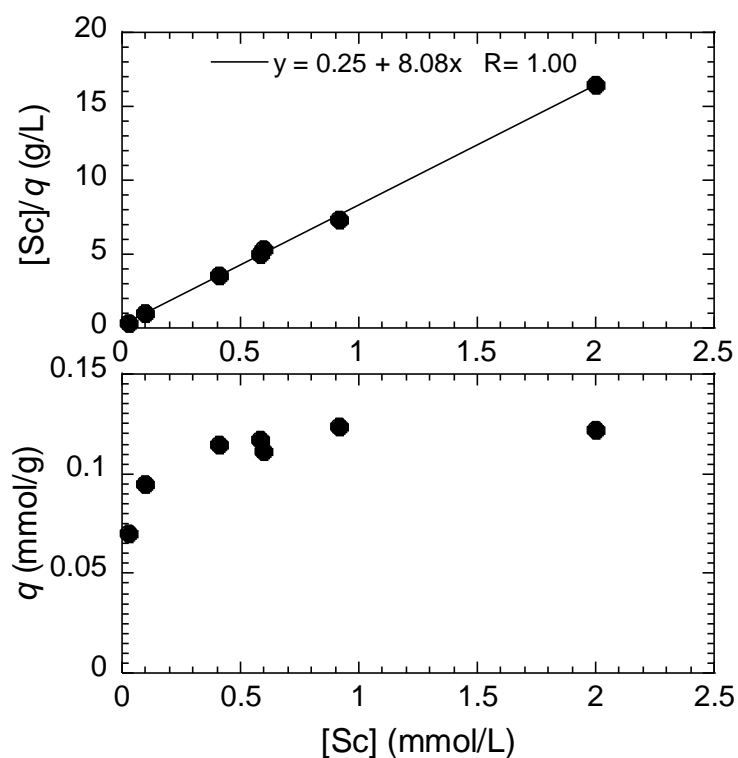


Figure 3.11. Langmuir isotherm model of SIRs with different concentration of organic solvent; (Cyanex 272/1-octanol) = 0.05 mol/L/0.03 mol/L

Table 3.3. Maximum adsorption amount and adsorption equilibrium constant of Sc with SIRs.

SIR	q_0 (mmol/g)	K (L/mmol)
(a) 0.05 mol/L/0.00 mol/L	0.179	31.6
(b) 0.05 mol/L/0.01 mol/L	0.176	32.1
(c) 0.05 mol/L/0.03 mol/L	0.124	33.1

Elution of Sc from the loaded SIRs with different concentration of HCl was then investigated. The elution yield obtained was summarized in Figures 3.12 – 3.14. In all SIRs, the elution yield was increased with HCl concentration, although quantitative elution was not achieved from SIRs (a) 0.05 mol/L/0.00 mol/L and (b) 0.05 mol/L/0.01 mol/L. In the case of (c) 0.05 mol/L/0.03 mol/L, however, complete elution was achieved with 5 mol/L HCl solution. These results are consistent to the maximum adsorption amount shown in Table 3.3, indicating excess amount of 1-octanol in the SIR can decrease adsorption ability of Sc and can therefore increase elution yield of Sc.

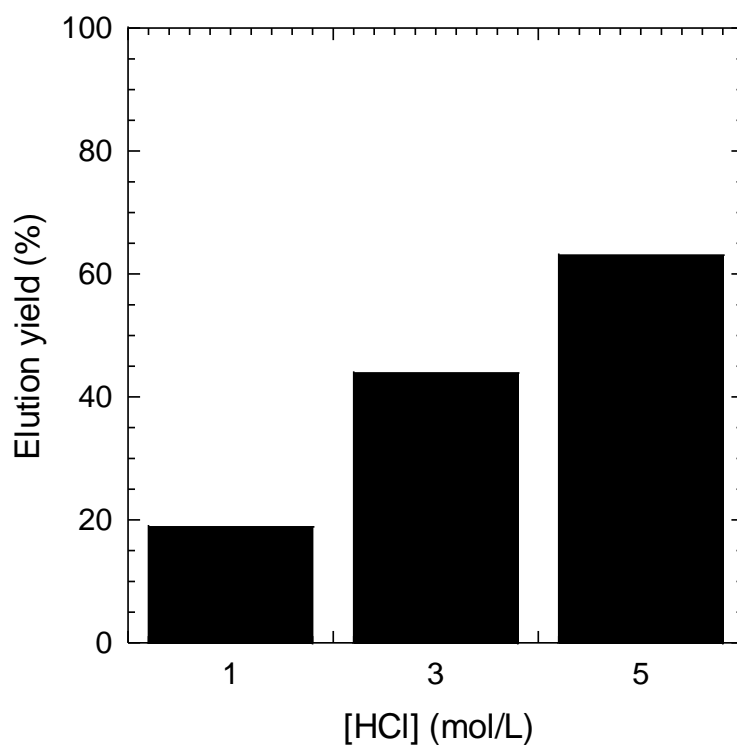


Figure 3.12. Elution yield of Sc with HCl solution from SIRs impregnated with organic solvent; (Cyanex 272/1-octanol) = 0.05 mol/L/0.00 mol/L

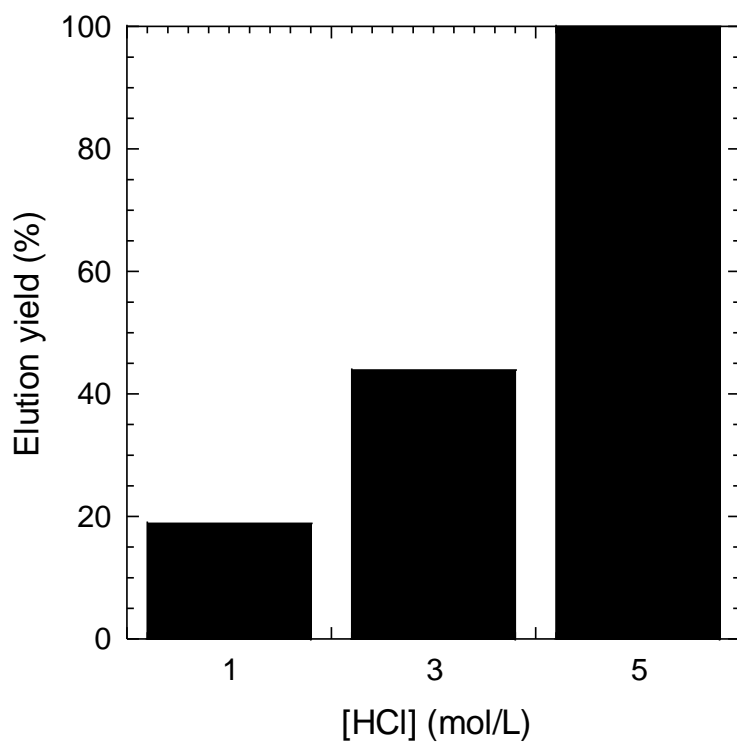


Figure 3.13. Elution yield of Sc with HCl solution from SIRs impregnated with organic solvent; (Cyanex 272/1-octanol) = 0.05 mol/L/0.01 mol/L

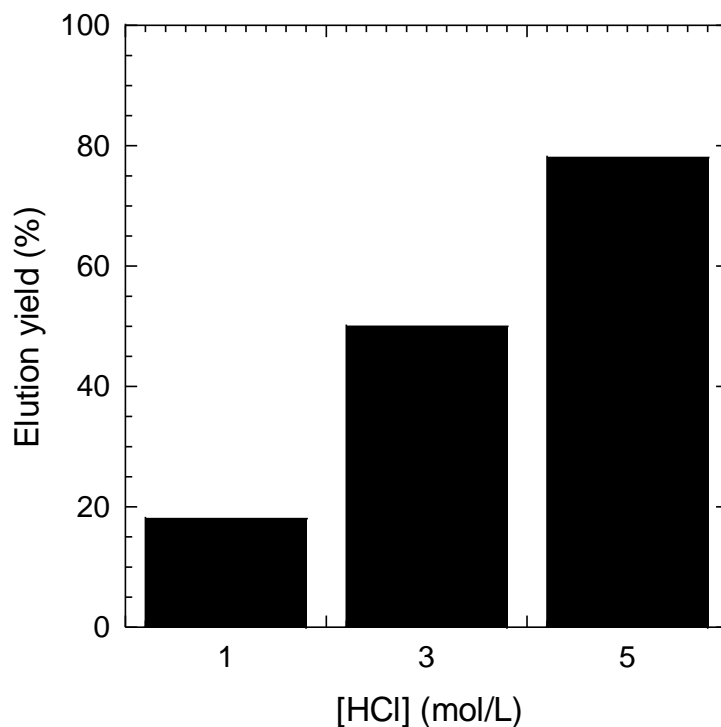


Figure 3.14. Elution yield of Sc with HCl solution from SIRs impregnated with organic solvent; (Cyanex 272/1-octanol) = 0.05 mol/L/0.03 mol/L

