Selective Recovery of Palladium from PGM Containing Hydrochloric Acid Solution Using Thiocarbamoyl-substituted Adsorbents

Kazutoshi HAGA*, Shiori SATO*, Muniyappan RAJIV GANDHI*, Manabu YAMADA** and Atsushi SHIBAYAMA*

*Department of Earth Resource Engineering and Environmental Science, Graduate School of International Resource Sciences, Akita University, Akita 010-8502, Japan
**Research Center for Advanced Materials for Breakthrough Technology, Graduate School of Engineering Science, Akita University, Akita 010-8502, Japan
E-mail:khaga@gipc.akita-u.ac.jp

Two thiocarbamoyl compounds, monomer-type 4-tert-butyl(dimethylthiocarbamoyloxy) benzene (1) and dimer-type 1,1′-bis(dimethylthiocarbamoyloxy)-2,2′-thiobis[4-tert-butylbenzene] (2), were impregnated on amberlite XAD-7 resin for selective recovery of palladium from platinum group metal solutions (PGM) containing a HCl solution. Pd(II)-ion adsorption performance of 1 and 2 impregnated resins were carried out in batch mode by varying HCl concentration, shaking time, Pd(II) concentration, and adsorbent amount. The monomer-impregnated adsorbent showed high Pd(II) sorption (94.1%) as compared with dimer-impregnated adsorbent (74.4%) in 1 M HCl media. Both monomer- and dimer-impregnated adsorbents exhibited a selective Pd(II) sorption from a mixed solution of PGM (Pd, Pt, and Rh). Pd(II)-ion desorption from Pd(II) adsorbed adsorbents were carried out using HCl-thiourea mixture as a desorption reagent. The results showed that both resins were suitable for selective separation of Pd(II) from PGM secondary resources.

Keywords: Platinum group metals, Thiocarbamoyl-impregnated adsorbents, Pd(II) recovery

1 INTRODUCTION

Impregnation of an organic extractant into a polymeric support offers several advantages over solvent extraction system, for example easy phase separation, nontoxic, eco-friendly and economical [1]. The advantages of extractant impregnated resin (EIR) were wide choice of reagents of desired selectivity, easy preparation, and easy to operate etc. [1]. EIR technology synergistically combines the advantages of both extraction and adsorption [2]. The concept of EIRs is based on the incorporation of extractants with selective extractability for metal species into a porous polymer by physical impregnation [2,3]. Thiocarbamoyl-based extractants are used as a versatile and selective extraction of transition metal ions [2]. In our previous study, solvent extraction of PGM from leach liquors of automotive catalyst using 2,2′-thiobis[4-tert-butylphenol] and their thiocarbamoyl derivative 1,1′-bis(dimethylthiocarbamoyloxy)-2,2′-thiobis[4-tert-butylbenzene] (2) was evaluated [4]. It was shown that thiocarbamoyl-based extractants, 4-tert-butyl(dimethylthiocarbamoyloxy)benzene (1) and 2, dissolved in CHCl₃ have an intrinsic selectivity for Pd(II) extraction [4]. However, the practical use of thiocarbamoyl-based extractants and other supramolecular extractants in solvent extraction is still limited because of their insolubility in the hydrocarbon diluents for practical applications [5-7]. Amberlite XAD-7 (XAD) is a polyacrylic acid ester resin with good chemical stability, high porosity, uniform pore size, high surface area, and a non-ionic structure [2]. Hence, we have developed green hydrometallurgical processes based on thiocarbamoyl possessing extractants impregnated on amberlite XAD-7 and used as an adsorbent for selective separation and recovery of Pd(II) from PGM solutions.

2 EXPERIMENT

2.1 Materials and methods

Stock HCl (1-6 mol/L) solution of Pd, Pt, and Rh ions were prepared using 1 g/L in 1 M HCl standard of Pd, Pt, and Rh solution (Wako Pure Chemical Industries, Ltd) respectively. p-tert-Butylphenol, N,N-dimethylthiocarbamoyl chloride, K₂CO₃, and acetone were also purchased from commercial sources and used without further purification. The concentration of each metal ion in its aqueous solution was determined using inductively coupled plasma atomic emission spectrometry instrument (ICP-AES) (SPS-3000, Seiko Instruments Inc. Japan).

