Vol. 23, No. 3(2024) Proc24380
Revista Mexicana de Ingeniería Química

Separation of palladium from waste electronic card leaching solutions by solvent extraction using a tertiary amine

Separación de paladio a partir de soluciones de lixiviación de tarjetas electrónicas de desecho mediante extracción por solventes utilizando una amina terciaria

G. Martínez-Ballesteros[1]*, J. L. Valenzuela-García[1]*, P. Guerrero-Germán[1], B. Valdez-Salas[2], A. Gómez-Álvarez[1]
[1]Department of Chemical Engineering and Metallurgy, University of Sonora, Blvd. Luis Encinas y Rosales s/n, Col. Centro, Hermosillo, Son., 83000, México.
[2]Engineering Institute, Autonomous University of Baja California, Avenida Álvaro Obregón s/n, Nueva, 21100 Mexicali, Baja California.
Received: July 13, 2024; Accepted: September 17, 2024

Abstract
In this research, waste electronic cards were processed to recover precious metals, presenting new challenges for the efficient extraction of metals of interest. After a pretreatment that removed base metals (Cu, Fe, Zn, and Ni), via pressure leaching with sulfuric acid and oxygen, precious metals were leached in a chloride medium, resulting in an aqueous solution containing Ag, Au, Pt, and Pd chlorides. Palladium was recovered from this solution using a solvent extraction process, which concentrated the chloride solution with a tertiary amine extractant. The process achieved over 95% extraction efficiency for palladium at a pH of 1.5 and a phase ratio of 1.2:1. Extraction isotherms indicated a higher loading capacity with a 12% tertiary amine concentration diluted in kerosene. A McCabe-Thiele diagram showed that three theoretical stages were needed for effective extraction. To determine best re-extraction conditions, thiourea ($CS(NH_2)_2$) in 0.5 M HCl was used, and the aqueous phase ratios were varied. A stripping efficiency of over 98% for palladium was achieved using 1 M thiourea at a phase ratio of 5:1 and ambient temperature (25 °C). Thus, palladium can be selectively extracted from a chloride solution using solvent extraction with a tertiary amine, yielding a concentrated solution.
Keywords: Palladium, Solvent Extraction, Tertiary Amine, Chloride ions.

Resumen
En esta investigación se procesaron tarjetas electrónicas de desecho para recuperar metales preciosos. Un pretratamiento permitió separar metales base (Cu, Fe, Zn y Ni) utilizando lixiviación a presión con ácido sulfúrico, después los metales preciosos fueron lixiviados con ácido clorhídrico, obteniendo una solución acuosa de Ag, Au, Pt y Pd en medio cloruro. El paladio fue separado mediante extracción por solventes, utilizando extractante amina terciaria, alcanzando una extracción superior al 95%, bajo condiciones de pH 1.5 y una relación de fases de 1.2:1. Las isotermas de extracción mostraron que las aminas terciarias al 12% de concentración tienen una mayor capacidad de carga. Análisis del diagrama de McCabe-Thiele indicó que son necesarias tres etapas teóricas para lograr una extracción eficiente. Para determinar las condiciones de reextracción, se utilizó tiourea ($CS(NH_2)_2$) en una solución de HCl 0.5 M, variando las relaciones de fases. Se obtuvo una eficiencia de despojamiento de más del 98% para el paladio al emplear una concentración de tiourea 1 M y una relación de fases de 5:1 a temperatura ambiente (25 °C). Así el paladio puede ser extraído selectivamente de una solución de cloruros mediante extracción por solventes con amina terciaria, obteniéndose paladio en una solución concentrada.
Palabras clave: Paladio, Extracción por Solventes, Amina Terciaria, Iones Cloruros.

*Corresponding author. *E-mail*: guadalupe.martinezballesteros@unison.mx; jesusleobardo.valenzuela@unison.mx;
https://doi.org/10.24275/rmiq/Proc24380
ISSN:1665-2738, *issn-e*: 2395-8472

1 Introduction

Electronic and electrical equipment waste (WEEE) represents a valuable source of raw materials. In 2019, WEEE generation was approximately 54 million tonnes (MT), expecting that by 2030 this will increase to 75 MT, of which only 15-20% of the world's e-waste is recycled annually(Fontana *et al*., 2018; Forti *et al*., 2020; Shittu *et al*., 2021). This percentage of WEEE recycling is mainly due to two factors: The first factor is the lack of awareness of the pollution problems that this type of equipment can cause when discarded. The second factor is due to the composition of these scraps, which is much more complex and varied than that in natural mines; this leads to the recovery processes of valuable metals being carried out in more stages for the efficient and environmentally friendly processing of WEEE (Duan *et al*., 2012).