3.3.3. Column experiments

Column adsorption of Sc and Y from binary solution was finally investigated. In this case, SIR with 0.05 mol/L of Cyanex 272 and 0.01 mol/L of 1-octanol was used as adsorbent, and adsorption – elution processing was repeated for three times. Adsorption was carried out by frontal mode, and then the loaded metals were eluted with 5 mol/L HCl solution. Figure 3.15–20 show breakthrough and elution curves of the metals in each cycle. In the case of 1st cycle, Sc was completely adsorbed until bed volume of ca. 40, while Y was hardly adsorbed and was immediately broken through. Complete elution of both metals was also achieved with 5 mol/L HCl solution. In the cases of 2nd and 3rd cycles, however, adsorption amount of Sc was decreased, compared to the 1st cycle, to 84% and 69%. In addition, elution yield of Sc was also decreased to 87% and 85%. This might be due to the leakage of 1-octanol, and incomplete elution of Sc at the 2nd cycle leads dramatical decrease in the adsorption amount in the 3rd cycle.

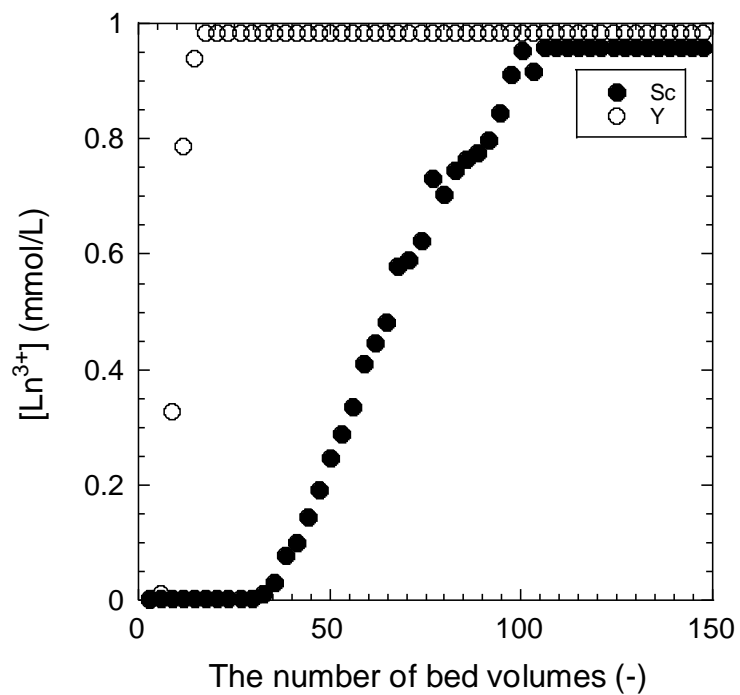


Figure 3.15. 1st breakthrough curve of Sc with SIR impregnated with organic solvent; (Cyanex 272/1-octanol) = 0.05 mol/L/0.01 mol/L

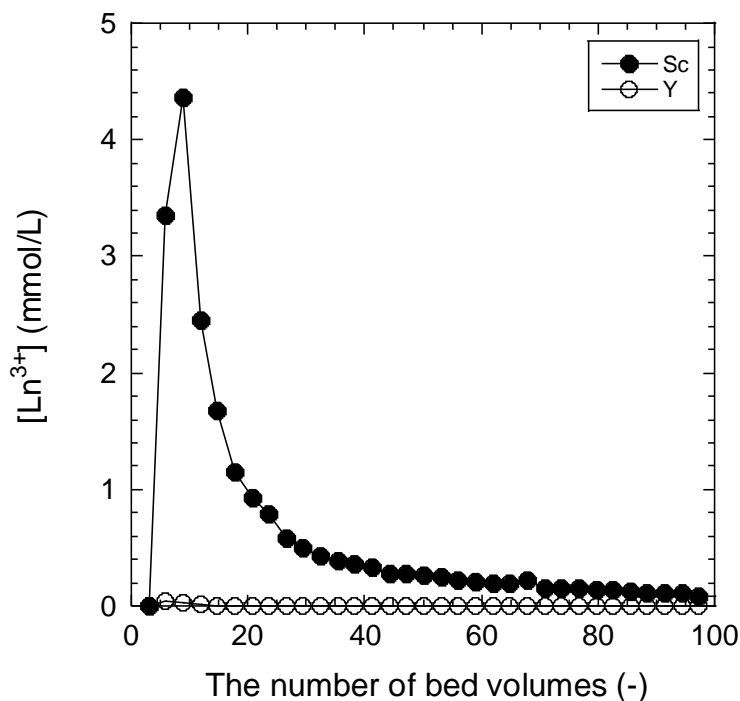


Figure 3.16. 1st elution curve of Sc with HCl solution from SIR impregnated with organic solvent; (Cyanex 272/1-octanol) = 0.05 mol/L/0.01 mol/L

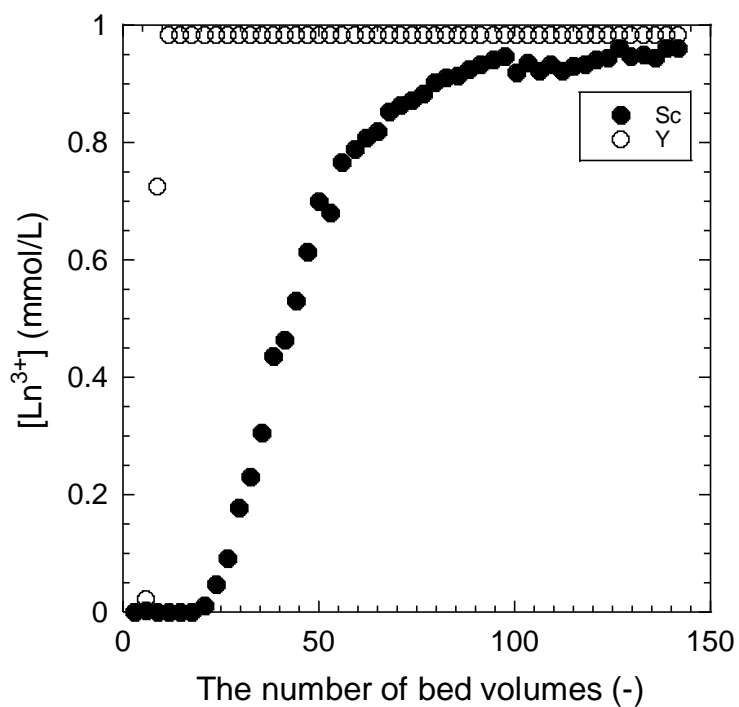


Figure 3.17. 2nd breakthrough curve of Sc with SIR impregnated with organic solvent; (Cyanex 272/1-octanol) = 0.05 mol/L/0.01 mol/L

