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https://hdl.handle.net/2324/7330566

出版情報：Journal of Chemical Engineering of Japan. 56 (1), 2023-07-03. Society of Chemical Engineers, Japan
バージョン：

Journal of Chemical Engineering of Japan

ISSN: 0021-9592 (Print) 1881-1299 (Online) Journal homepage: www.tandfonline.com/journals/tjce20

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To cite this article: Mayu Kamisono, Takafumi Hanada & Masahiro Goto (2023) Green Leaching of Metallic Platinum Using an Ionic Liquid with Synergistic Organic Acid–Chlorinating Agent Additives, Journal of Chemical Engineering of Japan, 56:1, 2228363, DOI: 10.1080/00219592.2023.2228363

To link to this article: https://doi.org/10.1080/00219592.2023.2228363

JOURNAL OF CHEMICAL ENGINEERING OF JAPAN
2023, VOL. 56, NO. 1, 2228363
https://doi.org/10.1080/00219592.2023.2228363

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SHORT COMMUNICATION

Green Leaching of Metallic Platinum Using an Ionic Liquid with Synergistic Organic Acid–Chlorinating Agent Additives

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ABSTRACT

This study explored the potential for an environmentally friendly method for refining difficult-to-solubilise noble metals (notably platinum). Conventional noble-metal refining processes rely on the use of strong inorganic acids and oxidants, which cause significant environmental impact. To overcome these challenges, we propose a non-aqueous direct leaching process using an ionic liquid, an organic acid, and a chlorinating agent. Our findings indicate that trihexyl(tetradecyl)-phosphonium chloride ($P_{66614}Cl$) in combination with methanesulfonic acid and trichloroisocyanuric acid effectively solubilises metallic platinum. We investigated the leaching mechanism using ultraviolet–visible spectroscopy and confirmed that Pt(0) was oxidised to Pt(IV) to form $PtCl_6^{2-}$. Recovery of Pt from Pt-loaded $P_{66614}Cl$ was achieved by stripping with ammonium nitrate solution. This work advances the development of sustainable refining methods for noble metals.

ARTICLE HISTORY
Received 26 February 2023
Accepted 18 June 2023

KEYWORDS
Ionic liquid; Non-aqueous leaching; Platinum; Oxidative dissolution; Sustainable metallurgy

1. Introduction

Noble metals (NMs), such as gold, palladium, and platinum (Pt), are used as industrial catalysts and in electronic components. However, their relative scarcity and uneven distribution pose worldwide political and economic challenges that render them costly. Therefore, not only primary but also secondary resources have attracted attention for a more stable and sustainable supply of NMs (Zupanc et al. 2023). In particular, NM recovery from secondary resources, such as waste electric and electronic equipment, provides advantages in terms of CO_2 emissions (Rocchetti et al. 2013).

Conventional hydrometallurgical refining processes, which use strong inorganic acids and oxidants such as aqua regia to dissolve chemically inert NMs, are associated with environmental concerns due to the generation of large quantities of acidic wastewaters and usage of volatile organic solvents. However, the recent development of solvents such as ionic liquids (ILs) and deep eutectic solvents has made it possible to eliminate the use of volatile organic solvents in solvent-extraction systems (Dwamena 2019; Wongsawa et al. 2020). Additionally, processes such as adsorption (Nikoloski et al. 2015), membrane separation (Fontàs et al. 2007), and precipitation (Matsumoto et al. 2021), offer alternatives to solvent extraction in metal separation. Despite these efforts to develop environmentally friendly methods for metal separation, research on benign leaching of NMs has yet to make significant progress; hence, alternative methods for NM dissolution have been pursued, particularly the use of non-aqueous solvent systems as a replacement for harmful inorganic acids, in an effort to achieve more sustainable and selective dissolution of NMs (Li and Binnemans 2021).

