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Homogeneous Liquid-Liquid Extraction (HoLLE) of Palladium in Real Plating Wastewater for Recovery

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Abstract

On the basis of homogeneous liquid-liquid extraction (HoLLE) with Zonyl FSA to plating water containing 1 mg palladium, 96.6% of the palladium was extracted into the sedimented liquid phase. After phase separation, the volume ratio (Va/Vs) of the aqueous phase (Va) and the sedimented liquid phase (Vs) was 556 (50 mL → 0.09 mL). The assessment of the potential implementation of this procedure to wastewater treatment showed that HoLLE was satisfactorily achieved when the volume was scaled up to 1000 mL. Moreover, HoLLE was conducted to real palladium plating wastewater generated in the plating industry. 94.5% of the palladium was extracted into the sedimented liquid phase. After phase separation, the volume ratio (Va/Vs) of the aqueous phase (Va) and the sedimented liquid phase (Vs) was 500 (50 mL → 0.1 mL). In addition, HoLLE could separate palladium from coexisting metals in real plating wastewater. This knowledge is expected to lead to the development of new separation and concentration technologies of rare metals from real plating wastewater.

1. Introduction

The multi-functionalization and miniaturization of electronic devices is accompanied by a growing density of their components. Highly efficient electronic devices contain many parts, such as connectors and sensors, in-

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volving precious metal plating. Gold plating is widely implemented in wiring and contact materials in the electronic industry because it provides excellent corrosion resistance and electric conductivity [1] [2]. However, the need for cost reducing approaches has prompted researchers to seek substitutes for gold plating. Specifically, plating processes using palladium and its alloys have been applied to electronic materials since the 1960s [3] [4]. Palladium plating provides superior chemical and mechanical properties that fulfill the characteristic requirements for the surface treated electronic components [5]-[7].

Recently, the potential use of plating wastewater as a metal resource has attracted considerable attention. Currently, most plating wastewater treatment procedures rely on sludge reclamation after pH adjustment. In Japan, plating industries have been reported to produce 50,000 tons of sludge per year, and almost all of this sludge is reclaimed [8]. Plating wastewater treatment is commonly conducted in solutions containing various metals. Contamination by other metals makes selective metal recovery difficult. It was expected that the spent plating water with the targeting metal could be isolated to avoid contamination by other metals. The metal recovery from plating wastewater has been examined by several methods such as cementation [9], precipitation [10], electrowinning [11]-[13], solid phase extraction [14] [15], and solvent extraction [16]-[18]. In addition, the metal recovery from palladium plating water has been performed by electrochemical method [19], and ion exchange resin [20].

Precious metal recovery from plating wastewater relies on economically and environmentally suitable hydrometallurgical technologies such as solvent extraction, which has been extensively applied at the industrial scale [21]-[23]. In the general solvent extraction, an interface exists between the aqueous phase and the water-immiscible organic solvent phase. Thus, mechanical shaking is required, which increases the surface area of the contact interface and causes the solute to move through the interface. On the other hand, homogeneous liquid-liquid extraction (HoLLE) has proven an effective metal recovery technology. In this method, the target solute (metal) is concentrated into small liquid phase on the basis of its phase separation from homogeneous water [24]. No interface is observed between the aqueous and organic solvent phases because the solution is homogeneous under initial conditions. In other words, the surface area of the interface is infinitely large. Therefore, HoLLE does not require vigorous mechanical shaking. Furthermore, HoLLE can achieve 100 - 100,000 fold concentration down to very low sample volumes in a few minutes [25]. In addition to various metal separation and concentration [26] [27], rare metal concentration from used home appliances has been achieved by HoLLE [28].

To lower the wastewater treatment costs, the volume of the plating wastewater is often reduced by heat treatment in a specialized facility. Therefore, an effective metal extraction system is required. To meet this requirement, in this study, an extraction system exploiting the high efficiency and recovery of HoLLE was developed for palladium plating wastewater.

