

Powerful Concentration of Rhodium in Plating Wastewater Using Homogeneous Liquid–Liquid Extraction (HoLLE) and Study for Scale-up

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Abstract

A powerful technique for the concentration of rhodium (Rh) in plating wastewater was developed. The technique entails complexing Rh with 1-(2-pyridylazo)-2-naphthol (PAN) followed by homogeneous liquid–liquid extraction (HoLLE) with Zonyl FSA. The optimum HoLLE conditions were determined as follows: [ethanol]_T = 30.0 vol.%, pH = 4.00, and Rh: PAN = 1:5. Under these optimum conditions, 88.1% of Rh was extracted into the sedimented liquid phase. After phase separation, the volume ratio [aqueous phase (V_a) / sedimented liquid phase (V_s)] of V_a and V_s was 1000 (50 mL → 0.050 mL). We then applied the new method to wastewater generated by the plating industry. The phase separation was satisfactorily achieved when the volume was scaled up to 1000 mL of the actual wastewater; 84.7% of Rh was extracted into the sedimented liquid phase. After phase separation, V_a/V_s was 588 (1000 mL → 1.70 mL).

Keywords: Homogeneous liquid–liquid extraction; HoLLE; Zonyl FSA; Rhodium; Plating wastewater

1. Introduction

Ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt) belong to the platinum group metals (PGMs), which possess superior heat and corrosion resistance properties. PGMs have been widely used in electronic devices due to their excellent physical and chemical properties. In 2013, the total world productions of Pd and Pt were 203,000 kg and 184,000 kg, while the total production of other PGMs (Ru, Rh, Os, and Ir) was 67,700 kg (Loferski, 2015). Because PGM production is unevenly distributed, and the prices of PGMs exhibit large fluctuation, securing PGMs is a global issue.

PGMs have been widely separated and purified using hydrometallurgical methods. Among these methods, solvent extraction is the most commonly used industrial process and is used in INCO's Acton refinery (Barnes & Edwards, 1982). Rh is recovered from the residual liquid in the distillation and solvent extraction of Ru, Pd, Os, Ir, and Pt owing to the most difficult step in the extraction of PGMs (Tanaka, Koyama, Narita, & Oishi, 2011). This is because Rh ions are more strongly hydrated than other PGMs; thus, Rh exhibits extreme inertness during the extraction process (Yan & Alstad, 1995). As a soft acid, Rh can be selectively extracted using soft donor base with nitrogen or sulfur atoms (Kumar, Lee, Kim, & Sohn, 2009; Shaikh, Lande, & Arbad, 2011). A variety of nitrogen-based extractants, such as alamine 304-1 (Sun, J.Y. Lee, & M.S. Lee, 2011), tri-octylamine (Jaree & Khunphakdee, 2011), and N-decylpyridine-4-amine (Bagal, Sakhare, Lande, & Arbad, 2014), and a variety of sulfur-based extractants such as dialkyl sulfoxides (Preston & Preez, 2002) and trialkylphosphine sulphide (Rizvi, Mathur, Murali, & Iyer, 1996), have been investigated for Rh extraction.

Although solvent extraction is a useful separation and purification method, it has several drawbacks related to operability and efficiency. In general, solvent extraction requires mechanical shaking to increase the surface area between the aqueous and water-immiscible organic solvent phases. In contrast, in homogeneous liquid–liquid extraction (HoLLE), no interface exists between the aqueous and water-immiscible organic solvent phases; that is, the initial condition is a homogenous solution (Igarashi & Yotsuyanagi, 1988). The HoLLE procedure is