Studies have explored the use of halogen–halide polar organic solvent systems (Nakao 1992 1999), dihalogen–sulphur-containing ligand adducts (Cau et al. 2003), aromatic thiol ligands (Räisänen et al. 2007), “organic aqua regia” formed by thionyl chloride and pyridine (Lin et al. 2010), and various oxidant–ligand systems for the solubilisation of NMs. However, only a few studies have reported successful dissolution of Pt in non-aqueous systems. Sulphur-containing triiodide ligands (Bigoli et al. 2001), water-immiscible solvents, and HCl–oxidant mixtures (Nguyen et al. 2022) have been proposed as means of dissolving Pt. Although trihalide species are promising oxidants for NMs in organic solvents and ILs, solubilising Pt remains challenging, partly due to the loss of reactive trihalide species at elevated temperatures (van den Bossche et al. 2021). Moreover, the complexity of solvent and ligand synthesis hinders the economic viability of NM refining.

In this study, we focused on the facile and benign dissolution of Pt into ILs, with the synergistic combination of organic acids and chlorinating agents to generate chlorine gas in situ for efficient Pt dissolution. A phosphonium-based IL was used as the solvent owing to its high capacity for platinum extraction (Firmansyah et al. 2020). The superiority of this leaching solvent was exhibited by comparison with water and conventional organic solvents. The dissolution mechanism of Pt into ILs was investigated by kinetic analysis and ultraviolet–visible (UV–vis) spectroscopy.

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Recovery of Pt from the IL was demonstrated via stripping with various aqueous solutions.

2. Experimental

2.1 Chemicals

Platinum powder, 28% ammonia, and thiourea were purchased from Fujifilm Wako Chemical Ltd., Japan. Trihexyl(tetradecyl)phosphonium chloride ($P_{66614}Cl$) was purchased from Sigma-Aldrich Co., USA. Trichloroisocyanuric acid (TCCA) and methanesulfonic acid (MSA) were purchased from Tokyo Chemical Industry Co., Ltd., Japan. *n*-Dodecane, 1-propanol, 5 M nitric acid, 99% ammonium nitrate, and 5 M hydrochloric acid were purchased from Kishida Chemical Co., Ltd., Japan. Milli-Q water was used to prepare the series of aqueous solutions used in this work.

2.2 Method for Leaching of Pt Powder

The effects of additive agents, leaching solvent, and leaching time on Pt dissolution were investigated. Undiluted $P_{66614}Cl$ was used as the leaching solvent. After screening several combinations of chlorinating agents and organic acids, TCCA and MSA were used as additive agents to enhance Pt dissolution. All experiments were performed at a solid-to-liquid ratio of 0.5 g/L, stirring at 400 rpm at 353 K for 24 h.

After leaching, the resulting mixture was completely separated into the solvent and residue components by centrifugal separation at 20 000 *g* for 10 min at 298 K. The Pt concentration in the leaching solvent was measured by an inductively coupled plasma optical emission spectrometer (Optima 8300, PerkinElmer, USA). Leaching performance (%L) was measured using the following equation:

$$\%L = \frac{C_{M,\ leaching\ solvent}}{C_{M,\ all\ metal}} \times 100 \tag{1}$$

where $C_{M,\ leaching\ solvent}$ is the concentration of metal M in the leaching solvent after reaction and $C_{M,\ all\ metal}$ is the concentration of metal M assuming all Pt powder is leached. UV–vis spectra of the leaching solvents were measured at 298 K using a UV–vis spectrometer (JASCO V-750, Japan).

2.3 Method of Pt Ion Stripping from Leach Solution

To strip Pt from the solvent, an aqueous phase containing the stripping reagent was vigorously mixed with the leach solution at a volume ratio of 2:1 using a vortex mixer at 298 K for 24 h. The two solutions were then completely separated by centrifugation at 10,000 *g* for 1 min at 298 K. Stripping performance (%S) was measured using the following equation:

$$\%S = \frac{C_{M,\ leaching\ solvent} - C_{M,\ after\ stripping}}{C_{M,\ leaching\ solvent}} \times 100, \tag{2}$$

where $C_{M,\ leaching\ solvent}$ is the concentration of metal M in the leaching solvent after reaction and $C_{M,\ after\ stripping}$ is the concentration of metal M in the leaching solvent after stripping.