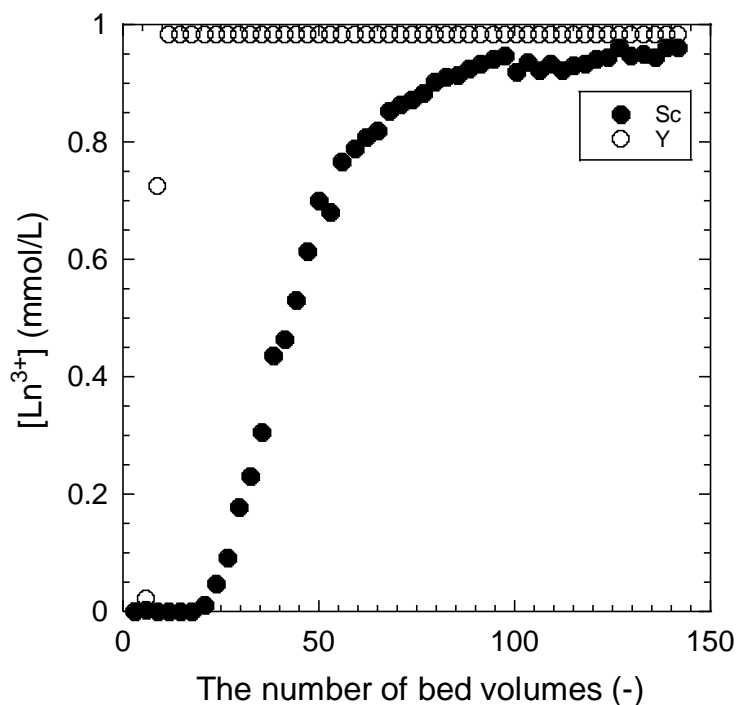


Figure 3.18. 2nd elution curve of Sc with HCl solution from SIR impregnated with organic solvent; (Cyanex 272/1-octanol) = 0.05 mol/L/0.01 mol/L

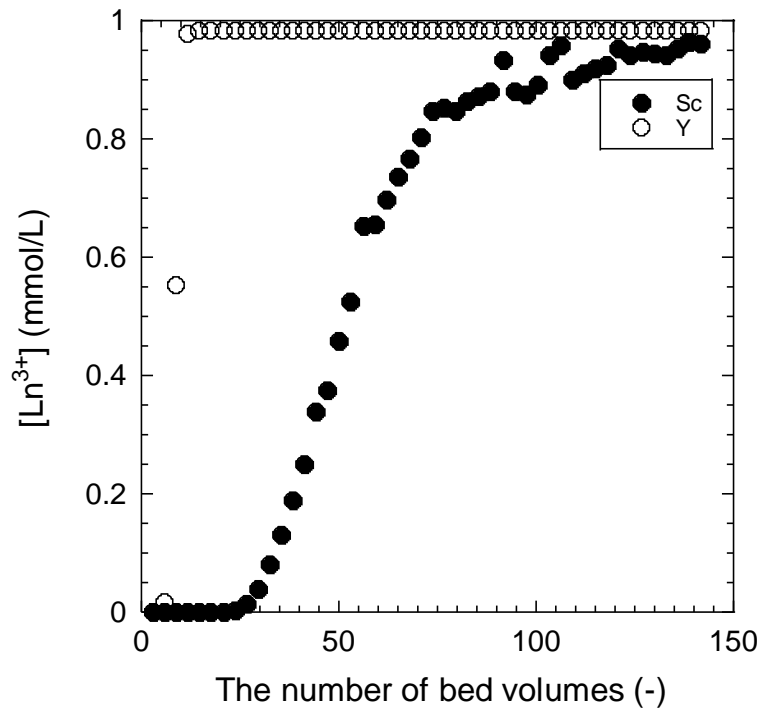


Figure 3.19. 3rd breakthrough curve of Sc with SIR impregnated with organic solvent; (Cyanex 272/1-octanol) = 0.05 mol/L/0.01 mol/L

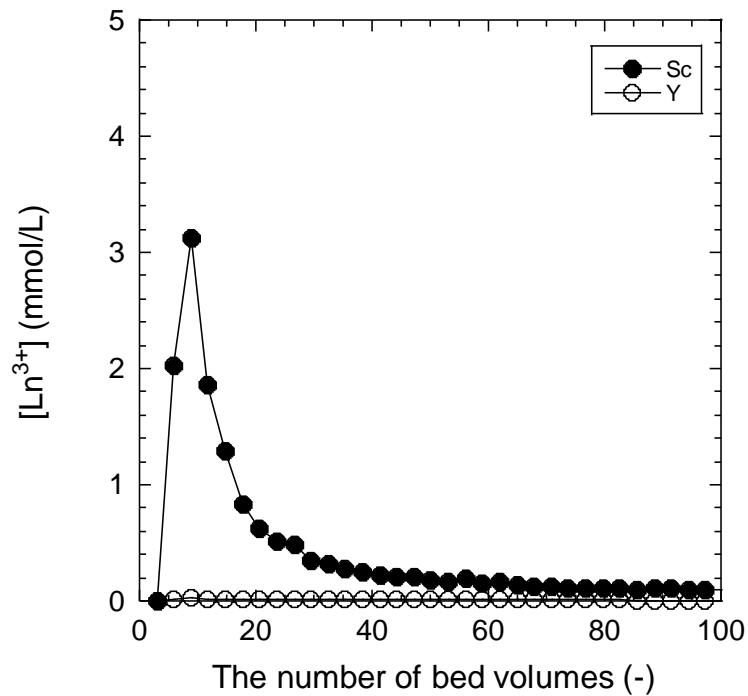


Figure 3.20. 3rd elution curve of Sc with HCl solution from SIR impregnated with organic solvent; (Cyanex 272/1-octanol) = 0.05 mol/L/0.01 mol/L

3.4. Conclusion

- (1) The extraction of Sc and Y was proceeded with the conventional cation exchange mechanism, and separation factor of the two metals is extremely high of 2.82×10^5 .
- (2) Complete stripping was achieved by addition of 1-octanol / Cyanex 272 of more than 6.
- (3) Sc was successfully adsorbed with the all SIRs, while Y was hardly adsorbed. Adsorption of Sc by SIRs was of Langmuir adsorption model.
- (4) The adsorption amount of Sc was decreased as the amount of 1-octanol increases, and thus complete elution of Sc from the adsorbent was achieved with 5 mol/L HCl.
- (5) Sc was selectively adsorbed with the SIR by chromatographic separation, while Y was hardly adsorbed. Sc adsorbed was completely eluted with 5 mol/L HCl.

Chapter 4

Separation of Scandium and Yttrium Using Carboxylic Acid

4.1. Introduction

Separation of scandium (Sc) from yttrium (Y) in aqueous chloride media by solvent extraction and SIR using Versatic acid 10 was investigated. Versatic acid 10 was adopted due to commercial availability and lower pK_a value which proposes higher stripping yield than Cyanex 272. Conventional slope analysis method revealed the extraction equilibrium formulation of the metals. Then Versatic acid 10 and 1-octanol impregnated SIR was employed to batch and column chromatography to recover Sc and Y.

4.2. Experiments

4.2.1. Reagents

Versatic acid 10 was supplied by HEXION Specialty Chemicals Co., Ltd (Tokyo, Japan), scandium oxide and yttrium oxide were supplied by Nippon Yttrium Co., Inc. (Fukuoka, Japan). IP Solvent 2835, a synthetic isoparaffinic hydrocarbon having 99.8 vol % or more iso-paraffin was supplied by Idemitsu Kosan Co., Ltd (Tokyo, Japan). Diaion HP2MG, a methacrylic ester copolymer containing no functional group, was supplied by Nippon Rensui Co., Ltd. (Tokyo, Japan). All other organic and inorganic reagents were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) as analytical-grade reagents.

4.2.2. Solvent Extraction

4.2.2.1. Extraction

Aqueous rare earth chloride solutions were prepared by dissolving each oxide in 1 or 2 mol/L HCl solution, and then diluted with deionized water to obtain 1 mmol/L Sc or Y aqueous solutions. The pH of the aqueous solution was adjusted using HCl or NaOH. Organic solutions were prepared by diluting Versatic acid 10 in IP Solvent 2835. Concentrations of the extractant as a dimeric species base are shown in the Figure captions. Extraction of Sc and Y was carried out by shaking the organic and aqueous solutions at a volume ratio of 1 : 1 at 298K for more than 6 h. Concentrations of the metals in the resultant aqueous solutions were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu ICPE-9000) and those in the organic solutions were calculated based on material balance. The pH was measured by a pH meter (Horiba F-74).