straightforward and only requires the addition of reagents due to the large surface area of the interface. In HoLLE, the target solute is concentrated into a small secondary phase through the effect of some stimulation such as pH, or light. HoLLE has been widely used to extract target solutes such as indium (In) (Kato, Igarashi, Ishiwatari, Furukawa, & Yamaguchi, 2013), cobalt (Co) (Kato, Igarashi, Saito, Ando, & Asano, 2014), rare earth elements (Saito, Ohno, Igarashi, Kato, & Yamaguchi, 2015), and Pd (Kato, Igarashi, Ohno, Saito, & Ando, 2016), although the target solute is not limited to metals. Additionally, HoLLE can be applied to organic compounds (Takagai & Igarashi, 2002) and biological materials (Sudo & Igarashi, 1996). With respect to trace amounts of metals, nanofiltration (Otero-Fernandez et al., 2017) and solid-phase extraction (Molaei, Bagheri, Asgharinezhad, Ebrahimzadeh, Shamsipur, 2017) have been reported. However, there is still room for improvement in contact probability, and interfacial area, and other factors. These problems can be solved using HoLLE because the initial condition is a homogeneous solution and the surface area of the interface is infinitely large. On the other hand, Murata and Ikeda studied the high solubility of propylene carbonate in water at high temperature as homogeneous liquid–liquid extraction (Murata & Ikeda, 1969). In similar studies, some ionic liquid solutions form one homogeneous phase above the upper critical solution temperature or below a lower critical solution temperature (Lamb & Peterson, 1995; Mori et al., 2015; Hoogerstraete, Onghena, & Binnemans, 2013; Depuydt, Liu, Glorieux, Dehaen, & Binnemans, 2015). Such homogeneous liquid–liquid extraction was applied to the extraction of metal ions (Mori et al., 2015; Hoogerstraete, Onghena, & Binnemans, 2013; Depuydt, Liu, Glorieux, Dehaen, & Binnemans, 2015). Compared with homogeneous liquid–liquid extraction based on temperature, HoLLE based on pH-dependent phase separation can be used to achieve 100–100,000-fold concentration in several minutes down to micro-volume levels (Takagai & Igarashi, 2002). For this reason, HoLLE based on pH-dependent phase separation was investigated.

In the treatment of wastewater from the plating industry, the volume of wastewater is often reduced by heating, evaporation, and other processes because it is difficult to treat the wastewater at own facility in plating industry. Thus, HoLLE represents a promising strategy to concentrate Rh from plating wastewater. Herein, we used 1-(2-pyridylazo)-2-naphthol (PAN) as a soft donor base containing nitrogen to extract Rh (Cheng & Bray, 1955; Stokely & Jacobs, 1963). In this study, Zonyl FSA was used as a phase separation agent with an acid dissociation constant (pKa) of approximately 6 (Sudo & Igarashi, 1996). It introduced a methylene chain as a spacer between the perfluoroalkyl group and carboxyl group in order to negate the effect of fluorine. Consequently, this method can apply complexation at mild pH because phase separation below pH 6 is possible.

2. Experimental

2.1 Reagents and Materials

Rh plating water comprising rhodium sulfate (0.2 wt%), sulfuric acid (4 wt%), phosphoric acid (1.4 wt%), and water was obtained from Ibaraki Plating Kogyo Co., Ltd. (Ibaraki, Japan). The Rh concentration of the real plating wastewater was determined as 708 mg L⁻¹ using inductively coupled plasma optical emission spectrometry (ICP-OES). Aqueous solutions of metal ions were prepared by diluting 1000 mg L⁻¹ standard solutions obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). A solution of Zonyl FSA [CF₃(CF₂)_nCH₂CH₂SCH₂CH₂CO₂H; n = 6–8; DuPont, Tokyo, Japan] was prepared by diluting pure Zonyl FSA with an equivalent amount of distilled water. All chemicals except Zonyl FSA were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All reagents used in this study were of analytical grade.

2.2 Apparatus

The following instruments were employed in this study: an M-12 pH meter manufactured by Horiba (Kyoto, Japan); an AS185 centrifugal separator manufactured by AS ONE Corporation (Osaka, Japan); a U-4100 UV-VIS spectrophotometer manufactured by Hitachi High-Technologies Corporation (Tokyo, Japan); and an ICP ULTIMA2 ICP-OES manufactured by Horiba (Kyoto, Japan).

2.3 Methods

2.3.1 HoLLE of a pure Rh solution

Rh standard solution (1,000 mg L⁻¹) was added to a 50-mL centrifuge tube such that 0.1 mg of Rh was added to the tube. PAN solution (5 mL, 0.025%) and ethanol (2 mL) were then added to the centrifuge tube, and the volume was adjusted to 30 mL with phthalate pH standard solution (pH 4). The solution was heated for 60 min at 90 °C to form Rh-PAN complexes and then allowed to rest for 60 min at room temperature. Subsequently, phthalate pH standard solution (11 mL) and ethanol (8 mL) were added to the centrifuge tube, followed by the addition of 50 v/v% Zonyl FSA (1 mL). After shaking gently, the solution was centrifuged at 2,500 rpm for 30 min in order to hasten phase

separation. After phase separation, the sedimented liquid phase was collected using a microsyringe. The volume of the sedimented liquid phase was determined using a 0.1-mL microsyringe.