3. Results and Discussion

3.1 Impact of additive agents

Metallic Pt is much less soluble than metallic gold, even in aqua regia (Shibata et al. 2001). To overcome this challenge, TCCA and MSA were used as additive agents in this study. TCCA has been previously used to dissolve metallic gold in acetone with the aid of quaternary ammonium salts (Feng et al. 2020), while MSA has been lauded for its biodegradability and low volatility, making it an environmentally friendly organic acid (Binnemans and Jones 2023). $P_{66614}Cl$, a hydrophobic IL, has been used as an efficient extractant for NM ions (Nguyen et al. 2016). Based on these prior findings, we hypothesised that the combination of undiluted IL, TCCA, and MSA would form an effective leaching solvent for metallic Pt.

The impact of these additive agents on the leaching performance of Pt is shown in Figure 1. We found that Pt powder was barely leached using either the IL alone or the IL with MSA, and only slightly dissolved in the IL with TCCA. The minor dissolution of Pt in the IL with TCCA was attributed to the slight generation of chlorine gas from TCCA as an oxidant. Remarkably, when the IL was combined with TCCA and MSA, over 75% of Pt was efficiently leached. The oxidation of Pt with TCCA appeared to be augmented by MSA, which facilitated the efficient solubilisation of Pt into the IL.

3.2 Impact of solvent

The impact of different solvents on leaching was investigated. Leaching efficiencies of Pt with TCCA and MSA were evaluated using four different solvents: water, 1-propanol, *n*-dodecane, and the IL $P_{66614}Cl$. The results are presented in Figure 2. Pt was scarcely leached by water, 1-propanol, or *n*-dodecane, even with the addition of TCCA and MSA. These results suggest that $P_{66614}Cl$ plays a crucial role in Pt leaching, potentially by stabilizing the anion complex of dissolved Pt through the P_{66614} cation (Nguyen et al. 2016). Furthermore, when the reaction vials containing the first three leaching solvents were opened after leaching, a gas was

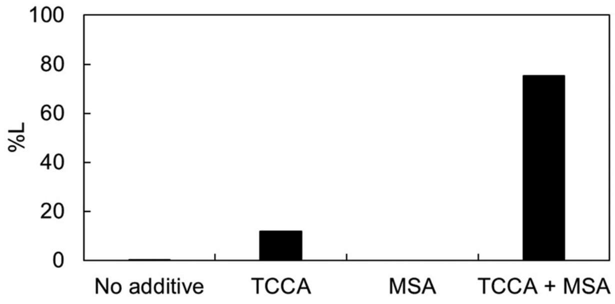

Figure 1. Impact of additive agents on leaching performance of Pt. Solvent: $P_{66614}Cl$. Additive agents: MSA 13.8 wt.%, TCCA 5.3 wt.%. Conditions: 0.5 g/L, 353 K, 400 rpm, 24 h.

emitted. This observation suggests that a chlorine gas, acting as an oxidant for Pt, was produced by reaction with TCCA and MSA, but was not consumed for Pt oxidation in these solvents.

3.3 Kinetics of leaching of Pt powder

Figure 3 shows the variation in leaching efficiency with time. The leaching efficiency was 80% after 24 h and increased to 90% after 48 h. Equations (3) and (4), which are frequently used in kinetic analyses of metal leaching based on the shrinking-core model (Cao et al. 2006), were used to determine the leaching mechanism:

$$kt = x; \tag{3}$$

$$kt = 1 - (1 - x)^{\frac{1}{3}}. \tag{4}$$

where k is the kinetic constant, t is the reaction time, and x is the leaching efficiency, respectively.

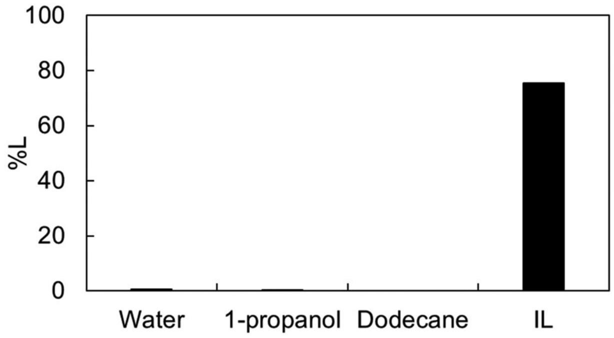

Figure 2. Impact of solvent on leaching of Pt powder. Additive agents: MSA 13.8 wt.%, TCCA 5.3 wt.%. Conditions: 0.5 g/L, 353 K, 400 rpm, 24 h.