As minerals are non-renewable resources and WEEE is an important secondary source for obtaining metals, some researchers are currently attempting to recover metals through hydrometallurgical processes. The first step of hydrometallurgical processes consists of extracting metals from the leaching solution in an acidic or alkaline medium, and the second step consists of purifying the solution (Marsden & House, 2006).

Due to the chemical and physical properties of platinum-group metals (PGMs), substitution by other metals is difficult. The need for PGMs is increasing with the development of industry, and minerals that contain PGMs are rare. There are only 70 thousand tons of PGM proven reserves around the world; they are mainly concentrated in South Africa, Russia, Zimbabwe, and the United States, which make up 89.9%, 5.6%, 1.7%, and 1.3% of the world's PGM reserves, respectively (Wang *et al*., 2021; Wang *et al*., 2023). This is why the recovery of PGMs through the recycling of WEEE is important. In the hydrometallurgical treatment of these wastes, PGMs are leached together with other metals using chloride-based solutions (Sun & Lee, 2011).

Since the wastes from electrical and electronic devices are multi-metallic materials, meaning that the solutions from leaching would not only contain palladium and platinum but also other metals such as gold, silver, copper, lead, and aluminum, there is a necessity for a process in which the metal or metals of interest can be separated from the solutions. Chemical precipitation is a conventional method widely used due to its cost-effectiveness and simplicity. The greatest disadvantages of this process are the high consumption of chemical products and slow kinetics, in addition to the fact that solid–liquid separation must be carried out. It is necessary to develop more environmentally friendly hydrometallurgical techniques to replace conventional chemical precipitation (Zheng *et al*., 2021). Solvent extraction has been extensively applied for the separation and purification of palladium (Rane, 2019); for this reason, various researchers have carried out research on the concentration and purification of leaching solutions from WEEE or catalysts through the solvent extraction process (Faye & Inman, 1963; Nguyen *et al*., 2015; Swain *et al*., 2010).

Solvent extraction is a process that makes it possible to selectively and efficiently transfer the ionic species of interest present from an aqueous phase to an organic phase. The aqueous phase is the solution from leaching; meanwhile, the organic phase contains the extractant, which, in this research, was used as a tertiary amine in a diluent (Aguayo *et al*., 2007). The extractant is responsible for selectively extracting the metal of interest. Tertiary amines are among the extractants that have been used in recent years for the extraction of platinum and palladium from chlorinated solutions (Nguyen *et al*., 2015; Tang *et al*., 2021). Tertiary amines can act as a kinetic accelerator, reducing equilibrium times to minutes, but no information has been published on the effect of the amines on selectivity of palladium–platinum separation (Kislik, 2011).

Different investigations have been carried out on the purification of palladium or platinum from chlorinated synthetic solutions via solvent extraction with different extractants based on amines (Alguacil *et al*., 1997; Islam *et al*., 2022; Lee *et al*., 2009; Lee *et al*., 2010; Tang *et al*., 2021), oximes (Jackson, 1998; Rane & Venugopal, 2006), triphosphoric acid (Rovira *et al*., 1999), phosphonic acid (Bandekar & Dhadke, 1998), thiourea (Uheida *et al*., 2002), phosphonium (Jin *et al*., 2021), and N-methyl-N-isopropyl octanthioamide (Wang *et al*., 2023). Most investigations are mainly based on leaching solutions from spent automobile catalysts (Barakat *et al*., 2006) and, as platinum is the metal to be separated from palladium, they are based mainly on platinum. However, waste electronic cards also contain other basic and precious metals, then selective leaching is required primarily due to the high concentration of base metals (Martinez-Ballesteros *et al*., 2021; Segura-Bailón & Lapidus-Lavine, 2023); therefore, in the purification of leaching solutions for this type of material, other metals such as gold and silver must be considered.