4.2.2.2. Stripping

Stripping experiments were carried out using the metal loaded organic solution. In this case, the extraction was carried out in the same manner as described above, and the metal loaded organic solution was used in the stripping experiments. Stripping was

performed by contacting the loaded organic solution with different concentrations of HCl (2 – 3 mol/L) at a volume ratio = 1 : 1, and the mixture was shaken at 298K for more than 3 h. The concentrations of the metals in the resultant aqueous solutions were determined by ICP-AES and those in the organic solutions were calculated based on material balance.

4.2.3. Solvent impregnated resin

4.2.3.1. SIR preparation

The SIR was prepared by the following method [14, 15, 41]. HP2MG was washed with methanol and dried in vacuo. Washed HP2MG (2.5 g) was then immersed overnight in a 0.2 mol/L Versatic acid 10 – toluene solution (50 mL). The toluene was then removed by evaporation, and the resin dried in vacuo for 24 h. The amount of Versatic acid 10 impregnated in the resin was 8.23 mmol/g. Coating of SIRs were conducted using PVA, of polymerization degree ca. 2000, crosslinked by glutaraldehyde (GA). The prepared SIR (3 g) was immersed in an aqueous solution (50 mL) containing 3 wt% PVA and 1 wt% acetamide and the mixture was shaken for 17 h. The resultant suspension was then mixed with 1 mol/L KCl aqueous solution (10 mL) and the mixture was shaken for 24 h. The pre-treated SIR was filtered and resuspended in a 0.32 mol/L H₂SO₄ solution (10 mL) for 1 h. 0.32 mol/L GA aqueous solution (10 mL) was then added, followed by shaking the mixture for 24 h, to complete crosslinking. The coated SIR obtained was filtered, washed with deionized water, and then dried. Hereafter, SIR used in the present study was all coated SIR.

4.2.3.2. Batch Experiments

Aqueous rare earth chloride solutions were prepared by dissolving each oxide in 1 or 2 mol/L HCl solution, and then diluted with deionized water to obtain 1 mmol/L Sc and Y aqueous solutions. The pH of the aqueous solution was adjusted using HCl or NaOH. The SIR (20 mg) was added to 20 mL of aqueous solution, and the suspended mixture was shaken at 298 K for 24 h. The concentrations of the metal ions were determined, after filtration of the resin, with an ICP-AES. The amount of adsorbed metal ion, q (mmol/g), is defined as:

$$q = \frac{([M]_{ini} - [M]_{eq}) \times L}{w} \quad (4-1)$$

where $[M]_{ini}$ and $[M]_{eq}$ are initial and equilibrium concentrations of metals in the solution (mmol/L), respectively, V is the volume of the solution (L), and W is the weight of the resin (g). Elution experiments were carried out using the metal loaded SIR. In this case,

the adsorption was carried out in the same manner as described above, and the metal loaded SIR was used. Elution was performed by adding 10 mg of metal adsorbed SIR to 10 mL of different concentrations of HCl (1 – 3 mol/L), and the mixture was shaken at 298K for more than 24 h. The concentrations of the metal ions were determined with ICP-AES. The elution yield was calculated by material balance.

4.2.3.3. Column experiments

SIR (weight = 1.0 g, wet volume = 2.6 mL) was packed into a glass column of 100 mm in length and 8 mm in diameter, and then deionized water was fed to the column to wash the adsorbent for 12 h. Aqueous feed solution containing $[Sc^{3+}] = [Y^{3+}] = 1$ mmol/L at $pH_{ini} = 4.01$ was fed to the column at flow rate of 0.20 mL/min {space velocity (S.V.) = $6\ h^{-1}$ }, using a peristaltic pump (EYELA KP-11). The metal ions loaded into the columns were eluted with 3 mol/L HCl, which is determined by the preliminary study by comparing various acids and bases. The effluents were collected with a fraction collector (EYELA DC-1500). The number of bed volumes of the effluent is defined as:

$$\text{Bed Volume} = \frac{v \times t}{V} \quad (4-2)$$

where v , t , and V are the flow rate of the solution (mL/min), time the solution was applied (min), and the wet volume of the adsorbent (mL).

4.3. Results and Discussions

4.3.1. Solvent extraction

Figure 4.1 shows the effect of time on the extraction of Sc. It reached equilibrium in 3 h. Thus, the extraction is conducted for 3h. Figure 4.2 shows the effect of pH on the extraction yield of Sc and Y. Extraction of Sc proceeds at pH 3 – 4, while extraction of Y proceeds at pH > 4.5. Thus, separation of Sc from Y is expected to be achieved at pH 3 – 4. Figure 4.3 shows the effect of pH on the distribution ratio of Sc from pH 3.1 to 3.5 where extraction of Y hardly occurs. For Sc, a linear relationship with a slope of 3 between pH and $\log D$ was obtained, indicating that the extraction proceeds by cation exchange between scandium and the three protons.