2. Materials and Methods

2.1. Reagents and Materials

Palladium plating consisting of dichlorotetraammine palladium (1 wt%), ammonium nitrate (15 wt%), and water (84 wt%) received from Ibaraki Plating Kogyo Co., Ltd. (Ibaraki, Japan) was used in this study. The palladium concentration of the plating water in this experiment was determined to be 4.34 $g \cdot L^{-1}$ by inductively coupled plasma optical emission spectrometry (ICP-OES). Aqueous metal ion solutions were prepared by diluting 1000 $mg \cdot L^{-1}$ standard solutions obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). A Zonyl FSA $(CF_3(CF_2)_nCH_2CH_2SCH_2CH_2CO_2H$, n = 6 - 8, DuPont, Tokyo, Japan) solution was prepared by diluting the pure substance with an equivalent amount of distilled water. Nitric acid, hydrochloric acid, ammonia, and other basic chemicals were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All the reagents used in this study were of analytical grade.

2.2. Apparatus

The following instruments were utilized in this study: an M-12 pH meter manufactured by Horiba (Kyoto, Japan), a 7780 centrifugal separator manufactured by Kubota (Tokyo, Japan), an XGT-5000WR X-ray fluorescence spectrometer manufactured by Horiba (Kyoto, Japan), and an ICP ULTIMA2 ICP-OES manufactured by Horiba (Kyoto, Japan).

2.3. Methods

2.3.1. HoLLE of a Pure Palladium Solution

A 1000 mg·L^{-1} palladium standard solution was added to a 50 mL centrifuge tube such that 1 mg of palladium was placed in the tube. 13.4 M ammonia (1 mL) was then added to the centrifuge tube, and the volume was adjusted to 30 mL with distilled water. The pH of the solution was adjusted to 2.0 using 5 M nitric acid. Next, acetone (10 mL) and 50 v/v% Zonyl FSA (1 mL) were added to the mixture, and the volume was adjusted to 50 mL with distilled water. The solution was centrifuged at 2500 rpm for 30 min. After phase separation, the sedimented liquid phase was collected using a microsyringe.

2.3.2. HoLLE of Palladium Plating Water

Palladium plating water (30 mL) containing 1 mg palladium was added to a 50 mL centrifuge tube, and the pH of the solution was adjusted to 2.0 using 5 M nitric acid. Next, acetone (11 mL) and 50 v/v% Zonyl FSA (1 mL) were added to the mixture, and the volume was adjusted to 50 mL with distilled water. The solution was centrifuged at 2500 rpm for 30 min. After phase separation, the sedimented liquid phase was collected using a microsyringe.

3. Results and Discussion

3.1. HoLLE of a Pure Palladium Solution

The performance of HoLLE was evaluated for a palladium-ammine complex in weakly acidic aqueous media using Zonyl FSA. Upon the addition of 13.4 M ammonia, the orange-colored palladium standard solution instantly became colorless and transparent, suggesting the formation of the palladium-ammine complex. On the basis of palladium-ammine complex, phase separation was satisfactorily completed by HoLLE in weakly acidic aqueous media. After phase separation, approximately 100 μL of each aqueous and sedimented liquid phase were collected using a microsyringe. These solutions were then dropped onto a filter paper and analyzed by X-ray fluorescence. The results of the analyses are shown in **Figure 1**. A peak for palladium was not detected in the X-ray fluorescence spectrum of the aqueous phase, but was observed in the spectrum of the sedimented liquid phase. The volume ratio can be calculated as follows:

$$\text{Volume ratio} = \left(\text{mL of the aqueous phase}\right)/\left(\text{mL of the sedimented liquid phase}\right) = 50/0.1 = 500$$
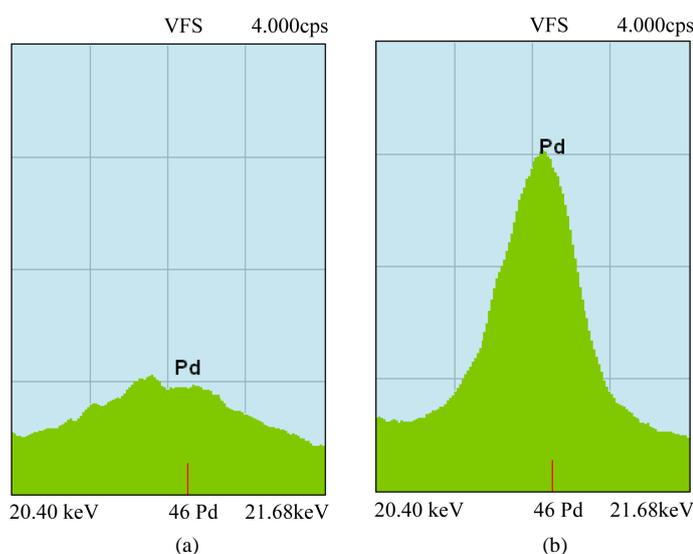