Figure 1 shows a diagram of the process to which waste electronic cards can be subjected to recycle the metals. First, the epoxy material is removed by means of a solution of 10 M sodium hydroxide. Once the particle size is obtained, the first stage is to subject the material to pressure leaching with sulfuric acid to pass the base metals into a solution (Martinez-Ballesteros *et al*., 2023). The solid waste is subjected to a second stage of pressure leaching with hydrochloric acid and sodium hypochlorite for the dissolution of precious

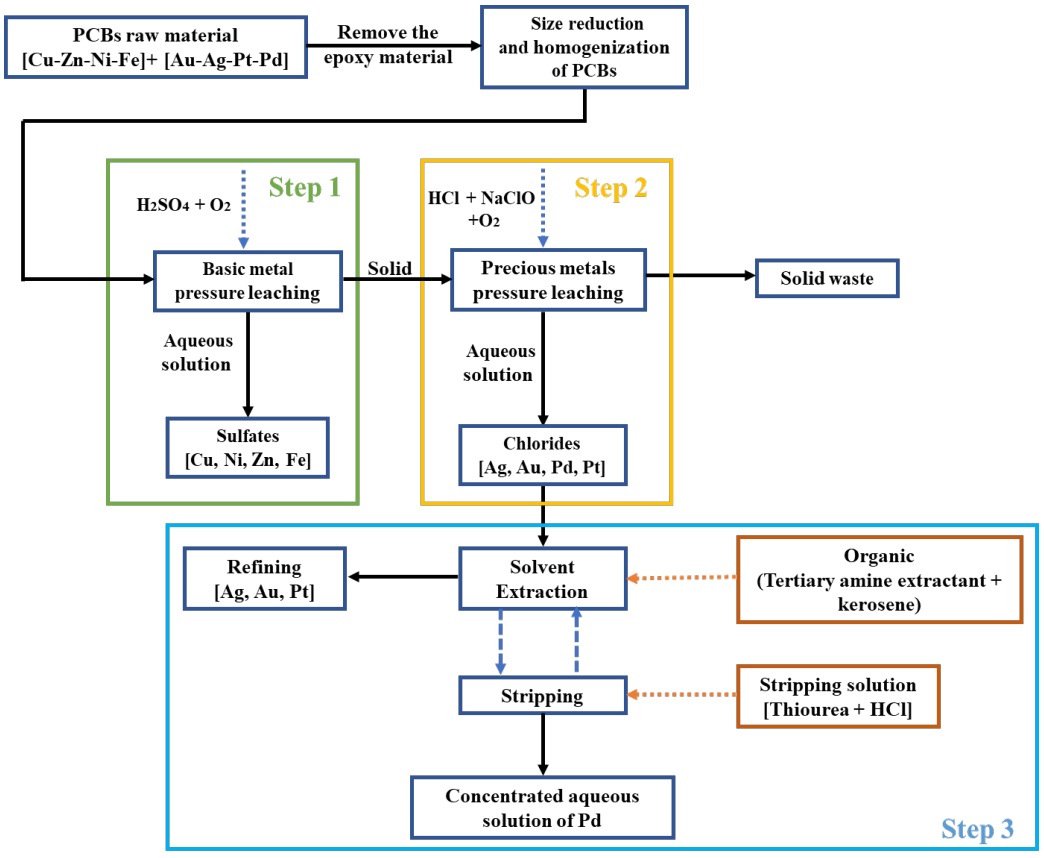

Figure 1. Diagram of metal recycling process for waste electronic cards.

metals (Martinez-Ballesteros *et al*., 2021).

In the present research, the solvent extraction process was used for the aqueous separation of palladium from leach solutions (Step 3 of Figure 1), using a tertiary amine as an extractant, and kerosene as a diluent. The aqueous:organic (AQ:ORG) phase ratio, the concentration of the extractant in the diluent, and the pH of the leaching solution were varied to determine the best conditions for the separation of palladium from the other metal ions present in the solution. In addition, the McCabe-Thiele diagrams were built to determine the number of steps required the extraction process. The effects of the thiourea ($CS(NH_2)_2$) concentration in the stripping solution and the phase ratio were also studied to determine the best conditions for the stripping step and regenerate the amine extractant.