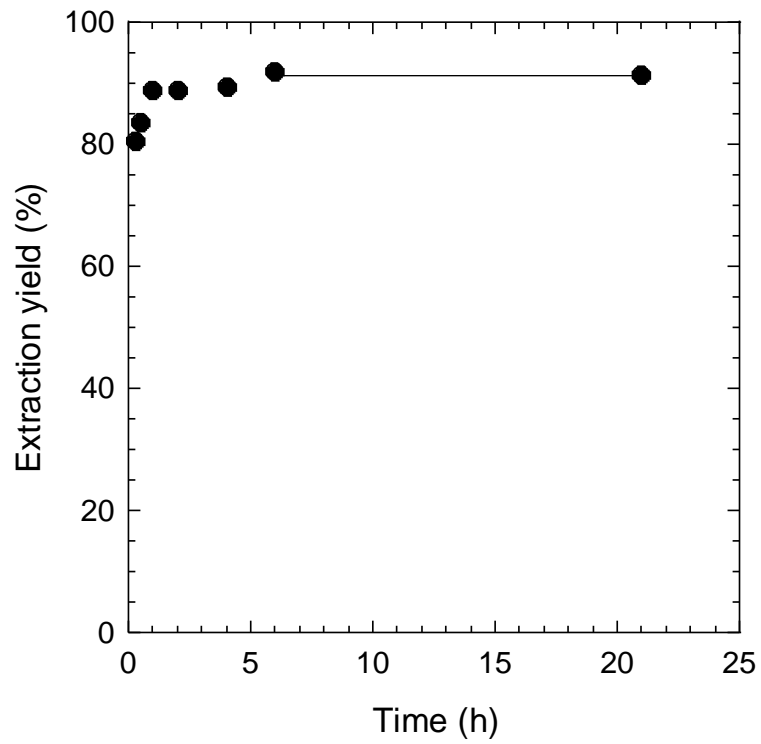


Figure 4.1. Effect of time on the extraction of Sc

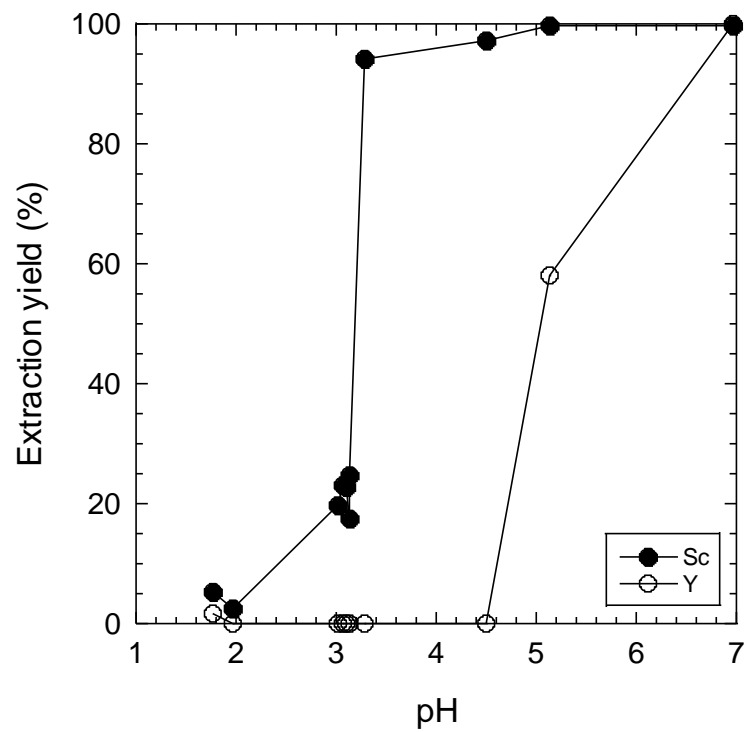


Figure 4.2. Effect of pH on the extraction yield

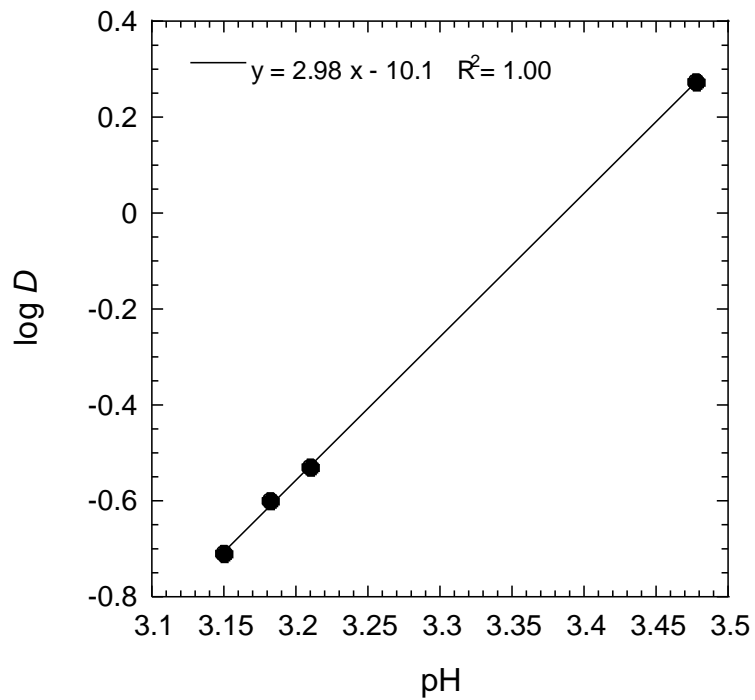


Figure 4.3. Effect of pH on the distribution ratios of Sc.

$[(\overline{\text{RH}})_2]_{\text{feed}} = 0.0354 \text{ mol/L}$, $[\text{1-octanol}] = 0.01 \text{ mol/L}$, $[\text{Sc}]_{\text{feed}} = 1.00 \text{ mmol/L}$

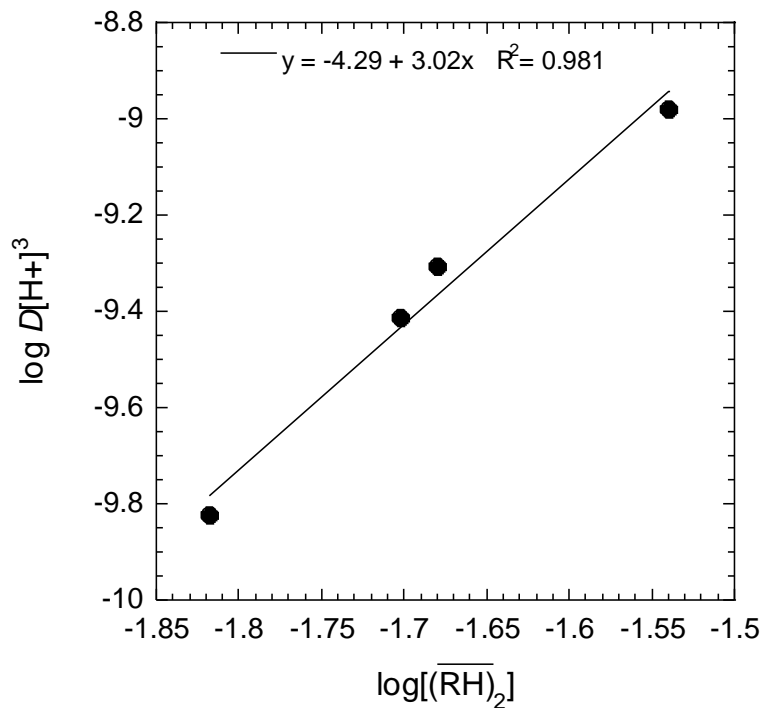
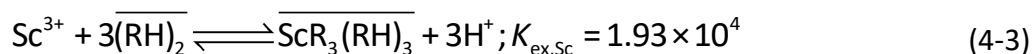


Figure 4.4. Effect of concentration of dimeric extractants on the normalized distribution ratios of Sc. $[(\overline{\text{RH}})_2]_{\text{feed}} = 0.0354 \text{ mol/L}$, $[\text{Sc}]_{\text{feed}} = 1.00 \text{ mmol/L}$

Figure 4.4 shows the effect of the concentration of the dimerized extractant on the distribution ratio. The relationship between $\log D[\text{H}^+]^3$ and $\log[(\text{RH})_2]_{\text{feed}}$ for Sc showed a dependency of slope 3, so that three dimeric extractants participate in the extraction of each metal ion. Based on the results of the slope analysis, the extraction equilibrium for Sc is formulated as Eq. (4-3).



K_{ex} value for Sc is 1.93×10^4 which is quite high, and it implies the stripping of Sc is expected to be difficult. Stripping of the loaded Sc was then investigated. Table 4.1 lists the stripping yields of Sc from the loaded organic solutions containing Versatic acid 10 with different concentrations of HCl. The stripping yield of Sc reached 100 % by 3 mol/L HCl.

Table 4.1. Stripping yield of Sc using different concentrations of HCl

[HCl] (mol/L)	Stripping rate (%)
1	49.2
2	87.7
3	100

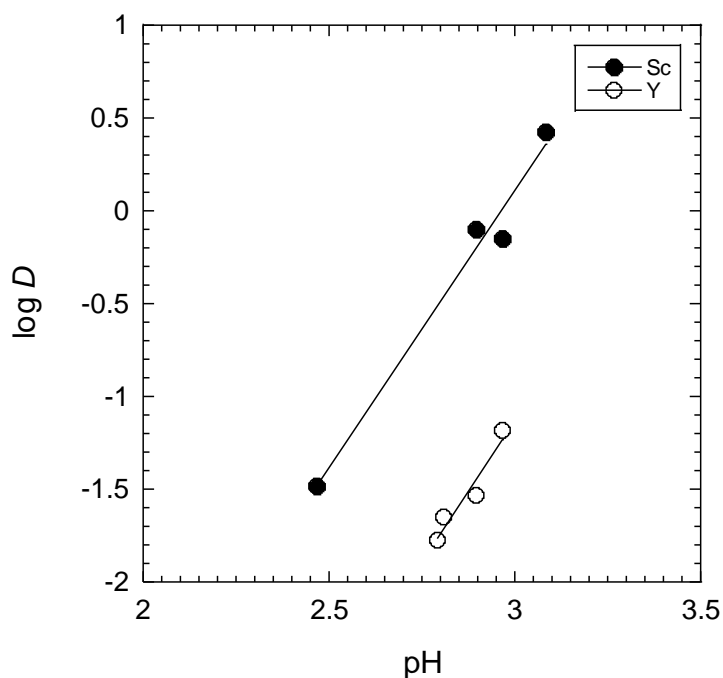


Figure 4.5. Effect of pH on the distribution ratios of Sc and Y.

