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Research Article

Separation and Recovery of Palladium (II) and Platinum (IV) from Automotive Catalysts by Solvent Extraction Using Tri-n-butyl Phosphate and Aliquat 336

Mustafa AKÇİL ^{a,*}, Çağrı EYÜBOĞLU ^a

^a Department of Metallurgical and Materials Engineering, Faculty of Technology, Sakarya University of Applied Sciences, Sakarya, TURKEY

* Corresponding author's e-mail address: makcil@subu.edu.tr

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ABSTRACT

Pt, Pd, Fe, Ni, and Cr are among the metals found in spent automotive catalysts, which are both environmentally critical and economically beneficial. In this study, solvent extraction methods were utilized to separate and recover palladium (Pd) and platinum (Pt) from wasted car catalyst. The synthetic leach liquor employed in this investigation contains (mg/L): Pd-140, Pt-500, Ni-800, Fe-2000 and Cr-150. The variation of tri-n-butyl phosphate (TBP) in Shellsol D70 from 0.1 to 2 M revealed selective and quantitative Pd extraction even at the lowest extractant concentration. Stripping Pd from loaded organic (LO) phase using 1 M thiourea and 1 M HCl yielded stripping efficiency of 99%. The use of Aliquat 336 at concentrations ranging from 0.05 to 0.5M in the extraction of Pt from Pd free raffinate demonstrated selective extraction of Pt, reaching 99.7% at 0.2M. The use of a McCabe-Thiele plot in 0.2M Aliquat 336 is expected to result in the extraction of more than 99% of Pt in two stages when an A/O phase ratio of 3 is used. The stripping efficiency of Pt from loaded organic (LO) at O/A ratio 6 with 0.5 M thiourea (tu) and HCl was 99.9 percent.

Keywords: Automotive Catalyst, Shellsol D70, Aliquat 336

Tri-n-bütül Fosfat ve Aliquat 336 Kullanarak Otomotiv Katalizörlerinden Paladyum (II) ve Platin (IV)'in Çözücü Ekstraksiyonu ile Ayrılması ve Geri Kazanımı

Öz

Kullanılmış otomotiv katalizörlerinde bulunan metaller arasında çevresel olarak kritik ve ekonomik olarak faydalı olan Pt, Pd, Fe, Ni ve Cr bulunmaktadır. Bu çalışmada, atık otomobil katalizörlerinden paladyum (Pd) ve platin (Pt) ayırmak ve geri kazanmak için çözücü ekstraksiyon yöntemleri kullanılmıştır. Bu çalışmada kullanılan sentetik liç likörü (mg/L olarak) şunları içermektedir: Pd-140, Pt-500, Ni-800, Fe-2000 ve Cr-155. Shellsol D70 içindeki tri-n-bütül fosfat (TBP) konsantrasyonunun 0.1'den 2 M'ye değişimi, en düşük ekstraktör konsantrasyonunda bile seçici ve nicel Pd ekstraksiyonunu ortaya koymuştur. Yüklü organik (LO) fazdan 1 M tiourea ve 1 M HCl kullanılarak Pd'nin sıyırılması %99 sıyırma verimliliği sağlamıştır. Pd'siz rafinatın Pt'nin ekstraksiyonunda 0.05'ten 0.5 M'ye kadar konsantrasyonlarda Aliquat 336 kullanımı, 0.2 M'de %99.7'ye ulaşan seçici Pt ekstraksiyonunu göstermiştir. 0.2 M Aliquat 336 kullanılarak yapılan bir McCabe-Thiele plotunun, 3 A/O faz oranı kullanıldığında iki aşamada %99'dan fazla Pt ekstraksiyonu ile sonuçlanması

beklenmektedir. Yüklü organikten (LO) 0.5 M tiyourea (tu) ve HCl ile 6 O/A oranında Pt'nin sıyırılma verimliliği %99.9 olmuştur.

Anahtar Kelimeler: Otomotiv Katalizörü, Shellsol D70, Aliquat 336

I. INTRODUCTION

Platinum group metals (PGMs) consist of six elements: Rhodium, ruthenium, palladium, platinum, iridium and osmium. These metals are used in areas such as catalysts, both in the petrochemical and automotive industries [1], hydrogen fuel cells [2] and electronic devices [3]. Platinum and palladium are sought-after elements whose prices are constantly rising.