2 Methodology

The solution obtained from the leaching, which contained platinum and palladium (Table 1), was concentrated using the solvent extraction process and separation funnels, in which the leaching solution (aqueous phase) and the solvent (organic phase) were added, followed by manual stirring for 3 minutes. Finally, it was left to rest so that the phases could separate, thus allowing for the aqueous solution to be removed from the organic phase; a tertiary amine (R_3NH) was used as an extractant. To carry out the stripping of the organic phase, thiourea and hydrochloric acid (0.5 M) were mixed in a solution and stirred for five minutes. In the extraction stage, the concentrations of the extractant in the organic phase (8, 10, and 12 % v/v), the pH of the leaching solution (0.1, 0.5, 1, 1.5, and 2), and the ratio of the aqueous–organic phases (AQ:ORG) (0.8:1, 1:1, and 1.2:1) were varied; each test was performed in triplicate. In the stripping stage, the AQ:ORG phase ratio (2:1, 5:1, and 10:1) and the thiourea concentration (0.1, 0.3, 0.5, 0.8, and 1 M) were varied; each test was performed in triplicate.

The extraction reaction for palladium and platinum chloride ions using tertiary amine extractant is as follows (Eq. 1 and Eq. 2) (Ritcey & Ashbrook, 1984):

$$PdCl_{6AQ}^{2-} + 2R_3NH^+Cl_{ORG}^- \rightarrow (R_3NH)_2(PdCl_6^{2-})_{ORG} + 2Cl_{AQ}^- \quad (1)$$

$$PtCl_{6AQ}^{2-} + 2R_3NH^+Cl_{ORG}^- \rightarrow (R_3NH)_2(PtCl_6^{2-})_{ORG} + 2Cl_{AQ}^- \quad (2)$$

Additionally, when thiourea was used the stripping

reactions for palladium and platinum can be represented as follows (Eq. 3 and Eq. 4) (Calla-Choque & Nava-Alonso, 2020; Sun & Lee, 2011):

$$(R_3NH)_2(PdCl_6^{2-})_{ORG} + 2(NH_2)_2CS_{AQ} \rightarrow PdCl_4((NH_2)_2CS)_{2AQ} + 2R_3NH^+Cl^-_{ORG} \quad (3)$$

$$(R_3NH)_2(PtCl_6^{2-})_{ORG} + 2(NH_2)_2CS_{AQ} \rightarrow PtCl_4((NH_2)_2CS)_{2AQ} + 2R_3NH^+Cl^-_{ORG} \quad (4)$$

To determine the isotherm equilibrium for the construction of McCabe–Thiele diagrams for both the extraction and stripping stages, the AQ:ORG ratio was varied (10:1, 5:1, 2:1, 1:1, 1:2, 1:5, and 1:10). For the stripping stage, the concentration of thiourea that resulted in the highest stripping percentage was used. The metal ions concentration in the aqueous phase was determined by the atomic absorption spectroscopy technique (Perkin Elmer model AAnalyst 400 atomic absorption equipment, PerkinElmer Inc, Waltham, MA, USA), and the metal ions concentration in the organic phase was determined using a mass balance with Equation 5:

$$V_{AQ}([M]_i - [M]_f)_{AQ} = V_{ORG}([M]_f - [M]_i)_{ORG} \quad (5)$$

where V_{AQ} is the volume of the aqueous solution, V_{ORG} is the volume of the organic solution, $[M]_i$ is the concentration of the metal at the start of the reaction, $[M]_f$ is the concentration of the metal at the end of the reaction, AQ is the aqueous phase, and ORG is the organic phase. The pH of the aqueous solution was varied by sodium hydroxide.

Table 1. Concentration of metals in the aqueous phase.

Metals	Ag	Au	Pd	Pt
Concentration (mg/L)	10	10	1	3

3 Results and discussion

3.1 Palladium extraction mechanism

Figure 2 shows the metal extraction kinetics. After 1 minute, the extraction of gold and silver remained constant, with extraction percentages greater than 80% for $AgCl_3^{2-}$ and 98% for $AuCl_4^-$. Meanwhile, the extraction of platinum ions remained constant after 2 minutes, achieving an extraction percentage greater than 95%, and palladium ions achieved equilibrium after 2.5 minutes, obtaining an extraction percentage greater than 98%. Then 3 minutes equilibrium time was considered for all experiments in extraction.