Figure 1. XRF evaluation after the HoLLE of palladium from HNO$_3$ solution. (a) Aqueous phase, (b) Sedimented liquid phase. Added palladium weight: 1 mg, [Ammonia]$_T$ = 0.267 M, pH 2.00, [Acetone]$_T$ = 20 vol.%, [Zonyl FSA]$_T$ = 1.00 vol.%, (XRF measurement conditions: X-ray diameter: 1.2 mm, time: 300 s, voltage: 50 kV).

The ICP-OES analysis of the aqueous phase revealed that 100% of the palladium was quantitatively extracted into the sedimented liquid phase, indicating that it was possible to concentrate palladium via HoLLE using Zonyl FSA.

3.2. Optimization of HoLLE Conditions for a Pure Palladium Solution

HoLLE using Zonyl FSA was reversible with the pH change in the solution, corresponding to below and above the pKa of Zonyl FSA [28]. This phase separation was achieved in the presence of hydrochloric acid, sulfuric acid, or nitric acid. The volume of the sedimented liquid phase was approximately 100 µL upon the addition of acids. The palladium recovery amounted to 98.3% in hydrochloric acid, and was lower than that in sulfuric acid and nitric acid. After phase separation, the pH of the aqueous phase was 1.52 and 2.09 in sulfuric and nitric acid, respectively. Considering the treatment of the aqueous phase, nitric acid was chosen for the remainder of the experiment because palladium recoveries were equivalent in sulfuric and nitric acids. Moreover, optimum condition of pH in nitric acid was confirmed (**Table 1**). When phase separation was satisfactorily completed, the pH before and after the phase separation was acidic. Recoveries for all the above mentioned conditions in nitric acid were 100% by phase separation. Moreover, the pH correlated with the acid dissociation constant (pKa = 6.5 [29]) during HoLLE. On the basis of these results, it was confirmed that phase separation was completed and recovery was 100% under pH 2.0 before phase separation. The pH before phase separation was set at 2.0 for the remainder of the experiment.

Next, the effect of the water-soluble organic solvent on palladium recovery was evaluated because this organic solvent significantly contributes to phase separation. When dioxane, tetrahydrofuran, or acetone was added, the phase separation was satisfactory. This suggested that the formation of the sedimented liquid phase depended on the solubility of Zonyl FSA in the water-soluble organic solvent. The volume of the sedimented liquid phase amounted to approximately 100 µL in dioxane and acetone but was a little larger in tetrahydrofuran (approximately 130 µL). The palladium recovery was 94% in dioxane, which was lower than that in tetrahydrofuran and acetone. Consequently, acetone was chosen for the remainder of the experiment. The acetone concentration was then optimized when it was 0 - 30 vol.%. Insoluble matter, which was believed to be Zonyl FSA, was detected near the sedimented liquid phase when the acetone concentration was 0 - 2 vol.%. This insoluble matter persisted even when the sedimented liquid phase formed from 6 - 12 vol.% acetone. Because the sedimented liquid phase was satisfactorily formed in 16 - 30 vol.% acetone, the palladium recovery was evaluated in this concentration range. Approximately 95% of the palladium was extracted in the sedimented liquid phase for these acetone concentrations (**Figure 2**). Therefore, the acetone concentration was set at 22 vol.% for the remainder of the experiment.

Finally, the influence of Zonyl FSA concentration on HoLLE was determined (**Figure 3**). The phase separation was satisfactory when the Zonyl FSA concentration was 0.3 - 1.5 vol.%. In addition, the volume of the sedimented liquid phase was proportional to the Zonyl FSA concentration. The palladium recovery increased with

Table 1. Influence of pH on the HoLLE of palladium from HNO_3 solution.