Modern cars are equipped with catalytic converters that convert toxic exhaust components such as NO_x, unburnt C_xH_y and CO into non-toxic N₂, H₂O and CO₂ [4]. The exhaust gas conversion activity of autocatalysts decreases over time due to the deposition of impurities, unburnt hydrocarbons or the sintering process at high operating temperatures. When the regeneration of autocatalysts is no longer practical, they are considered solid waste [5,6].

PGMs, which are considered critical metals, are in short supply and increasing demand will put significant pressure on the market. Therefore, all potential PGM sources need to be considered and residues such as used automotive catalytic converters are important secondary resources in this regard.

Hydrometallurgy and pyrometallurgy are the two main methods for recovering PGMs from secondary raw materials [7]. Recycling platinum group metals from secondary raw materials is not only beneficial for the environment (less waste) but also for the economy. Hydrometallurgy (also known as the "wet process") is considered more beneficial than pyrometallurgical processes because it produces less waste and consumes less energy. In addition, hydrometallurgy allows the recovery of components from very dilute solutions and the separation not only of the main products but also of some by-products, resulting in a more environmentally friendly approach.

The PGMs have similar physical and chemical properties, which makes separation by chemical precipitation methods difficult [8]. Hydrometallurgical leaching followed by solvent extraction to separate metals offers several advantages over conventional precipitation methods due to its higher selectivity, the washing step to achieve high metal purity and the complete removal of metals through multi-stage extraction steps [9-12].

In this work, a simple, efficient and environmentally friendly process is developed for the extraction of Pd and Pt from chloride liquors of spent autocatalysts using commercially available phosphorus- and amine-based extractants. The optimization of the process parameters includes the removal of base metal impurities, the influence of the extractant concentration, the phase ratio and stripping.

II. MATERIALS AND METHODS

A. AQUEOUS AND ORGANIC SOLUTIONS

Aqueous feed solution which is similar to the chloride leach liquor of a spent automobile catalyst containing, Pd and Pt as well as other base metal impurities (Cr, Ni, and Fe) was prepared by dissolving analytical grade salts of NiCl₂.6H₂O (99.9% purity, Sigma-Aldrich), CrCl₃.6H₂O (98% purity, Sigma-Aldrich), FeCl₃.6H₂O (99.5% purity, Merck), PdCl₂ (99.9% purity, Alfa Aesar) and PtCl₄ (99.9% purity, Sigma-Aldrich) in 3M HCl. To adjust the pH, analytical grade of NaOH (99.9% purity, Merck) and HCl (37%, Sigma-Aldrich) diluted in deionised water were used. TBP (tri-n-butyl

phosphate) from Fluka and Aliquat 336 (quaternary amine) from Merck Millipore were used without further purification. Shellsol D70 was used as a diluent and phase modifier. The metal contents in the synthetic solutions were verified via Shimadzu AA-7000 Atomic Absorption Spectrophotometer. The chemical composition of the synthetic solution is shown in Table 1.

Table 1. Chemical composition of the synthetic solution

Element	Ni	Fe	Cr	Pd	Pt
Concentration (mg L ⁻¹)	800	2000	150	140	500

B. EXPERIMENTAL PROCEDURE

Magnetic stirrer hot plates were used as mixing reactors in the current study, along with 500 ml beakers. The aqueous and organic solutions were preheated to 40 °C using a water heating bath. For each experiment, the aqueous solution was in contact with a various volume of organic solution to measure the equilibrium distribution of metals between the aqueous (aq) and organic (org) phases. An adjustable pipette was used to add NaOH (5 mol L⁻¹) as needed to adjust the pH of the solution during agitation. After the agitation was complete, the pH was measured, and the dispersion was transferred into separation funnels to allow the two phases to separate. After phase separation was completed, the aqueous phases were collected from the separation funnels and diluted to the concentration range required for analysis. After phase separation was complete the aqueous phases were collected from the separation funnels and diluted to the concentration range required for analysis by AAS, and the samples were analysed. The metal content of the organic phase was calculated using a mass balance based on AAS measurements. The metal ion extraction percentage (E) was calculated using the following equations:

$$E = \frac{[M]_{org}}{[M]_{aq}} \times 100 \quad (1)$$

where [M]_{org} and [M]_{aq} denote the concentration of metal ions in the organic and aqueous phase (mg L⁻¹), respectively.