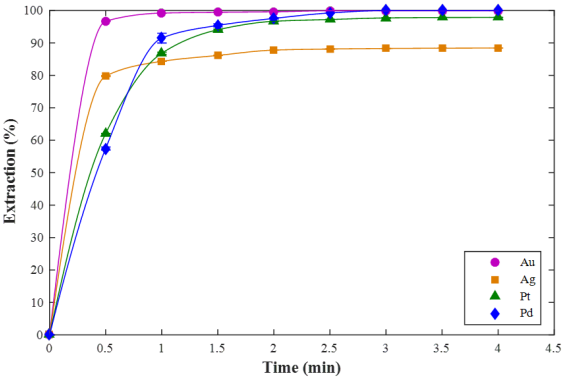

Figure 2. Metal extraction kinetics using 12% extractant v/v at an AQ:ORG phase ratio of 1.2 and pH of 0.1.

3.2 Metals extraction vs. pH

Based on the Eq. 1 the equilibrium constant can be described as a function of concentrations as:

$$K = \frac{[(R_3NH)_2M]_{ORG}[H^+]_{AQ}}{[(R_3NH)_2]_{ORG}[H_2O][M]_{AQ}} \quad (6)$$

and defining $M = PdCl_6^{-2}$. The equilibrium constant for H_2O is:

$$K_{H_2O} = \frac{[H^+][OH^-]}{[H_2O]} \quad (7)$$

by taking $[H^+]$ from Eq. 7 and substituting in Eq. 6:

$$K = \frac{[(R_3NH)_2M]_{ORG}K_{H_2O}}{[(R_3NH)_2]_{ORG}[H^+][M]_{AQ}} \quad (8)$$

and considering the distribution coefficient D:

$$D = \frac{[M]_{ORG}}{[M]_{AQ}} = \frac{[(R_3NH)_2M]_{ORG}}{[M]_{AQ}} \quad (9)$$

Dependence of the distribution coefficient and operation parameters can be described by the following equation

$$\log D = \log K' - pH + \log[(R_3NH)_2]_{ORG} \quad (10)$$

Defining P as the percentage of extraction:

$$D = \frac{P}{100 - P} \quad (11)$$

substituting Eq. (11) into Eq. (10):

$$\log P - \log(100 - P) = \log K' - pH + \log[(R_3NH)_2]_{ORG} \quad (12)$$

Sigmoid curves will be obtained when plotting the extraction (%) vs. pH. The position of each curve on the pH axis will depend only on the equilibrium constant K' and the concentration of the extractant.