2.3.2 HoLLE of Real Rh Plating Wastewater

Real Rh plating wastewater was added to a 50-mL centrifuge tube such that 0.1 mg of Rh was added to the tube. PAN solution (5 mL, 0.025%) and ethanol (2 mL) were then added to the centrifuge tube, and the volume was adjusted to 30 mL with phthalate pH standard solution (pH 4) and small amounts of 5-M nitric acid to adjust the pH to 4.0. The solution was heated for 180 min at 90 °C to form Rh-PAN complexes and allowed to rest for 60 min at room temperature. Then, phthalate pH standard solution (11 mL) and ethanol (8 mL) were added to the centrifuge tube, followed by the addition of 50 v/v% Zonyl FSA (1 mL). After shaking gently, the solution was centrifuged at 2,500 rpm for 30 min in order to hasten phase separation. After phase separation, the sedimented liquid phase was collected using a microsyringe. The volume of the sedimented liquid phase was determined using a 0.1-mL microsyringe.

2.3.3 HoLLE for Scale-Up to Real Rh Plating Wastewater

Real Rh plating wastewater was added to a beaker such that 2 mg of Rh was added to the beaker. PAN solution (100 mL, 0.025%) and ethanol (40 mL) were then added to the beaker, and the volume was adjusted to 600 mL with phthalate pH standard solution (pH 4) and small amounts of 5-M nitric acid to adjust the pH to 4.0. The solution was heated for 180 min at 90 °C to form Rh-PAN complexes and allowed to rest for 60 min at room temperature. The solution was moved from the beaker to the plastic vessel. Next, phthalate pH standard solution (220 mL) and ethanol (160 mL) were added to the plastic vessel, followed by the addition of 50 v/v% Zonyl FSA (20 mL). After shaking gently, the solution stood for about one hour. After phase separation, the sedimented liquid phase was collected by opening below cock of the plastic vessel. The volume of the sedimented liquid phase was determined using a 20-mL measuring glass.

3. Results and Discussion

3.1 Rh-PAN Complexes

Cheng and Bray first studied the use of PAN as an analytical reagent (Cheng & Bray, 1955). Stokely and Jacobs investigated Rh complexation with PAN for a spectrophotometric determination of Rh (Stokely & Jacobs, 1963). Rh-PAN complexes are easily prepared by heating in buffered, aqueous-alcoholic solutions. Because it is difficult to treat organic solvent as chloroform in a plating industry, ethanol is suitable in order to require environmental conscious system. Considering Rh-PAN complexation in buffered, aqueous-alcoholic solutions, PAN was selected in this study. Upon heating, the orange solution of Rh and PAN gradually became green, suggesting the formation of Rh-PAN complexes. Figure 1 shows the absorbance curves for the Rh-PAN complexes; the Rh concentration was proportional to the absorbance of the Rh-PAN complexes. The Rh-PAN complex had an absorbance maximum at 587 nm. On the basis of continuous variation method in absorbance at 587 nm, the Rh: PAN ratio was 1:1 (Figure 2).

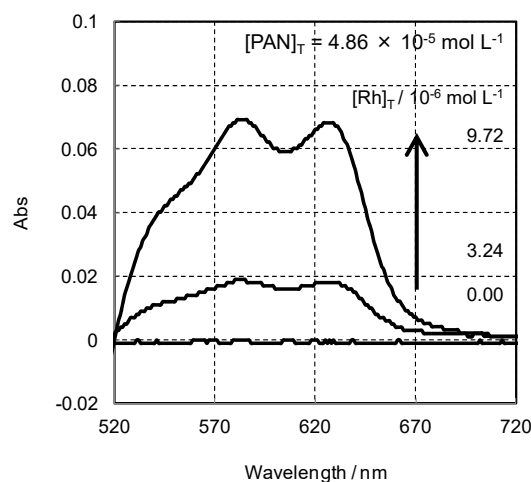


Figure 1. Absorbance curves for the rhodium(Rh)-1-(2-pyridylazo)-2-naphthol(PAN) complex. Complexing condition: 90 °C, 60 min., pH 4.01