The distribution ratio, D, was calculated as the concentration of metal present in the organic phase to that part in the aqueous phase at equilibrium. Separation factor ($\beta = D_{M1}/D_{M2}$), M₁ represents Pd and M₂ represents other metals (Pt, Cr, Fe and Ni), were calculated [13].

III. RESULTS AND DISCUSSIONS

A. PALLADIUM EXTRACTION with TBP

Effect of TBP concentration: TBP concentrations ranging from 0.1 to 2M in Shellsol D70 were used to extract Pd and other metals at pH 3.5. Quantitative extraction of Pd is possible with 0.5M TBP, whereas percentage extraction of other metals ranged from 1 to 5% (Fig. 1). The best separation factor was obtained with a concentration of 0.5M TBP and increasing the extractant concentration resulted in a decrease in β values due to co-extraction of other metals. Based on these findings, a TBP concentration of 0.5M appears to be the best for separating Pd from Pt and other base metals.

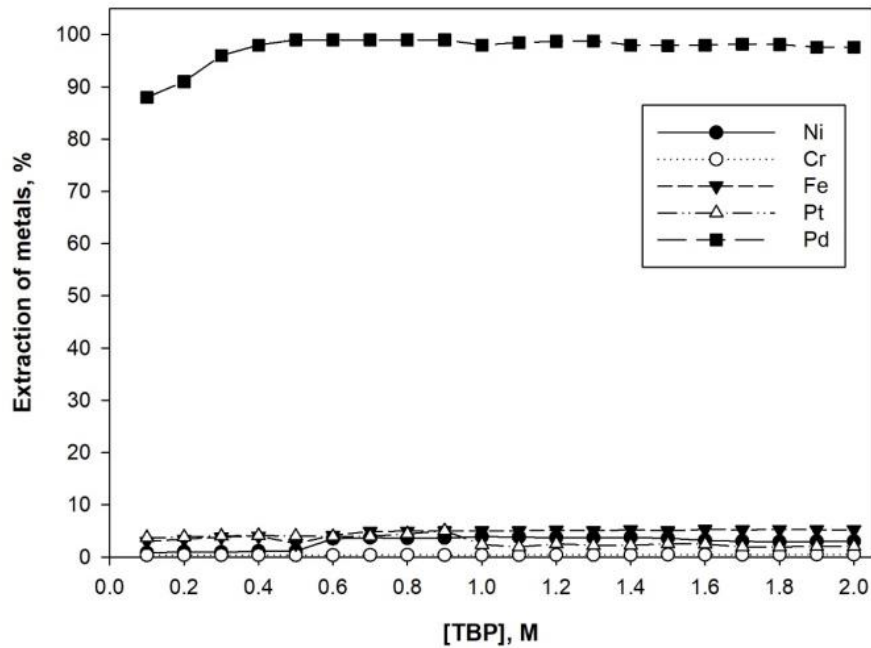


Figure 1. Effect of TBP concentration on the extraction of palladium and other metals at pH 3.5. Palladium: 140 mg/L, HCl: 1 M, A:O phase ratio= 1

Accordingly, McCabe–Thiele plot was obtained for the extraction of Pd with 0.5M TBP at A:O ratios from 1:2 and O:A ratios from 1:5 (Fig. 2). According to the extraction isotherm, a Pd extraction efficiency of 99.9% is achievable in two stages at an A/O phase ratio of 3. To reduce Pt co-extraction in the loaded organic phase, the extraction process was repeated at A/O phase ratios of 3.25 while maintaining the same Pd extraction efficiency. The results in Table 2 clearly showed that, a decrease in Pt co-extraction from 3% to 0.9%. Such a method can improve Pd selectivity and the purity of Pd strip solution. As a result of the Pd extraction process, 3.25:1 phase ratio (A:O) is used and the generated loaded organic (LO) contains 454.1 mg/L Pd.