$[(\text{RH})_2]_{\text{feed}} = 0.0354 \text{ mol/L}$, $[1\text{-octanol}] = 0.01 \text{ mol/L}$, $[\text{Sc}]_{\text{feed}} = [\text{Y}] = 1.00 \text{ mmol/L}$

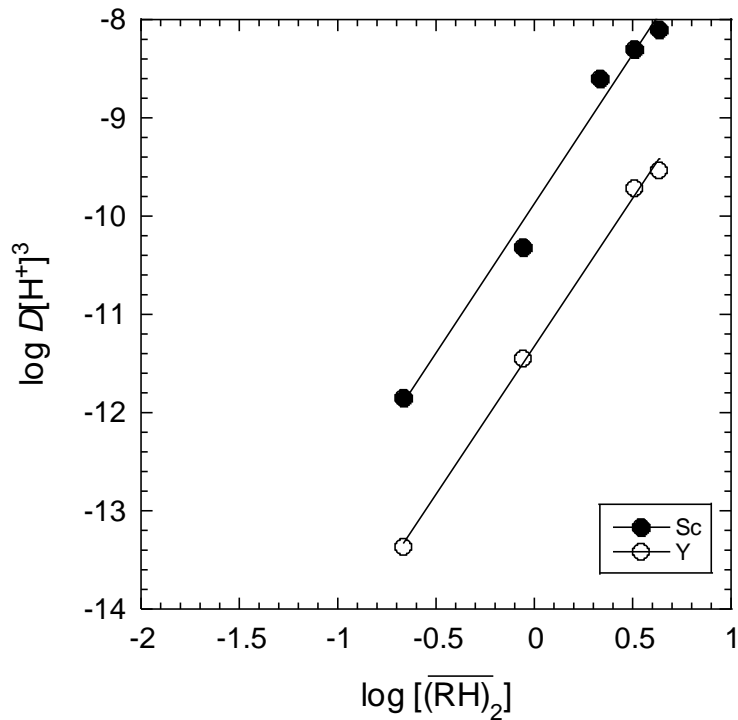
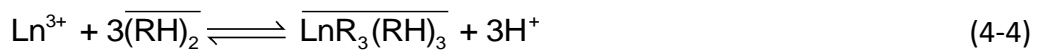


Figure 4.6. Effect of concentration of dimeric extractants on the normalized distribution ratios of Sc and Y. $[(\overline{\text{RH}})_2]_{\text{feed}} = 0.0354 \text{ mol/L}$, $[1\text{-octanol}] = 0.01 \text{ mol/L}$, $[\text{Sc}]_{\text{feed}} = [\text{Y}] = 1.00 \text{ mmol/L}$

Figure 4.5 shows the effect of pH on distribution ratio, and Figure 4.6 shows the effect of the concentration of dimerized Versatic acid 10 on the distribution ratio. As Figure 4.3 and Figure 4.4, three proton and three dimerized extractants were involved in cation exchange reaction. Thus, it was confirmed that 1-octanol was not involved in the extraction mechanism thus it was same as Versatic acid 10 single extraction.

The stoichiometry of the complex formation reaction for Sc and Y with Versatic acid 10 and 1-octanol is formulated as Eq. (4-4).



K_{ex} value for Sc is 1.32×10^{-10} and K_{ex} value for Y is 4.72×10^{-12} . Separation factor of Sc and Y was 2.79×10^1 . K_{ex} for Sc was less than that of Sc in the extraction with Versatic acid 10 in the absence of 1-octanol, which was expected from addition of 1-octanol as modifier.

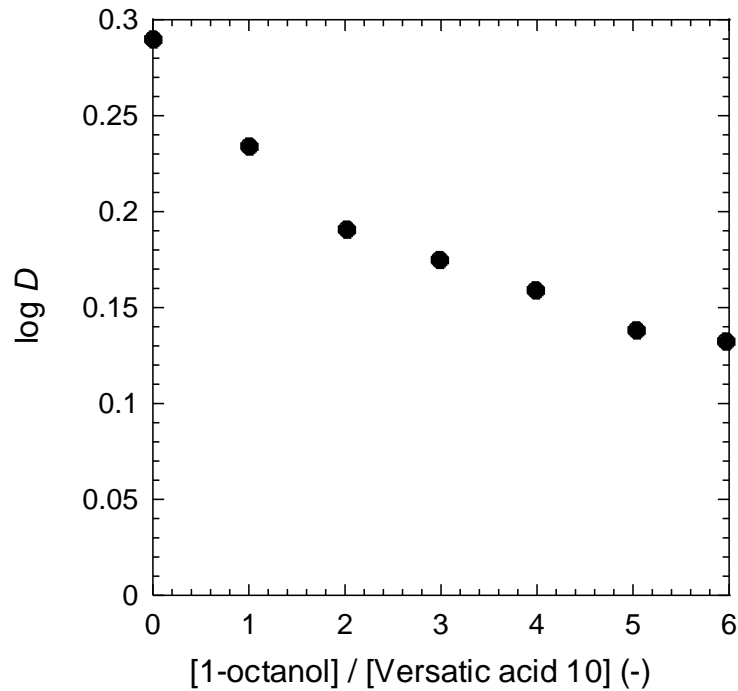


Figure 4.7. Effect of molar ratio of 1-octanol/Versatic acid 10 on the distribution ratio of Sc. $[(RH)_2]_{\text{feed}} = 0.0340 \text{ mol/L}$, $[Sc]_{\text{feed}} = 0.97 \text{ mmol/L}$

In Figure 4.7, the effect of ratio of 1-octanol/Versatic acid 10 on the distribution ratio was examined. Log D was decreased as the ratio of 1-octanol/Versatic acid 10 increases. Thus, increment of stripping yield is expected from the decrement of distribution ratio which also proposes lower extraction yield.

4.3.2. Batch experiments

Figure 4.8 shows the effect of pH on the adsorption of Sc and Y with Versatic acid 10 SIR in the binary solution. From pH 1.5 to 3.5 Sc and Y are adsorbed and Sc was maximum at pH 2.5, while Y was also maximum at pH 2.7.

Adsorption isotherm of Sc in pH 2.8 with Versatic acid 10 is shown in Figure 4.9. Assuming that the adsorption is of Langmuir mechanism, as shown in Eq. (4-5),

$$q = \frac{q_0 \times K \times [M]}{1 + K \times [M]} \quad (4-5)$$

then linearized Langmuir equation can be obtained, as Eq. (4-6).

$$\frac{[M]}{q} = \frac{1}{q_0} [M] + \frac{1}{q_0 \times K} \quad (4-6)$$

where q_0 is the maximum adsorption amount (mmol/g) and K is the adsorption equilibrium constant (L/mmol). From the linear relationship of the Langmuir mechanism, Figure 4.10, the adsorption of Sc with the Versatic acid 10 SIR is of Langmuir mechanism. The maximum adsorption amounts of Sc calculated was 0.139 mmol/g, and the adsorption equilibrium constant was 1.51 L/mmol, respectively. Elution of adsorbed Sc was then investigated. Table 4.2 lists the elution yields of Sc from the adsorbed resin with different concentrations of HCl. The stripping yield of Sc reached only 52.2 % by 3 mol/L HCl.