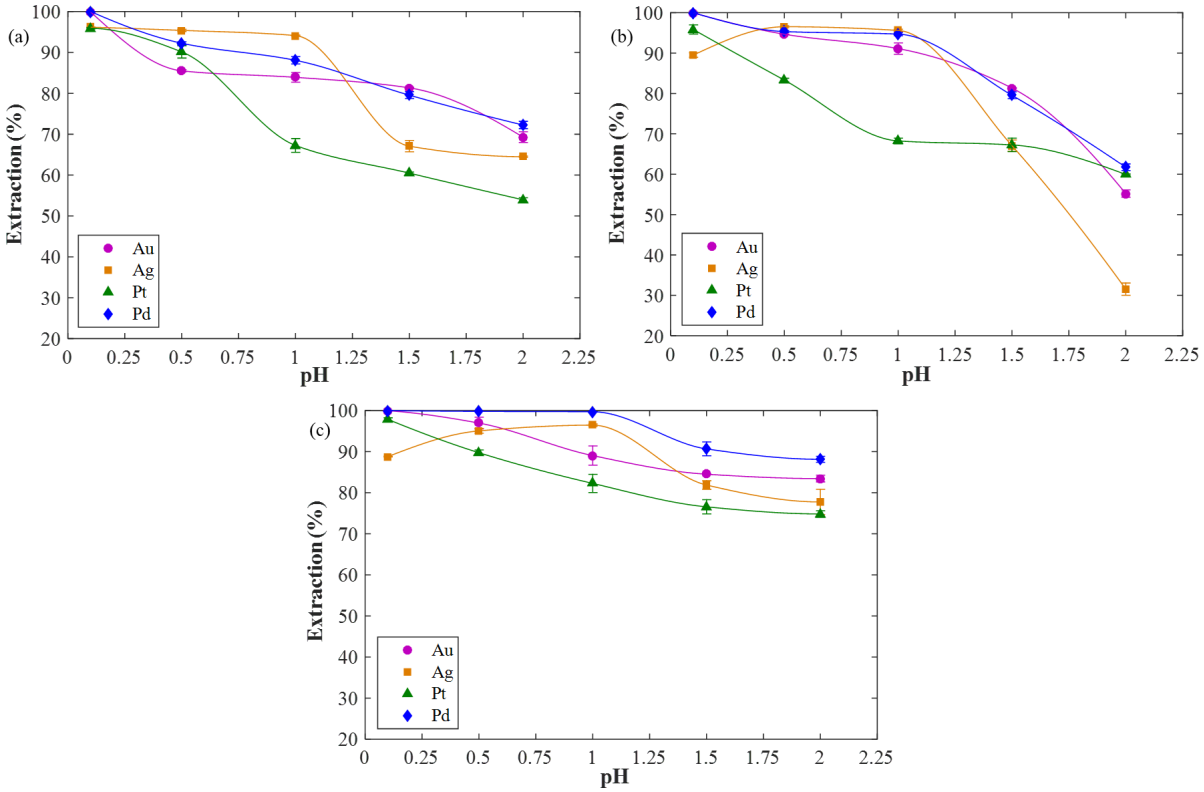

Figure 3. Extraction of metals (%) as a function of pH using 8% extractant v/v. (a) AQ:ORG = 0.8, (b) AQ:ORG = 1, and (c) AQ:ORG = 1.2.

Figures 3, 4, and 5 illustrate the effect of pH in the extraction of various metals from the aqueous solution when the concentration of the extractant in the organic phase is varied. Figure 3 shows the extraction percentage of different metals as a function of pH and different AQ:ORG ratios (0.8:1, 1:1, and 1.2:1) with 8% extractant v/v and 3 minutes of stirring. Figure 3(a) presents the extraction percentage at AQ:ORG ratio of 0.8, indicating that, as the pH increases, the extraction percentage of all metal ion decreases, with platinum having the lowest extraction percentage, less than 60%, at a pH of 2. Figure 3(b) displays the extraction graph for an AQ:ORG ratio of 1, showing that the extraction percentage decreases, with increases pH, with silver having the lowest extraction percentage, less than 35%, at a pH of 2. Figure 3(c) illustrates the extraction percentage at an AQ:ORG ratio of 1.2 where the extraction percentage of palladium remains above 98% at low pH but decreases below 90% when the pH exceeds 1. The best results are obtained using an 8% v/v extractant concentration at an AQ:ORG ratio of 1.2 and a pH of 0.1, achieving extraction percentages greater than 98% for $PdCl_6^-$, 98% for $AuCl_4^-$, 95% for $PtCl_6^-$ and less than 90% for $AgCl_3^{-2}$

Figure 4 shows the extraction percentages of different metal ions in the solution as a function of pH, using various AQ:ORG ratios (0.8:1, 1:1, and 1.2:1) with 10% extractant (v/v) and 3 minutes of stirring. Figure 4(a) shows the extraction results with an AQ ratio of 0.8. The extraction percentage of palladium ions remains above 95% at pH levels below 1.5. However, the extraction percentages of other metal ions decrease as the pH increases. Figure 4(b) presents the extraction percentages with an AQ:ORG ratio of 1. The extraction percentage of palladium ions stays above 95% across different pH values. Conversely, the extraction percentages of gold and platinum ions decrease as the pH increases. Figure 4(c) depicts the extraction results with an AQ:ORG ratio of 1.2. The extraction percentage of palladium ions remains greater than 90% across the various pH values used in this study. However, the extraction percentage of platinum ions decreases with increasing pH. The best results are obtained with a 10% v/v concentration at an AQ:ORG ratio of 1 and a pH of 1.5. Under these conditions, extraction percentages exceed 98% for both $PdCl_6^-$ and $AuCl_4^-$, while extraction percentages are less than 85% for $AgCl_3^{-2}$ and 75% for $PtCl_6^{-2}$.

Figure 5 illustrates the extraction percentages of different metal ions in the solution as a function of pH, using various AQ:ORG ratios (0.8:1, 1:1, and 1.2:1) with 12% extractant v/v. Figure 5(a) shows the extraction plot with an AQ:ORG phase ratio of 0.8, indicating that the extraction percentage of platinum ions decreases as the pH increases. Figure 5(b) presents the extraction isotherms for an AQ:ORG