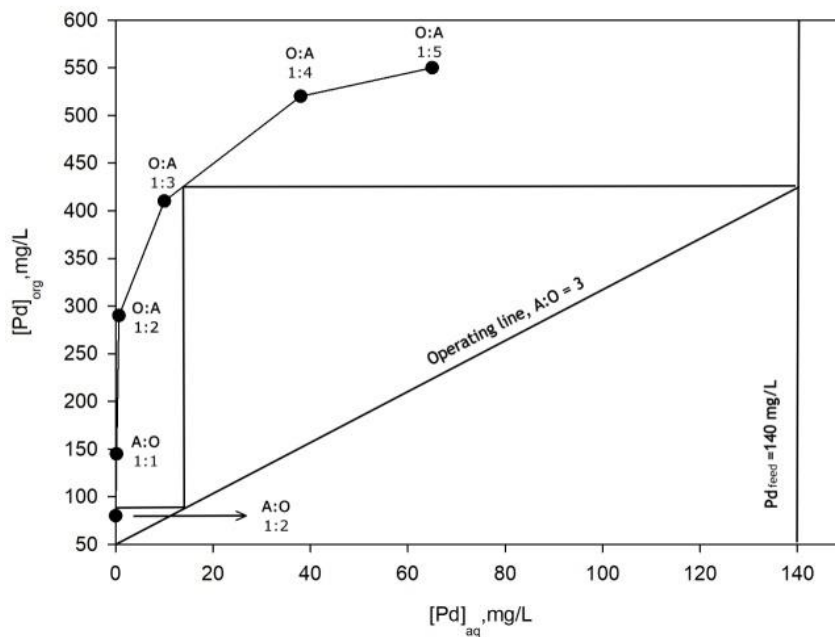


Figure 2. McCabe-Thiele plot for Pd extraction

Table 2. Results of Pd extraction at different phase

Phase Ratio (A:O)	Pd in LO, mg/L	Pd Extraction, %	Pt in LO, mg/L	Pt Extraction, %
3:1	419.6	99.9	45.3	3
3.25:1	454.1	99.8	17	1.1
3.5:1	489	99.8	13	0.9

LO = Loaded Organic

Stripping of Pd from loaded organic phase: It is critical in any commercial extraction process to continuously back-extract the metal from the loaded organic phase from the point of regeneration possibility and reuse for further extraction experiments. Pd was stripped from loaded organic (454.1 mg/L Pd) using different concentrations of HCl and in combination with thiourea (Table 3). Stripping of Pd with HCl is <2%. Among the various thiourea and HCl concentrations tested, 1 M thiourea and 1 M HCl gave Pd stripping of 99.9% from loaded organic phase in single stage.

Table 3. Effect of stripping reagents on Palladium stripping from loaded organic.

[HCl], M	[Thiourea], M	Pd stripping, %	[HCl], M	[Thiourea], M	Pd stripping, %
0.1	0	0	1.0	0.1	77.1
0.5	0	0	1.0	0.5	95.5
1.0	0	0	1.0	1.0	99.9
2.0	0	0	2.0	0.1	83.2
3.0	0	0.5	2.0	0.5	97.6
5.0	0	1.2	2.0	1.0	99.9

B. PLATINUM EXTRACTION with ALIQUAT 336

Effect of Aliquat 336 concentration: Fig. 3 depicts the extraction behaviour of platinum, chromium, iron, and nickel as a function of Aliquat 336 concentration in Shellsol D70 at pH 3.5. The percent extraction of Cr, Fe, and Ni in the studied concentration range is negligible. It was discovered that quantitative platinum extraction from Cr, Fe, and Ni is possible using 0.2M Aliquat 336. The co-extraction of Ni is 4.9%, indicating that platinum can be effectively separated from a Cr, Fe, and Ni mixture with a separation factor (β) of 15414. The value decreased to 3751 above 0.2M Aliquat 336 concentration due to nickel co-extraction. Based on these findings, 0.2M Aliquat 336 was chosen to ensure the best separation of platinum from Cr, Fe, and Ni.