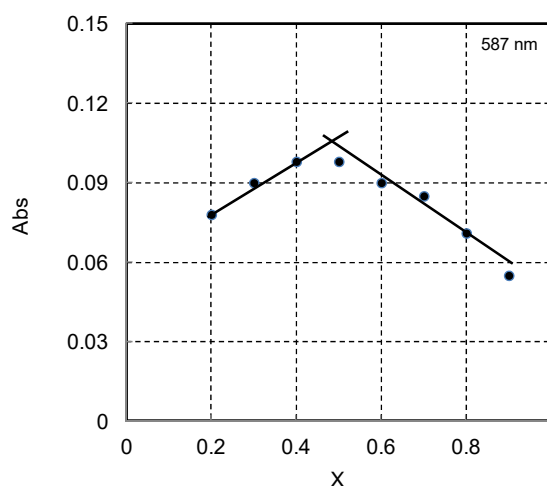


Figure 2. Continuous variation method in absorbance at 587 nm. $M + nX \rightarrow MX_n$, M: Rhodium, X: PAN, M: $(1 - x)$ mL, X: x mL, $[Rh] = [PAN] = 1.00 \times 10^{-3} \text{ mol L}^{-1}$, Total volume: 30 mL

3.2 HoLLE of Rh

HoLLE using a phase separation agent such as Zonyl FSA was reversible with the pH change in the solution, corresponding to below and above the pKa of phase separation agent such as Zonyl FSA (Igarashi & Yotsuyanagi, 1992). If the pH of the aqueous solution containing small amounts of a water-miscible organic solvent such as ethanol is lower than the acid dissociation constant of Zonyl FSA (pKa = 6.5) (Sudo & Igarashi, 1996), the target solute is concentrated into the sedimented liquid phase. In this study, we confirmed the behavior of HoLLE in a pure Rh solution. In particular, HoLLE using Zonyl FSA containing Rh-PAN complexes in weakly acidic media was examined. Phase separation was satisfactorily completed via HoLLE. The volume ratio, defined as volume ratio = (mL of the aqueous phase)/(mL of the sedimented liquid phase), was $50/0.085 = 588$. Therefore, we concluded that HoLLE can be used to concentrate Rh with a high volume ratio. The analysis of the aqueous phase using ICP-OES indicated that 74.0% of Rh was extracted into the sedimented liquid phase. It has been reported that the water content of the sedimented liquid phase was 5-% in the Zonyl FSA system (Sudo & Igarashi, 1996). Based on the low-water content of the sedimented liquid phase, the hydrophobic solute as Rh-PAN complex could be effectively extracted.

After confirming the ability of HoLLE to separate solutions containing Rh-PAN complexes, we optimized the experimental conditions. First, the effect of ethanol (the water-soluble solvent) on HoLLE was evaluated because ethanol affects the state of the sedimented liquid phase. The relation between the volume of the sedimented liquid phase and the ethanol concentration was linear for ethanol concentrations ranging from 18.0 vol.%–30.0 vol.%. At ethanol concentrations exceeding 30.0 vol.%, the volume of the sedimented liquid phase remained constant (Figure 3). Therefore, an ethanol concentration of 30.0 vol.% was selected for the remaining experiments. Then, we evaluated the effect of pH on HoLLE because pH contributes to Rh-PAN complexation and phase separation. Results state that the extraction percentage increased with increasing pH and exceeded more than 80.0% at pH values above 4.00. Moreover, the volume ratio was maximized at pH 4.00. Due to increasing water content in the sedimented liquid phase, the volume ratio at pH 4.50 was smaller than that at pH 4.00. Huang et al. found that surfactants can form vesicles in the ethanol-water-mixed solvents (Huang, Zhu, Zhao, & Zhang, 1997). Moreover, Lee et al. reported that surfactants can form vesicles at intermediate pH values close to the pKa of the molecules (Lee, Danino, & Raghavan, 2009). Based on these reports, it is considered that the water content of the sedimented liquid phase increased because Zonyl FSA forms vesicles at pH values close to the pKa. Thus, to obtain the optimum extraction percentage and volume ratio, a pH of 4.00 was chosen for the remaining experiments (Figure 4). Finally, we evaluated the effect of PAN concentration on Rh extraction. When the Rh: PAN ratio was less than 1:3, the extraction percentage of Rh was approximately 70.0%; however, at a ratio of 1:5, the extraction percentage was 88.1% (Figure 5). Based on these results, the Rh: PAN ratio was set at 1:5 in further experiments. Using the above optimum conditions for HoLLE, the volume ratio was calculated as follows:

$$\begin{aligned}\text{Volume ratio} &= (\text{mL of the aqueous phase})/(\text{mL of the sedimented liquid phase}) \\ &= 50/0.050 = 1000.\end{aligned}$$

Under the optimized conditions, 88.1% of Rh was extracted into the sedimented liquid phase, as determined by the ICP-OES analysis of the aqueous phase.