2.2 Synthesis of 4-tert-butyl(dimethylthiocarbamoyloxy) benzene (1) [8]

4-tert-butylphenol (1.50 g, 10.0 mmol), N,N-dimethyl(thiocarbamoyl) chloride (2.47 g, 20.0 mmol) and K₂CO₃ (2.76 g, 20.0 mmol) were stirred in acetone (100 mL) and were refluxed for 24 h under a nitrogen atmosphere. After the suspension had cooled, the solvent was removed in vacuo. The resulting solid material was dissolved in CHCl₃, and excess K₂CO₃ was quenched with 1 M HCl. The organic phase was then separated, washed with water, 5% KOH, and saturated NaCl, and dried over anhydrous Na₂SO₄. A brown solid was obtained by evaporation of the solvent. Recrystallization from CHCl₃ yielded 1 as a colorless crystal (yield: 2.18 g, 92%) [8].

Int. J. Soc. Mater. Eng. Resour. Vol.23, No.2, (Sep. 2018)
2.3 Synthesis of 1,1'-bis[(dimethylthiocarbamoyl)oxy]-2,2'-thiobis(4-t-butylbenzene) [4]:

2,2'-Thiobis(4-t-butyl) phenol (8.00 g, 24.2 mmol), N,N-dimethyl (thiocarbamoyl) chloride (7.93 g, 64.2 mmol), and K₂CO₃ (10.31 g, 74.6 mmol) were stirred in acetone (400 mL) and refluxed for 5 days under a nitrogen atmosphere. After the suspension was cooled to room temperature, the solvent was removed by evaporation in vacuo. The resulting oily material was dissolved in chloroform (350 mL), and the excess K₂CO₃ was quenched, with 10% HCl (350 mL) added to terminate the reaction. The organic layer was then separated, washed with water (350 mL × 2), and dried over anhydrous Na₂SO₄. The brown oil was obtained via evaporation of the solvent and was recrystallized from n-hexane/ethanol (5:1 v/v; 180 mL) to yield the crude form of the synthesized monomer-impregnated adsorbent (MTCA) and dimer-impregnated adsorbent (DTCA), respectively.

2.4 Preparation of 1 and 2 impregnated resins

The synthesized 1 and 2 extractants were impregnated on amberlite XAD-7 resin (supplied by Organo cooperation) CHCl₃ solutions of extractants 1 and 2 (1.0 mmol) were immersed for 24 h with 10 g of dry amberlite XAD-7. After that CHCl₃ was evaporated and resin was dried at 60°C. The quantity of extractant immobilized in the resin was calculated based on the difference in the mass of the extractant-impregnated resin and bare resin. The respective loadings of 1 and 2 in the resins were 0.145 and 0.066 mmol/g respectively. The 1 and 2 impregnated resins, namely as monomer-impregnated adsorbent (MTCA) and dimer-impregnated adsorbent (DTCA), respectively.

2.5 Adsorption experiment

Five milliliters metal solution and 0.2 g of an impregnated resin (monomer- and dimer-impregnated adsorbents) were fed into 5 mL polystyrene tube. The mixture was shaken vigorously at room temperature at 1800 rpm. After shaking, the solid and solution were separated by centrifugal separator and the metal concentration in the supernatant was determined by ICP-AES. The metal recovery experiments were conducted in 1 M HCl concentration and 60 min shaking time.

\[
\text{Adsorption capacity (mg/g), } q = [(C_0 - C_e) / m] \times V
\]

where q is adsorption capacity of the resin (mg metal ion/g resin), V is the volume of the metal ion solution (L), C₀ is the metal ion concentration before adsorption (mg/L), Cₑ is the metal ion concentration after adsorption (mg/L), and m is the weight of the resin (g).

2.6 Desorption experiment

MTCA and DTCA were mixed with 5 mL of 1 mol/L HCl solution containing 100 mg/L Pd and the mixture was shaken at 1800 rpm for 60 min at room temperature. The resulting solid was separated by centrifugal separator and the obtained solid was used in desorption experiment. Desorption conducted by mixing of Pd adsorbed resin (0.2 g) with 5 mL of diluted HCl, thiourea or mixture of HCl-thiourea solution. The mixture was shaken 1800 rpm for 60 min at room temperature, and the solid and solution were separated by centrifugal separator. The metal concentration in the supernatant was determined by ICP-AES.

The desorption percentage of Pd(II) was calculated by following equation (3). Desorption percentage of Pd(II) was calculated by following equation (3).

\[
\text{Desorption } (% \text{ of } Pd(II)) = [(C_i - C_f) / C_i] \times 100
\]

where Cᵢ is the weight of initially sorbed Pd(II) (mg/g) and Cᶠ is the equilibrium concentration of Pd(II) in the resin after recovery (mg/g).