Phase separation	Recovery (%)	pH (Before separation)	pH (After separation)
×	-	9.82	9.77
×	-	8.99	8.89
○	100	1.99	2.68
○	100	1.85	2.30
○	100	1.66	2.01
○	100	1.40	1.63
○	100	1.24	1.42
○	100	1.02	1.20

The pH (Before separation) was measured before addition of Zonyl FSA and acetone. Added palladium weight: 1 mg, $[Ammonia]_T = 0.267$ M, $[Acetone]_T = 20$ vol.%, $[Zonyl\ FSA]_T = 1.00$ vol.%.
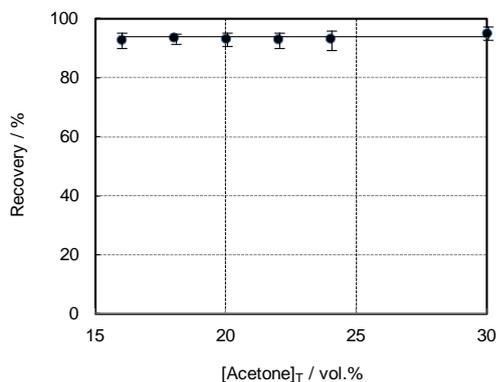
Figure 2. Influence of the acetone concentration on the HoLLE of palladium from HNO_3 solution. Added palladium weight: 1 mg, $[Ammonia]_T = 0.267$ M, pH 2.00, $[Zonyl\ FSA]_T = 1.00$ vol.%.

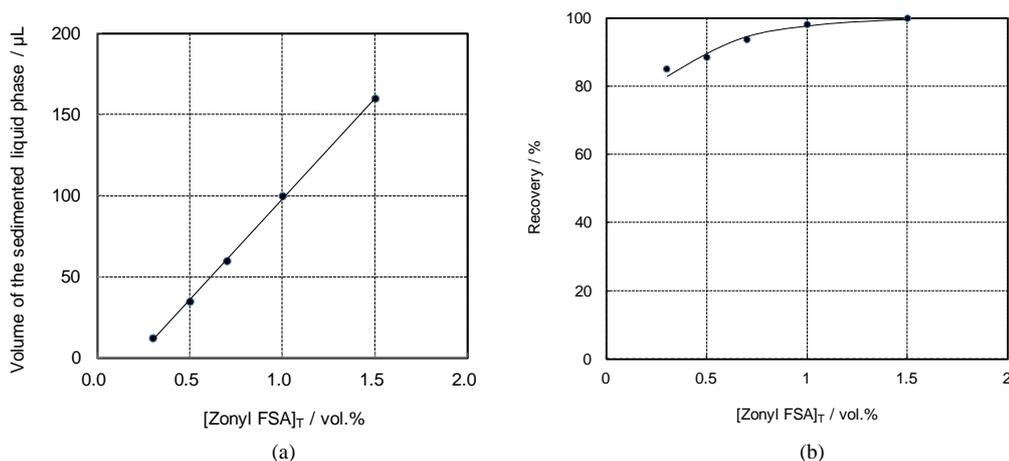(a)   (b)

Figure 3. Influence of the Zonyl FSA concentration on the HoLLE of palladium from HNO_3 solution. Added palladium weight: 1 mg, $[Ammonia]_T = 0.267$ M, pH 2.00, $[Acetone]_T = 22$ vol.%.

increasing Zonyl FSA concentration, and was almost 100% above 1.0 vol.% Zonyl FSA. Therefore, the Zonyl FSA concentration was set at 1.0 vol.% for the remainder of the experiment.

3.3. HoLLE of Palladium Plating Water

Palladium recovery from plating water containing a palladium-ammine complex was performed under the HoLLE conditions optimized for pure palladium solutions. Similar to the pure palladium solution, HoLLE was performed with and without ammonia addition for the plating water. The phase separation occurred in the absence of ammonia because the palladium-ammine complex already existed in the plating water. Therefore, the extraction was performed without ammonia addition. The phase separation of plating water with 1mg palladium was achieved by HoLLE using Zonyl FSA (Figure 4). Approximately 90 μL of each aqueous phase and sedimented liquid phase were collected using a microsyringe. These solutions were then dropped onto a filter paper and analyzed by X-ray fluorescence. The results of the analyses are shown in Figure 5. A peak for palladium was not detected in the X-ray fluorescence spectrum of the aqueous phase, but was observed in the spectrum of the sedimented liquid phase. The ICP-OES analysis of the aqueous phase showed that 96.6% of the palladium was extracted into the sedimented liquid phase. The volume ratio was calculated as follows:

$$\text{Volume ratio} = \left(\text{mL of the aqueous phase}\right)\big/\left(\text{mL of the sedimented liquid phase}\right) = 50/0.09 = 556$$

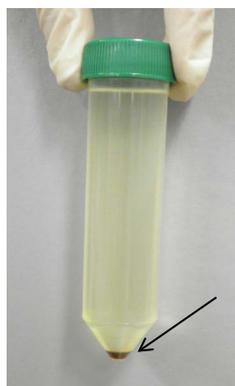These results suggest that the HoLLE-based approach effectively concentrated palladium from plating water.