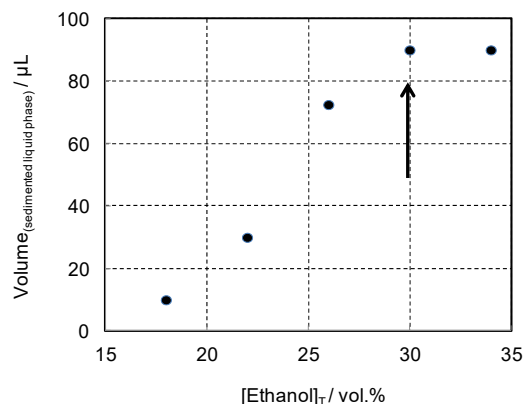


Figure 3. Effect of ethanol concentration on the HoLLE of Rh. $[\text{Rh}]_T = 1.94 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{PAN}]_T = 1.00 \times 10^{-4} \text{ mol L}^{-1}$, pH 4.01, $[\text{Zonyl FSA}]_T = 1.00 \text{ vol. \%}$

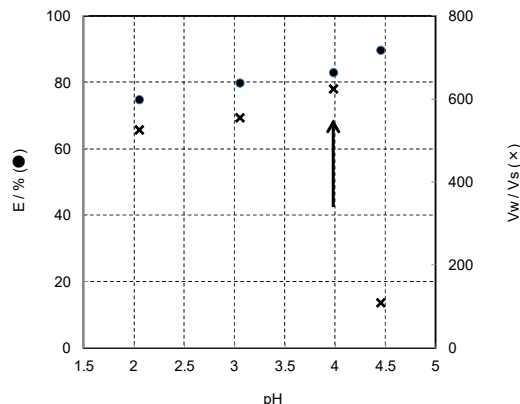


Figure 4. Effect of pH on the HoLLE of Rh. $[\text{Rh}]_T = 1.94 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{PAN}]_T = 1.00 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{Ethanol}]_T = 30.0 \text{ vol. \%}$, $[\text{Zonyl FSA}]_T = 1.00 \text{ vol. \%}$

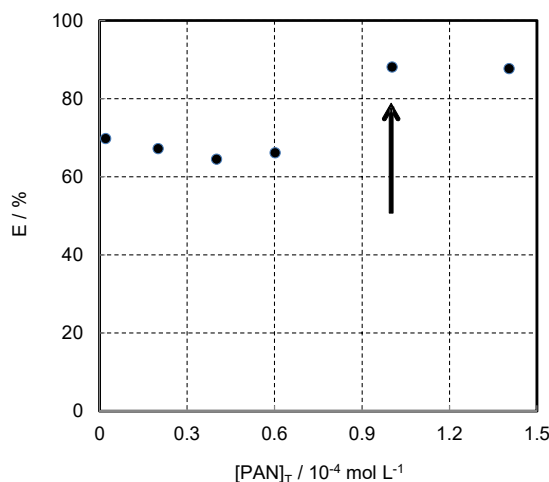


Figure 5. Effect of PAN concentration on the HoLLE of Rh. $[\text{Rh}]_{\text{T}} = 1.94 \times 10^{-5} \text{ mol L}^{-1}$, pH 4.01, $[\text{Ethanol}]_{\text{T}} = 30.0 \text{ vol.}\%$, $[\text{Zonyl FSA}]_{\text{T}} = 1.00 \text{ vol.}\%$

3.3 Scale-Up to Real Rh Plating Wastewater

HoLLE was first performed on real Rh plating wastewater using the same volume as above to confirm the applicability of this method to actual wastewater. The results indicated that phase separation was satisfactorily achieved (Figure 6). The volume ratio was calculated as follows:

$$\begin{aligned} \text{Volume ratio} &= (\text{mL of the aqueous phase})/(\text{mL of the sedimented liquid phase}) \\ &= 50/0.075 = 667. \end{aligned}$$

The ICP-OES analysis of the aqueous phase revealed that 86.4% of Rh was extracted into the sedimented liquid phase.