3 RESULTS AND DISCUSSION

3.1 Adsorption study

3.1.1 Effect of shaking time: The effect of shaking time on Pd(II) adsorption percentage of MTCA and DTCA in 1 mol/L HCl solution was investigated from 5 - 360 min. Figure 1 shows the Pd(II) adsorption percentage of MTCA and DTCA. Pd(II) adsorption percentage of MTCA was reached 80% in the first 5 min, 90% in 60 min and further increased to 97.7% in 240 min whereas DTCA showed only 78% of Pd(II) adsorption in 240 min. As a result, shaking time of 60 min is sufficient to obtain over 90% recovery of Pd(II) from 1 M HCl solution. Hence, further experiments were conducted in 1 M HCl concentration and 60 min shaking time.

3.1.2 Effect of HCl concentration: Figure 2 shows adsorption behavior of Pd(II) from different concentration of HCl solution (1-6 M) using 0.2 g of MTCA and DTCA. Ninety five% and 78% of Pd(II) was adsorbed on MTCA and DTCA in 1 mol/L HCl solution, respectively. HCl concentration increased from 1 M to 6 M, the adsorption percentage of Pd(II) on MTCA and DTCA decreased to 82% and 60%, respectively. MTCA showed high Pd(II) adsorption % in the HCl solution than DTCA. The reason behind high Pd(II) adsorption % of MTCA was due to the impregnated extractant on MTCA (0.145 mmol/g) is two-fold higher than DTCA (0.066 mmol/g). MTCA and DTCA are found to be very stable in HCl media and chemical structure of the impregnated extractants in the resin did not change after experiment. Hence the MTCA and DTCA adsorbents have high acid-resistivity and it is highly suitable for recovering Pd(II) from high acidity PGM leach liquors.
3.1.3 Effect of initial Pd concentration: The adsorption result of effect of initial Pd concentration on MTCA and DTCA was shown in Figure 3. The Pd(II)-loading capacity of MTCA and DTCA was investigated by varying the initial Pd(II) concentration from 0.05 to 1.0 g/L using a fixed contact time of 60 min using 1.0 M HCl as the medium. Pd(II) adsorption percentage was found to be 99% for MTCA and 94% for DMTCA at 0.05 g/L of initial Pd(II) concentration and Pd(II) adsorption percentage was decreased to 15.8% for MTCA and 12.5% for DMTCA at 1.0 g/L of initial Pd(II) concentration. Pd(II) sorption capacity by the MTCA and DTCA increased as the initial concentration increased. The maximum uptake of Pd(II) by MTCA and DTCA when the initial concentration of Pd(II) of 0.85 g/L was 7.9 and 6.2 mg/g (0.074 and 0.058 mmol/g), respectively (Figure 4).

3.1.4 Adsorption mechanism of Pd on adsorbent: Figure 5 shows relationship between impregnated amount of extractant in adsorbent and amount of adsorbed Pd on adsorbent. The slope analysis plot of MTCA and DTCA on Pd(II) sorption were determined. The slope for MTCA and DTCA was found to be 2:1 and 1:1, respectively. The slope value of 0.57 for MTCA indicates that MTCA: Pd ratio was found to be 2:1 and in the case of DTCA showed the slope value of 1.17 which indicated that DTCA: Pd ratio was found to be 1:1. These results were absolutely fitted with balance of sorption capacity and loading amount of extractant on resins. The proposed major adsorption mechanism of PdCl₄²⁻ ion on MTCA and DTCA were shown in Figure 6. Additionally, the sulfur in the crosslinking site of DTCA has a function to afford high PdCl₄²⁻ ion absorbability based on the hard-soft acid base theory [4].

3.1.5 Selective extraction of Pd from Pd, Pt, and Rh mixed solution: In order to study the selectivity of MTCA and DTCA for Pd(II) sorption, the adsorption studies were conducted from simulated mixed solution containing 100 mg/L of each Pt, Pd,
Rh. The result of the experiment was shown in Figure 7. The adsorption % of Pd was found to be 90% and 74% by MTCA and DTCA, respectively. MTCA and DTCA not adsorbed the Rh from solution and the adsorption % of Pt was found to be less than 2%.

3.2 Desorption study

For recovery of Pd ions from Pd adsorbed adsorbent, Pd desorption experiment were conducted with HCl, thiourea and mixture of HCl-thiourea. Pd(II) sorption experiments were conducted.

3.2.1 Desorption of Pd using HCl solution: Figure 8. shows the desorption behavior of Pd adsorbed resin using HCl solution. The Pd desorption percentages from Pd-adsorbed MTCA and DTCA was found to be below 25%.