Figure 4. Solutions obtained after HoLLE of palladium plating water.
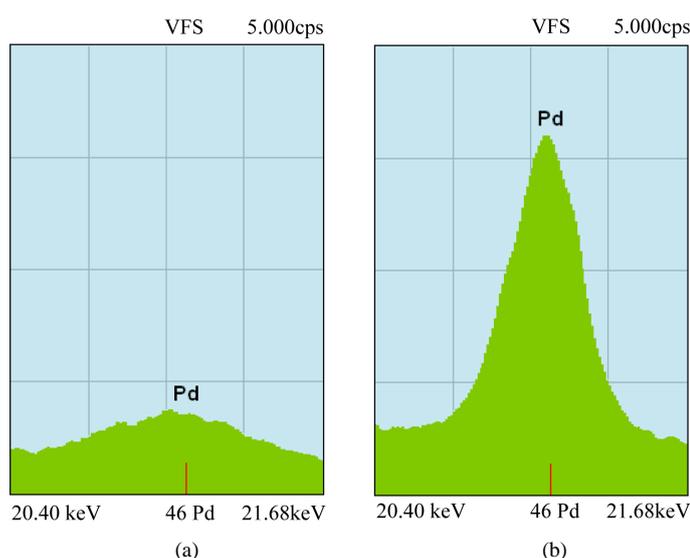

(a)　　　　　　　　　　　　　　(b)

Figure 5. XRF evaluation after the HoLLE of palladium from plating water. (a) Aqueous phase, (b) Sedimented liquid phase, Added palladium weight: 1 mg, pH 2.00, $[Acetone]_T = 22$ vol.%, $[Zonyl FSA]_T = 1.00$ vol.%, (XRF measurement conditions: X-ray diameter: 1.2 mm, time: 300 s, voltage: 50 kV).

To assess the applicability of this approach to industrial plating water, palladium was also concentrated from plating water by HoLLE. The total volume was increased to 1000 mL, which is twenty times higher than the original volume, whereas the remaining conditions were maintained identical to the optimized ones. Phase separation was satisfactorily completed (**Figure 6**). The ICP-OES analysis of the aqueous phase revealed that 99.9% of the palladium was extracted into the sedimented liquid phase. The volume ratio was calculated as follows:

$$\text{Volume ratio} = (\text{mL of the aqueous phase}) / (\text{mL of the sedimented liquid phase}) = 1000/2.5 = 400$$

This data showed that HoLLE resulted in high volume ratio and high recovery upon scale-up. Moreover, because of scale-up experiment without centrifugal separation, it was confirmed that phase separation was satisfactorily completed with only addition of reagents.

The palladium concentration of these plating water samples was 33.3 mg·L^{-1}, which was equivalent to 1 and 20 mg palladium in 30 and 600 mL solutions, respectively. Industrial plating wastewater results from a mixture of plating bath and rinse water bath and has been reported to contain 100 - 400 mg·L^{-1} of metals in Japan [30]. Therefore, the performance of HoLLE was evaluated in this concentration range. Under optimized HoLLE conditions, phase separation was satisfactorily completed for plating water containing 33.3 - 289 mg·L^{-1}. 88.0% of the palladium was extracted into the sedimented liquid phase from 289 mg·L^{-1} palladium plating water. This

Figure 6. Solutions obtained after HoLLE of palladium plating water (1000 mL).

confirms that HoLLE effectively extracted palladium from wastewater in plating facilities. In this concentration range, the recovery gradually decreased with increasing palladium concentration (**Figure 7**). A recovery of 96.6% was obtained from the 33.3 mg·L^{-1} palladium plating water, suggesting that HoLLE should be performed from slightly diluted solutions to reduce interferences from coexisting substances such as buffer solutions.