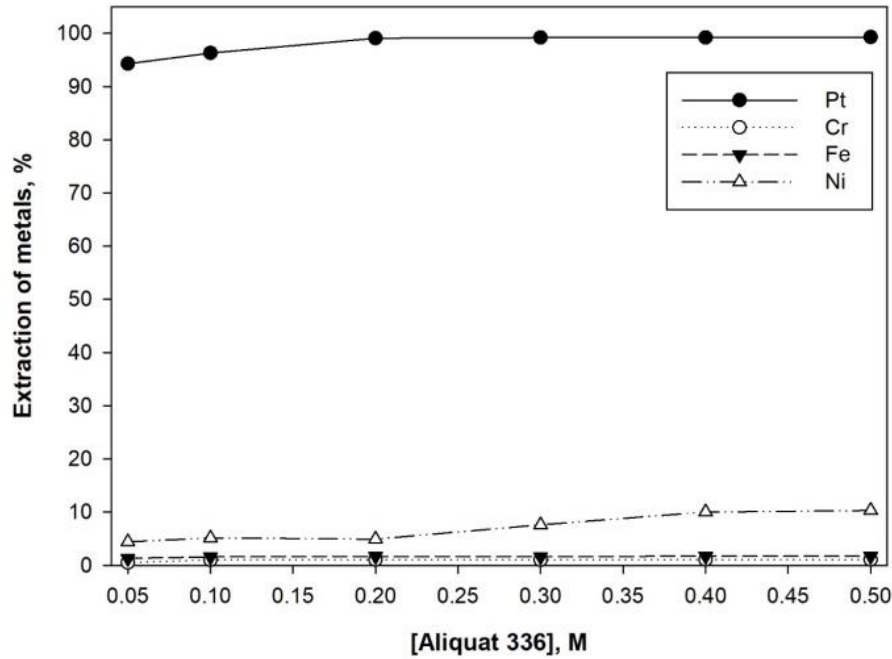


Figure 3. Effect of TBP concentration on the extraction of palladium and other metals. Palladium: 140 mg/L; HCl: 1 M.

To separate a specific metal/or group of metals from a mixture of metal ions in solution using selective extractants, an extraction isotherm (McCabe–Thiele plot) must be constructed by contacting the aqueous and organic phases at different volume ratios for a specified time. The operating line (a graphical representation of the system's mass balance) is the slope of which equals the A/O phase ratio. The extraction isotherm was created in this study by contacting the Pd free feed (500 mg/L Pt, 2000 mg/L Fe, 800 mg/L Ni and 150 mg/L Cr, pH 3.5) with 0.2 M Aliquat 336 at different A:O phase ratios ranging from 1 to 5 and O:A phase ratios ranging from 2 to 1. (Fig. 4). The McCabe–Thiele plot shows that at an A/O phase ratio of 3, complete platinum extraction efficiency can be achieved in three stages.