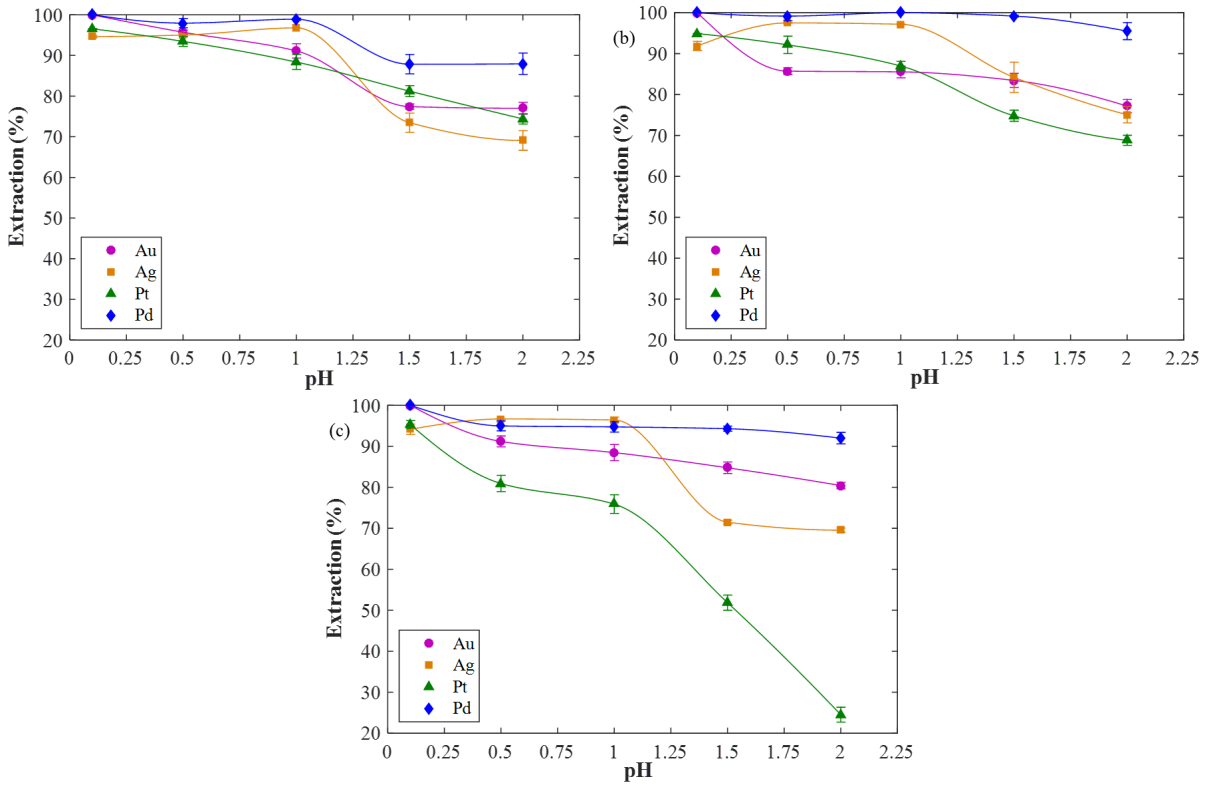

Figure 4. Extraction of metals (%) as a function of pH using 10% extractant v/v. (a) AQ:ORG = 0.8, (b) AQ:ORG = 1, and (c) AQ:ORG = 1.2.