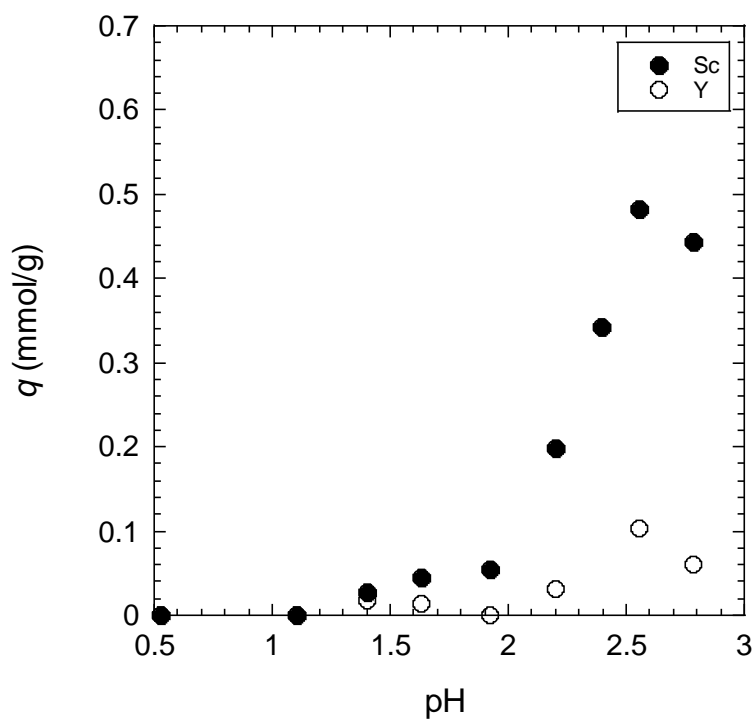


Figure 4.8. Effect of pH on the adsorption amount of Sc and Y

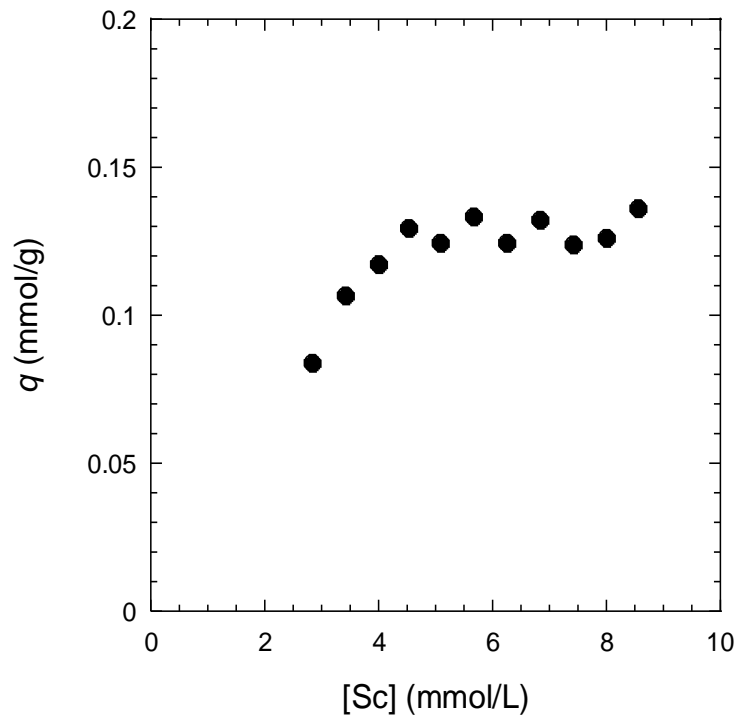


Figure 4.9. Adsorption isotherm of Sc with Versatic acid 10 + 1-octanol SIR

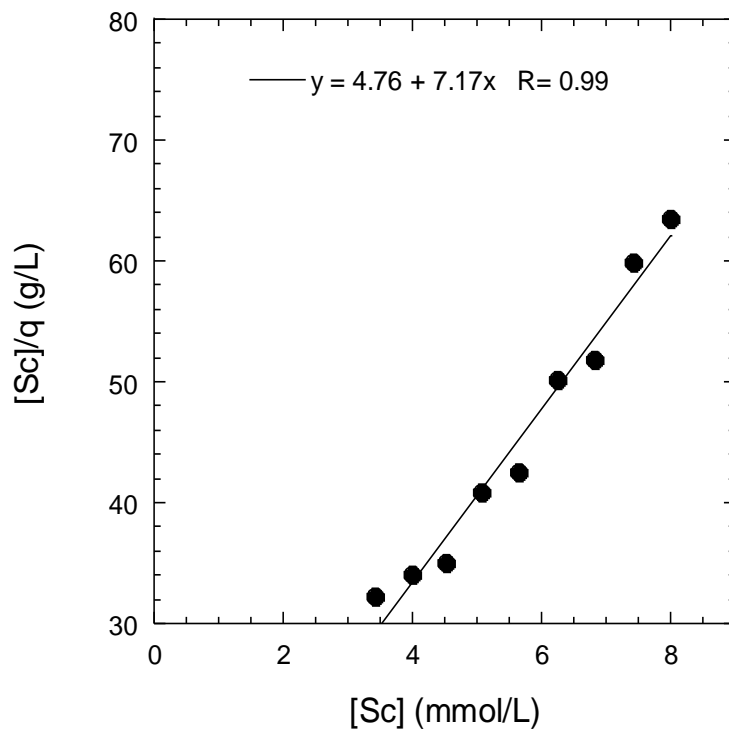


Figure 4.10. Langmuir isotherm of Sc with Versatic acid 10 + 1-octanol SIR

Table 4.2 Elution yield with different concentration of HCl

[HCl] (mol/L)	Stripping yield (%)
1	25.4
2	31.0
3	52.2

4.3.3. Column experiments

Column adsorption of Sc and Y from binary solution was investigated. In this case, SIR impregnating Versatic acid 10 and 1-octanol was used as adsorbent, and adsorption – elution processing was carried out. Adsorption was carried out by frontal mode, and then the loaded metals were eluted with 3 mol/L HCl solution. Figures 4.10 and 4.11 show breakthrough and elution cures of the metals.

Sc was completely adsorbed until bed volume of ca. 20, while Y was breakthrough bed volume ca. 20 and a little bit eluted. Complete elution of Sc and Y was also achieved with 3 mol/L HCl solution. Elution yield of Sc was 105.1%, and that of Y was 100%.

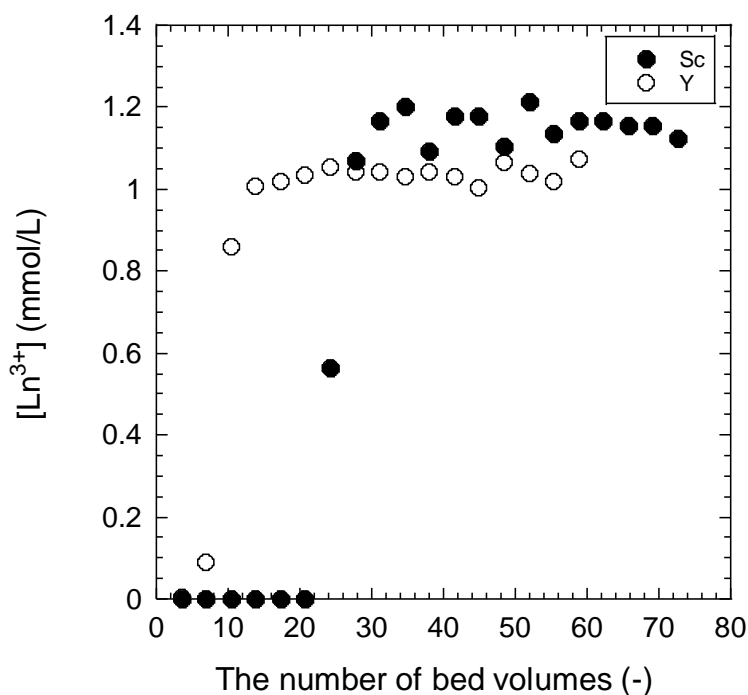


Figure 4.11 Breakthrough curve of Sc and Y with Versatic acid 10 and 1-octanol impregnated SIR

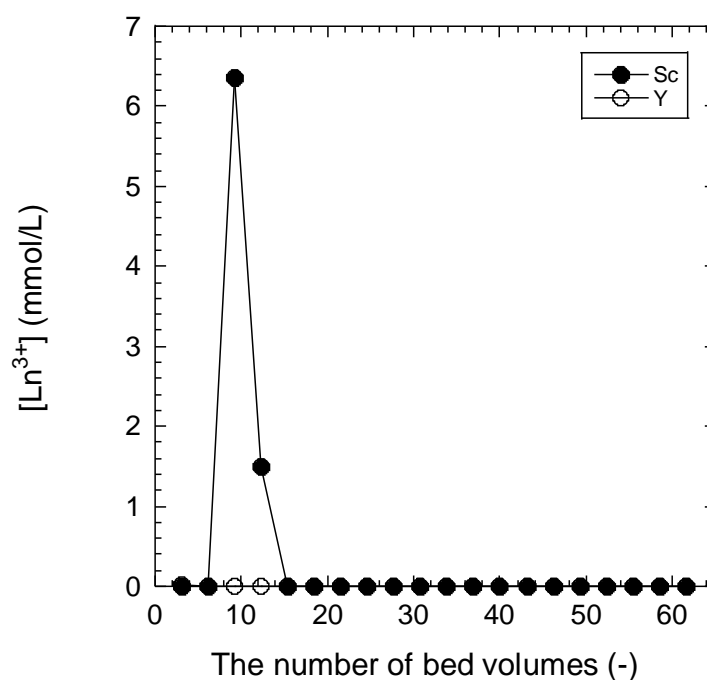


Figure 4.12 Elution curve of Sc and Y with Versatic acid 10 and 1-octanol impregnated SIR

4.4. Conclusion

Extraction and stripping of Sc with Versatic acid 10 and adsorption using Versatic acid 10 SIR were investigated with the following results.