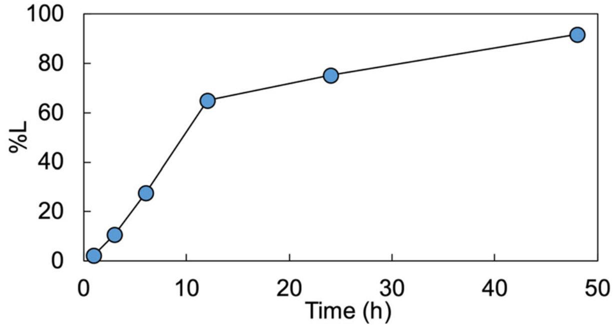

Figure 3. Variation in leaching efficiency with time. Solvent: $P_{66614}Cl$. Additive agents: MSA 13.8 wt.%, TCCA 5.3 wt.%. Conditions: 0.5 g/L, 353 K, 400 rpm, 1–48 h.

The kinetic plots for Eqs. (3) and (4) are shown in Figure 4. Notably, the linearity was greater when fitting the data to Eq. (3). Therefore, it was suggested that the leaching rate is controlled by diffusion-controlled reactions. The reason for the reaction proceeding in a diffusion-controlled reaction is due to the high viscosity of the IL.

3.4 Mechanism of Pt leaching in ionic liquid

The leaching mechanism of Pt by $P_{66614}Cl$-TCCA-MSA system was investigated via UV–vis spectroscopy. UV–vis spectra of the IL phase before and after leaching, along with that of an aqueous $PtCl_6^{2-}$ standard solution for reference, are shown in Figure 5. The spectra of IL after leaching (red line) and Pt standard solution (green dotted line) exhibited comparable peaks at around 260 nm, indicating the presence of $PtCl_6^{2-}$ (Glebov et al. 2015). Therefore, the metallic Pt was successfully oxidised from Pt(0) to Pt(IV) and formed $PtCl_6^{2-}$, which was stabilised by the IL cation.

3.5 Stripping of Pt ion from leaching solvent

Owing to the hydrophobic nature of the IL, the recovery of Pt and regeneration of the IL could be easily achieved by

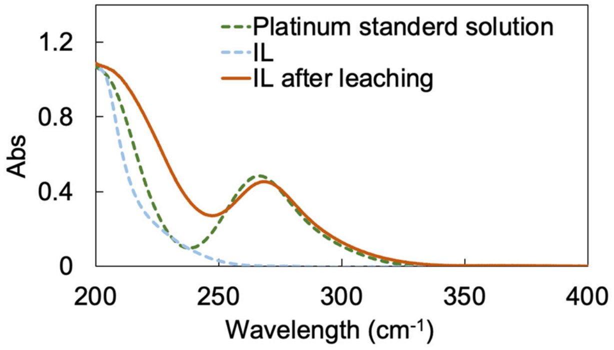

Figure 5. Ultraviolet–visible spectra of Pt standard solution (green dotted line), the IL before leaching (blue dotted line) and after leaching (red line). Condition: 298 K.

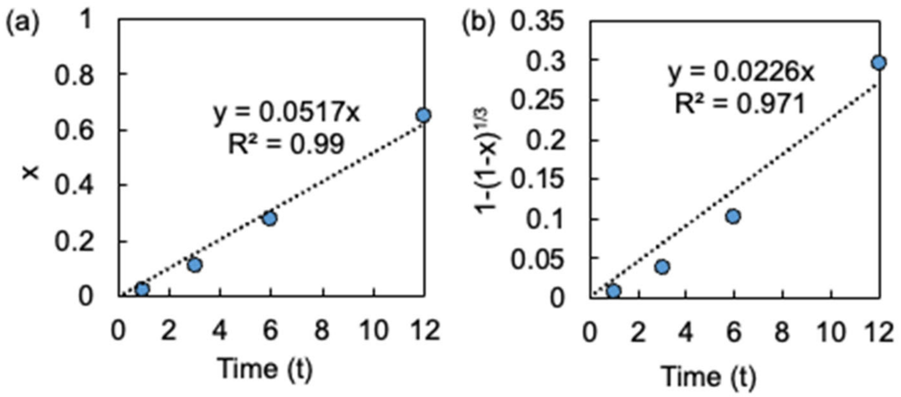

Figure 4. Kinetic plots for rate-limiting steps, corresponding to (a) diffusion and (b) surface chemical reaction.