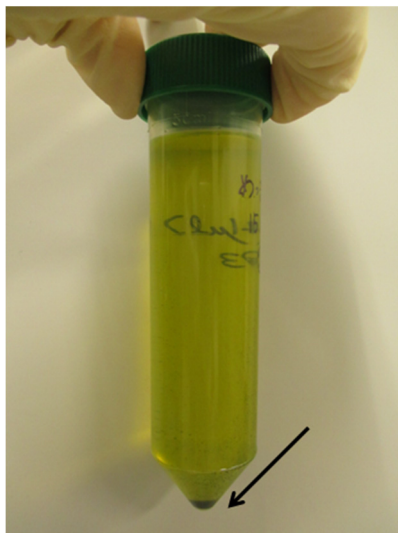


Figure 6. Solutions obtained after the HoLLE of real Rh plating wastewater. $[\text{Rh}]_{\text{T}} = 1.94 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{PAN}]_{\text{T}} = 1.00 \times 10^{-4} \text{ mol L}^{-1}$, pH 4.01, $[\text{Ethanol}]_{\text{T}} = 30.0 \text{ vol.}\%$, $[\text{Zonyl FSA}]_{\text{T}} = 1.00 \text{ vol.}\%$

We evaluated the potential of this method to scale-up to realistic volumes of actual plating wastewater. The total volume was increased to 1000 mL (20 times higher than the original volume), and the experimental conditions were the optimized conditions detailed above. The experiment was performed using a plastic vessel suitable in separation for treatment of several liters (Figure 7). Phase separation began in several minutes after the solution was added and mixed. Subsequently, a dark green sedimented liquid phase was formed, similar to that obtained in the above experiments. Phase separation was nearly completed in 1 h, and the volume ratio was calculated as follows:

$$\begin{aligned}\text{Volume ratio} &= (\text{mL of the aqueous phase})/(\text{mL of the sedimented liquid phase}) \\ &= 1000/1.70 = 588.\end{aligned}$$

The ICP-OES analysis of the aqueous phase indicated that 84.7% of Rh was extracted into the sedimented liquid phase. Thus, HoLLE can be used for the concentration of Rh in realistic volumes of plating wastewater.

Perfluoro compounds, such as Zonyl FSA, can be removed with back-extraction by adding solvent (Takagai & Igarashi, 2003), recovery using a chemically modified polymer gel (Butsugan & Igarashi, 2009), removal by solid-phase extraction (Japanese Standard Association, 2011), and reuse on the basis of the mixed solution (Saito, Ohno, Igarashi, Kato, & Yamaguchi, 2015). For example, rhodium leads to the formation of hydroxide, Zonyl FSA is recovered by a chemically modified polymer gel (Butsugan & Igarashi, 2009), and PAN remains in residual liquid after the Zonyl FSA of the sedimented liquid phase is dissolved in water at a higher pH value than its acid dissociation constant ($\text{pK}_a = 6.5$) (Sudo & Igarashi, 1996).

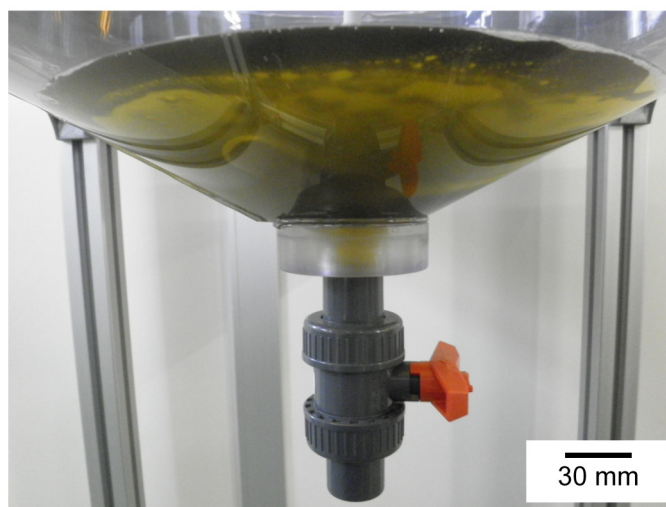


Figure 7. Plastic vessel used for the scaled-up experiment. $[\text{Rh}]_T = 1.94 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{PAN}]_T = 1.00 \times 10^{-4} \text{ mol L}^{-1}$, $\text{pH } 4.01$, $[\text{Ethanol}]_T = 30.0 \text{ vol.}\%$, $[\text{Zonyl FSA}]_T = 1.00 \text{ vol.}\%$

4. Conclusions

We successfully demonstrated the concentration of Rh. Under the optimized conditions, the extraction percentage was 88.1% and the volume ratio was 1,000 (50 mL \rightarrow 0.050 mL). We evaluated the potential of this method to scale-up using real plating wastewater; the results indicated that phase separation was satisfactorily completed with an extraction percentage of 84.7% and a volume ratio of 588 (1000 mL \rightarrow 1.70 mL). These findings are expected to facilitate the development of new concentration techniques to extract rare metals from plating wastewater.

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