3.2.2 Desorption of Pd using (NH$_2$)$_2$CS solution: Based on our previous studies and many other researcher reported that thiourea is very good stripping agents for Pd(II)[2,4-7]. Hence, desorption of Pd from adsorbent were conducted using 0.1-1.0 M thiourea solution. Figure 9 shows the desorption behavior of Pd adsorbed resin using thiourea solution. Pd desorption percentage was found to be 60-70% from Pd adsorbed MTCA and DTCA.

3.2.3 Desorption of Pd using mixture of HCl-thiourea solution: In order to achieve very high desorption % of Pd ions from Pd adsorbed MTCA and DTCA, the Pd desorption was conducted using mixture of 1 M of thiourea-1 M HCl and solution. Figure 10 shows the desorption behavior of Pd adsorbed resin using mixture
Selective Recovery of Palladium from PGM Containing Hydrochloric Acid Solution Using Thiocarbamoyl-substituted Adsorbents

of 1 M thiourea-1 M HCl solution is higher than the individual HCl and thiourea solution. Pd desorption percentages of Pd adsorbed MTCA and DTCA was found to be 100% and 91% respectively whereas 1 M thiourea solution showed about 75% and 12 M HCl solution showed below 25% of desorption.

4 CONCLUSION

The MTCA showed more effective for Pd(II) sorption than DTCA. Maximal Pd(II) sorption with the developed resins required a contact time of 60 min. Pd(II) sorption by the MTCA and DTCA was slightly influenced by the HCl medium and not decreased in the presence of Rh and Pt. The Pd(II) sorption capacity of MTCA was found to be 7.9 mg/g and Pd sorption % was found to be 95% in 1.0 M HCl. The Pd(II) sorption capacity of DTCA was found to be 6.2 mg/g and Pd sorption % was found to be 78% in 1.0 M HCl.

The desorption (%) for Pd(II) ions from the resin was 100% for MTCA and 91% for DTCA when a mixture of 1.0 M thiourea-HCl solution was used as a stripping agent. From these promising results, we can conclude that resins MTCA and DTCA have the potential for application as new adsorbents for the sorption and selective separation of Pd(II) ions from acid leach liquors of PGMs.

Acknowledgment: The authors sincerely acknowledge the financial support for this work that was provided by Tohoku Innovative Materials Technology Initiative for Reconstruction “High Efficiency Rare Elements Extraction Technology Area” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT). And this work was supported by the “JSPS KAKENHI Grant Number 16H04182 and 16K17941”

References

[1] Zagorodni A.A., “Ion exchange materials: Properties and applications” Elsevier, The Netherlands (2007).
[2] Yamada M.; Rajiv Gandhi M.; Kondo Y.; Haga K.; Shibayama A.; Hamada F., “Selective sorption of palladium by thiocarbonyl-substituted thiacalix[n]arene derivatives immobilized on amberlite resin: application to leach liquors of automotive catalysts” RSC Adv. 5, 60506-60517 (2015).
[3] Rajiv Gandhi M.; Yamada, M.; Kondo, Y.; Shibayama A.; Hamada F., “p-Sulfonatothiacalix[6]arene-impregnated resins for the sorption of platinum group metals and effective separation of palladium from automotive catalyst residue” J. Ind. Eng. Chem. 30, 20-28 (2015).
[4] Yamada M.; Rajiv Gandhi M.; Sato D.; Kaneta Y.; Kimura N., “Comparative study on palladium(II) extraction using thioamide-modified acyclic and cyclic extractants” Ind. Eng. Chem. Res. 55, 8914-8921 (2016).
[5] Rajiv Gandhi M.; Yamada, M.; Kondo, V.; Shibayama A.; Hamada F., “Rapid and selective extraction of Pd(II) ions using the SCS type pincer ligand 1,3-bis(dimethylthiocarbamoyloxy)benzene and its Pd(II) extraction mechanism” RSC Adv. 6, 1243-1252 (2016).
[6] Kimuro T.; Rajiv Gandhi M.; Kunda U.M.R.; Hamada F.; Yamada M., “Palladium(II) sorption of a diethylphosphate-modified thiacalix[6]arene immobilized on amberlite resin” Hydrometallurgy, 171, 254-261 (2017).
[7] Kunda U.M.R.; Yamada, M., “Sorption of palladium(II) using organophosphorus derivatives based on thiacalix[4]arene impregnated resins from hydrochloric media” Sep. Sci. Technol. 52, 1153-1159 (2017).
[8] Newman, M.S.; Karnes H.A., “The conversion of phenols to thiophenols via dialkylthiocarbamates” J. Org. Chem. 31, 3980-3984 (1966).