- (1) The extraction of Sc was proceeded by the conventional cation exchange mechanism and equilibrium constant was quite high at 1.93×10^4 .
- (2) The stripping yield of Sc from Versatic acid 10 reached 100% using 3.0 mol/L HCl solution as the stripping reagent.
- (3) The reaction stoichiometry was the same regardless of the presence or absence of 1-octanol, but the decrease of K_{ex} value was confirmed.
- (4) Versatic acid 10 with 1-octanol impregnated SIR can adsorbs Sc under specific pH region. Adsorption of Sc by Versatic acid 10 follows the Langmuir adsorption model and the maximum adsorption amounts of Sc was 0.139 mmol/g, and the adsorption equilibrium constant K was 1.51 L/mmol, respectively.
- (5) Sc was completely adsorbed until bed volume of 20, while Y was scarcely adsorbed. Complete elution of Sc and Y was also achieved with 3 mol/L HCl solution. Elution yield of Sc was 105.1%, and that of Y was 100%.

Chapter 5

Conclusion

In this study, following conclusions were obtained from research aimed at separating and recovering rare metals by applying coating-type SIR using amine, phosphate and carboxylic extractant.

In chapter 1, DHA-SIR and DOA-SIR possess the selective adsorption ability for Pt while other extractant did not. DHA-SIR is better than DOA-SIR from the view point of separation factor, while adsorption of other metals are suppressed in the batchwise adsorption system. Adsorption of Pt by DHA-SIR follows the Langmuir adsorption model and the maximum adsorption amounts of Pt was 5.434 mmol/g, and the adsorption equilibrium constant K was 0.533 L/mmol, respectively. Selective adsorption–elution of Pt and Pd using DHA-SIR and DHS-SIR can be achieved by sequential chromatographic system. Mutual separation of Pd and Pt can be achieved by DHS-SIR to separate Pd followed by DHA-SIR to separate Pt. The precipitation yield of Pt by adding NaBH₄ was increased with increase in pH, to reach 100% precipitation at pH > 10. Elementary Pt having the purity of 99.2% was obtained.

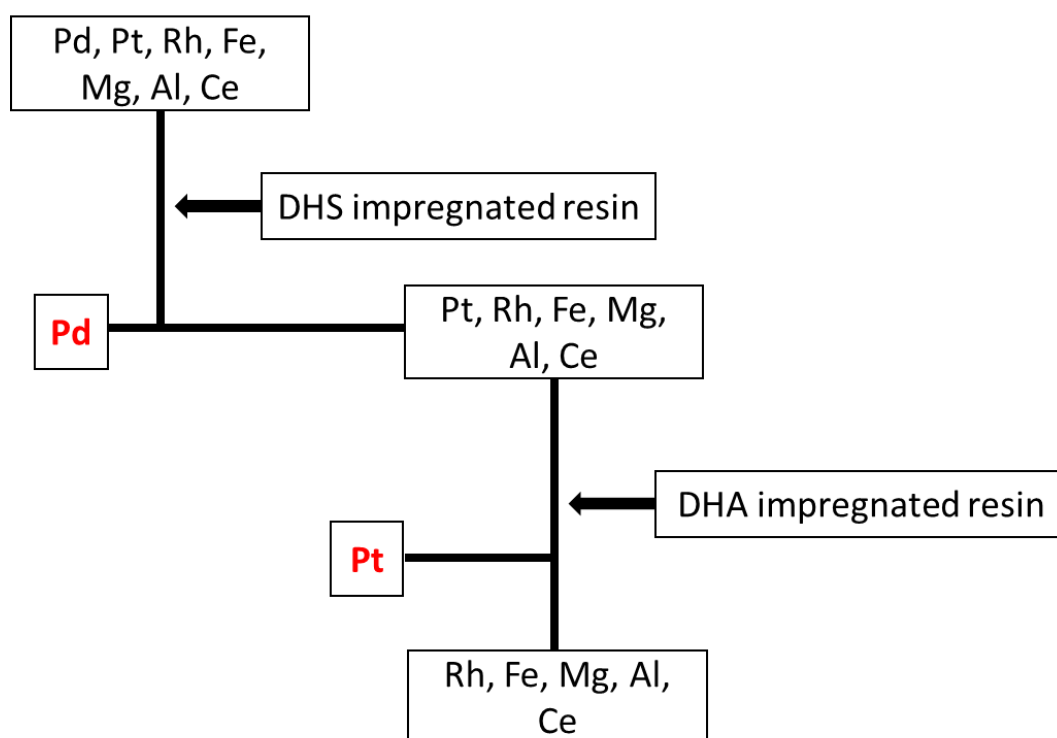
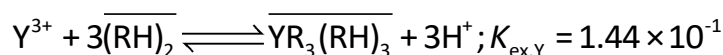
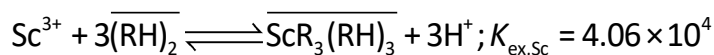


Figure 5.1. Flow chart of separation of Pt and Pd using solvent impregnated resin

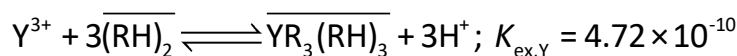
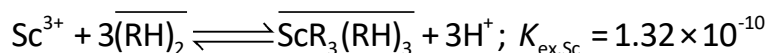
In chapter 2, separation and recovery of Sc and Y using solvent extraction method and coated SIR applying organophosphorus extractant was conducted. Extraction equilibrium relation and extraction equilibrium constant of Sc and Y using Cyanex272 are as follows.



Sc was successfully adsorbed with the all SIRs, while Y was hardly adsorbed. Adsorption amount of Sc was decreased as increasing the amount of 1-octanol, and thus complete elution of Sc from the adsorbent was achieved with 5 mol/L HCl. Adsorption of Sc by SIRs was of Langmuir adsorption model. The SIR could be applied for chromatographic separation of Sc and Y. Sc was selectively adsorbed with the SIR and adsorbed Sc was completely eluted with 5 mol/L HCl, while adsorption amount was decreased with repeated use.

In chapter 3, separation and recovery of Sc and Y using solvent extraction method and coated SIR applying carboxylic extractant was explored.

Extraction equilibrium of Sc with Versatic acid 10 was determined.



$$\frac{K_{\text{ex,Sc}}}{K_{\text{ex,Y}}} = 27.9$$

The stripping yield of Sc from Versatic acid 10 reached 100% using 3.0 mol/L HCl solution. Adsorption of Sc by Versatic acid 10 follows the Langmuir adsorption model and the maximum adsorption amounts of Sc was 0.139 mmol/g, and the adsorption equilibrium constant K was 1.51 L/mmol, respectively. The SIR could be applied for chromatographic separation of Sc and Y. Sc was selectively adsorbed with the SIR and adsorbed Sc was completely eluted with 5 mol/L HCl, while adsorption amount was decreased with repeated use.

For the future work, in order to apply to industrial scale, enhancement of purity of Pt up to 99.5% is necessary. Also, the development of solvents and SIRs possessing enough adsorption capacity for separation and recovery of Sc and high elution yield with low concentration of acid is required to make SIRs repeatedly used.

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