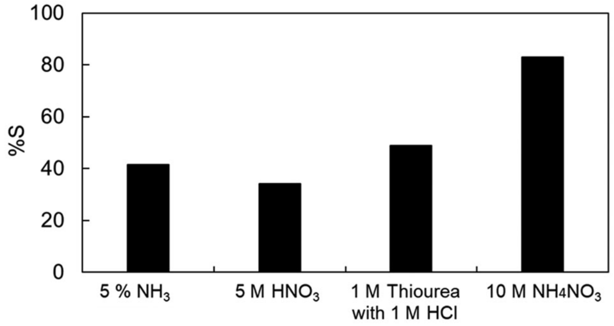

Figure 6. Stripping efficiencies of Pt from metal-loaded IL. Conditions: A:O = 2:1, 298 K, 24 h.

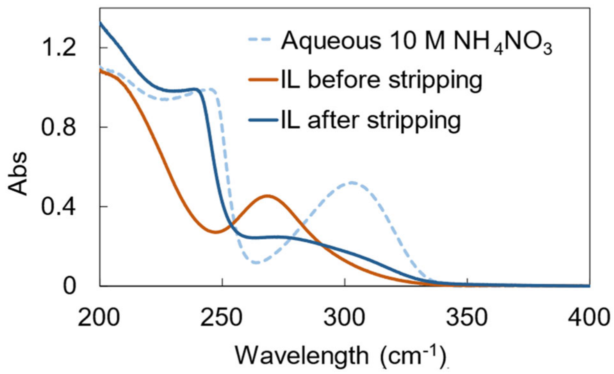

Figure 7. Ultraviolet–visible spectra of ionic liquid before and after stripping by 10 M NH_4NO_3 (red and blue lines, respectively) and aqueous 10 M NH_4NO_3 solution (blue dotted line). Condition: 298 K.

stripping using an appropriate aqueous solution. In this study, Pt was stripped from the IL using 5% NH_3, 5 M HNO_3, 1 M thiourea with 1 M HCl, and 10 M NH_4NO_3. Stripping efficiencies of Pt using the various stripping agents are shown in Figure 6. When 5% NH_3, 5 M HNO_3, and 1 M thiourea with 1 M HCl were used, the Pt stripping efficiency was less than 50%; conversely, 10 M NH_4NO_3 achieved a Pt stripping efficiency of up to 83%. UV–vis measurements were conducted to elucidate the mechanism. The UV–vis spectra of the IL phase (before and after stripping) and that of the aqueous NH_4NO_3 solution are shown in Figure 7. Compared with the spectrum of the IL before stripping (red line), the peak at 260 nm decreased, and a peak at 250 nm and a broad peak around 300 nm appeared in the spectrum of the IL after stripping (blue line). The latter is specific to nitrate ions which occurred in the aqueous NH_4NO_3 solution. Therefore, it was confirmed that the mechanism for $PtCl_6^{2-}$ stripping is an anion-exchange reaction with nitrate ions.

4. Conclusion

This study successfully demonstrated the leaching of metallic Pt using the phosphonium IL $P_{66614}Cl$ as a solvent, along with TCCA and MSA as additive agents. The use of the IL as the solvent, combined with the two different additive agents, was found to be critical for the efficient leaching of Pt. Pt that dissolved in the IL was efficiently stripped using 10 M NH_4NO_3, with the mechanism confirmed based on UV–vis spectroscopy to be an anion-exchange reaction with nitrate ions. Pt is widely used in various fields, especially in automotive exhaust catalysts, so the proposed method would be applicable to the refining of secondary resources.

Acknowledgements

This study was supported by the Environment Research and Technology Development Fund (Grant No. 3-2004) provided by the Ministry of Environment of Japan. We thank Kathryn Sole, PhD, from Edanz (https://jp.edanz.com/ac) for editing a draft of this manuscript.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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