The sedimented liquid phase contained palladium and Zonyl FSA. Back-extraction by addition of a solvent [31], recovery mediated by a chemically modified polymer gel [32], and scavenging by solid phase extraction [33] have been exploited to recover fluoro compounds. Therefore, it was thought that the metal could be isolated from the sedimented liquid phase by these methods.

3.4. HoLLE of Real Palladium Plating Wastewater

To confirm the effect of coexisting metals, except palladium, HoLLE was performed to real palladium-nickel plating wastewater generated in the plating industry. Plating water and plating wastewater in palladium-nickel plating compositions in palladium-nickel plating are shown in **Table 2**. Their base material was copper, and the plating metals consisted of nickel, gold, and palladium-nickel. During plating processes, the material passed through a plating bath and rinse water bath. It was confirmed that each metal concentration of plating wastewater was approximately 500 times lower than plating water (**Table 2**). The plating wastewater originated from diluted plating water because the base material and plating metal under palladium-nickel phase did not leach. The phase separation was satisfactorily completed in HoLLE for this plating wastewater. Further, the ICP-OES analysis of the aqueous phase revealed that 94.5% of the palladium was extracted into the sedimented liquid phase (**Table 3**). In addition, the recovery of the coexisting nickel and copper was 24.6% and 57.2%, respectively. In other words, the weight percentage of the three component metals in plating wastewater changed as Pd (62.1% → 86.0%), Ni (37.1% → 13.3%), and Cu (0.8% → 0.7%). Hence, it was confirmed that the palladium was conveniently separated from coexisting metals. It was considered that this separation was achieved because of the formation of a palladium-ammine complex and the ionization state of coexisting metals such as nickel and copper. The volume ratio was calculated as follows:

$$\text{Volume ratio} = \left(\text{mL of the aqueous phase}\right)/\left(\text{mL of the sedimented liquid phase}\right) = 50/0.1 = 500$$

These results show that it is possible to simultaneously concentrate palladium and separate coexisting substances.

4. Conclusion

Palladium was extracted from plating water by HoLLE in the presence of Zonyl FSA. For plating water with 1 mg palladium, palladium recovery amounted to 96.6%, and the volume ratio was 556 (50 mL → 0.09 mL). Performance assessment for the potential use of this approach for wastewater treatment demonstrated that the phase separation was satisfactorily achieved at the scaled-up volumes. Moreover, this extraction approach was applicable
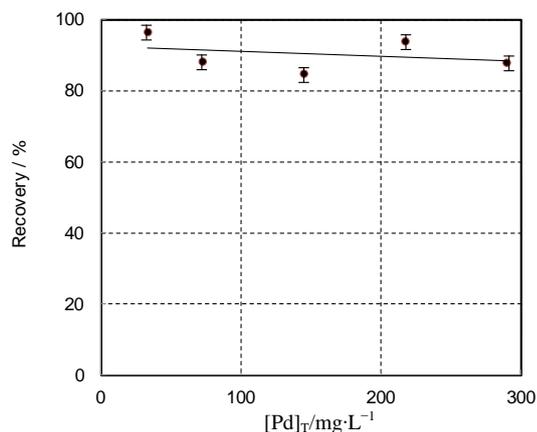
Figure 7. Influence of the palladium concentration on the HoLLE from plating water. pH 2.00, $[Acetone]_T = 22$ vol.%, $[Zonyl FSA]_T = 1.00$ vol.%.

Table 2. Concentration of plating water and plating wastewater in plating industry.

	Plating water (mg·L^{-1})	Plating waste water (mg·L^{-1})
Pd	15200	29.6
Ni	9280	17.7
Au	Not detected	Not detected
Cu	180	0.4

Table 3. Influence of coexisting substances on the HoLLE from plating wastewater.

	Weight in the plating waste water (mg)	Weight in the sedimented liquid phase (mg)	Recovery (%)
Pd	0.888	0.839	94.5
Ni	0.531	0.130	24.6
Au	Not added	-	-
Cu	0.012	0.007	57.2

to plating wastewater at standard industrial concentrations, as well as the real plating wastewater. This knowledge is expected to lead to the development of new separation and concentration technologies of rare metals from real plating wastewater.

Acknowledgements

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