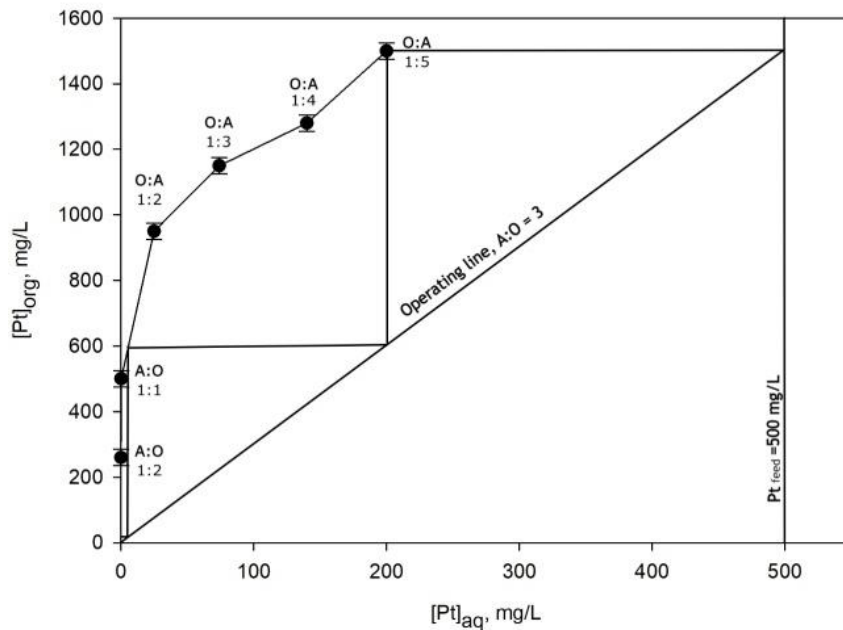


Figure 4. McCabe-Thiele plot for Pt extraction.

Stripping of Pt from loaded organic phase: To remove PGM ions, it is necessary to use a solution that has a very high concentration of either an acidic or basic aqueous solution and contains a reagent with sulphur, such as thiourea [14]. Pt was stripped from the loaded organic phase using HCl, NH₄Cl, NH₃, and an aqueous mixed solution of NH₃-NH₄Cl at a unit phase ratio as stripping reagents (Table 4). Due to their low stripping efficiency, these reagents were found to be unsuitable for platinum removal from loaded organic phases. Individual stripping of platinum from loaded organic phase with thiourea showed better platinum stripping efficiency but longer phase separation time and metal hydrolysis in strip solution. Finally, a 0.1–0.5M mixture of thiourea and HCl resulted in clear phase separation and quantitative stripping of platinum. In the current study, platinum was stripped from loaded organic phase using 0.1M HCl and 0.5M thiourea.

Table 4. Stripping of platinum from loaded organic phase.

Stripping reagent M	Pt stripping efficiency (%)	[HCl], M	[Thiourea], M	Pt stripping efficiency (%)
1 NH ₄ Cl	0.1	1-5	-	1-2.1
1 NH ₃	23.1	-	0.1-0.5	68-82
2 NH ₄ Cl	0.3	0.1	0.2	93.2
2 NH ₃	27.2	0.1	0.5	100
2 NH ₄ Cl + 0.1 NH ₃	3.5	0.2	0.2	98.3
2 NH ₄ Cl + 0.2 NH ₃	6.9	0.2	0.5	99.9
2 NH ₄ Cl + 0.5 NH ₃	14.6	0.5	0.2	99.7
2 NH ₄ Cl + 1 NH ₃	26.9	0.5	0.5	100

IV. CONCLUSION

In this study, a complete lab-scale hydrometallurgical process for the separation and recovery of Pd and Pt from synthetic chloride leach liquors of spent automobile catalyst was developed using solvent extraction.

Based on the experimental results, it can be concluded that the selective extraction of palladium (Pd) and platinum (Pt) from a mixed metal solution is highly efficient when using optimized concentrations of TBP and Aliquat 336 in the presence of a diluent like Shellsol D70.

For palladium, the optimal extraction conditions were found to be 0.5M TBP, which achieved quantitative extraction of Pd while minimizing the co-extraction of other metals such as chromium (Cr), nickel (Ni), and iron (Fe). The McCabe–Thiele plot further confirmed that at an aqueous-to-organic (A/O) phase ratio of 3:1, nearly complete Pd extraction (99.9%) could be achieved in just two stages, with a reduction in Pt co-extraction when the phase ratio was adjusted to 3.25:1.

For platinum, 0.2M Aliquat 336 was identified as the most effective concentration for separating Pt from Cr, Fe, and Ni. The McCabe–Thiele plot indicated that complete Pt extraction could be accomplished in three stages at an A/O phase ratio of 3:1. Additionally, the stripping of Pt from the loaded organic phase was most efficiently achieved using a mixture of 0.1M HCl and 0.5M thiourea, which facilitated clear phase separation and quantitative stripping.

In summary, the study demonstrates that by carefully controlling the extractant concentrations and phase ratios, it is possible to achieve high selectivity and efficiency in the extraction and separation of

Pd and Pt from a mixed metal solution. The methods outlined could significantly enhance the purity and recovery rates of these valuable metals in industrial applications.

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