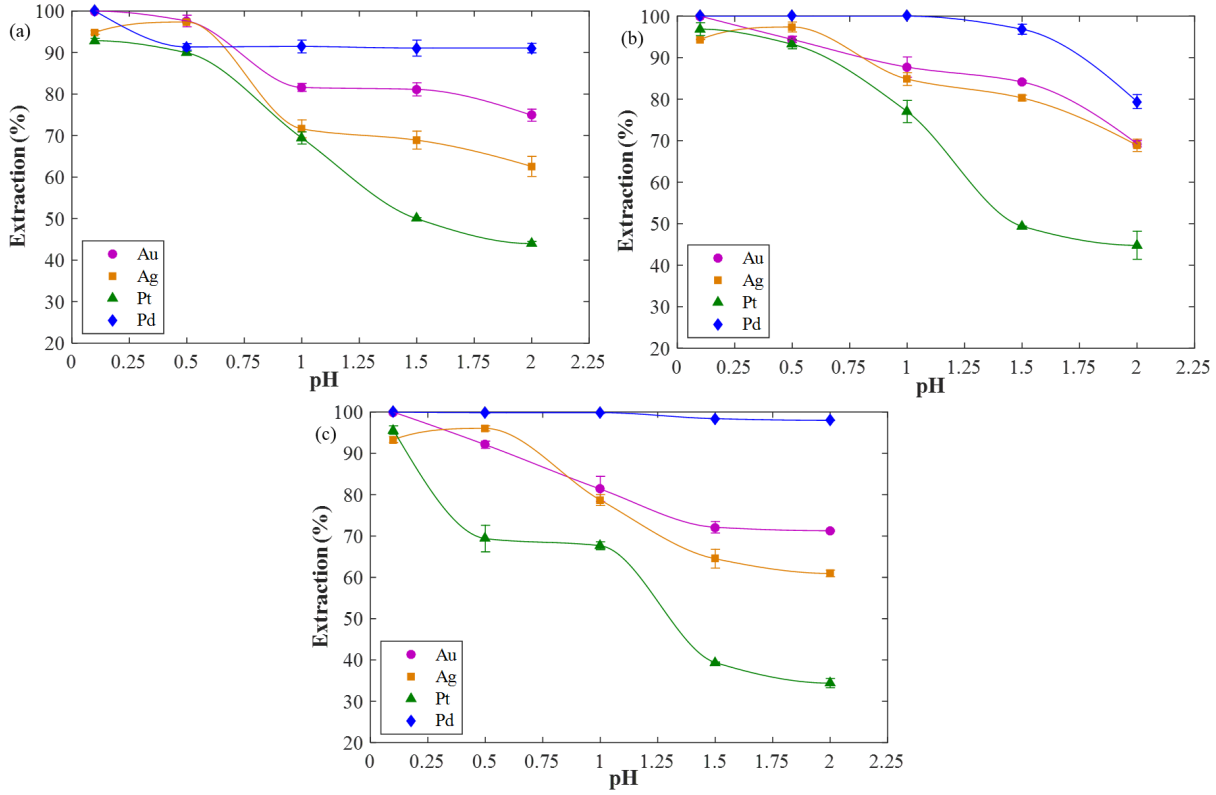

Figure 5. Extraction of metals (%) as a function of pH using 12% extractant v/v. (a) AQ:ORG = 0.8, (b) AQ:ORG = 1, and (c) AQ:ORG = 1.2.

ratio of 1, demonstrating that the extraction percentage of palladium ions remains above 95% at pH levels below 2, while the extraction percentage of platinum ions decreases with increasing pH. Figure 5(c) displays the extraction plot with an AQ:ORG ratio of 1.2, revealing that the extraction percentage of palladium ions stays above 98% at all pH levels tested, whereas other metal ions show varying extraction percentages depending on the pH. The best results are obtained using a 12% v/v extractant concentration at an AQ:ORG ratio of 1.2 and a pH of 2. Under these conditions, the extraction percentages are greater than 98% for $PdCl_6^-$, less than 68% for $AuCl_3^{-2}$, 75% for $AuCl_4^-$ and 40% for $PtCl_6^{-2}$.

In the previous graphs, it can be determined that the best conditions for carrying out the extraction of palladium ions are as follows: an AQ:ORG ratio of 1.2, a pH of 1.5, and a 12% extractant concentration v/v. Under these conditions, an extraction percentage greater than 98% is obtained for palladium ions, while extraction percentages below 80% are obtained for the other metal ions.

Platinum and silver ions may face stronger competition from other metal ions, leading to decreased extraction efficiency for these specific ions (Radzyminska-Lenarcik *et al*., 2021). Tertiary amines can extract more than 95% of platinum and palladium ions in a chloride medium under various conditions, as observed in the study by Swain *et al*. (2010). Therefore, a selective extraction process would be necessary for each of these metals (Swain *et al*., 2010).

As shown in the graphs above, gold extraction exceeds 98% when a pH of 0.1 is applied, regardless of the extractant percentage or ratio. This aligns with the findings of Doidge *et al*. (2019), who demonstrated that a tertiary amine can effectively extract gold in a chloride medium (Doidge *et al*., 2019).

3.3 *Extraction isotherms*

Once the solution contents are known, judgments about which metals can be separated should be made based on the extraction isotherms available. In this research it was used tertiary amine extractant (R_3NH) diluted in kerosene for palladium extraction.

Figure 6 shows the extraction isotherms at different extractant concentrations for the extraction of palladium from chloride solutions. The best results are obtained using a 12% v/v extractant concentration. This concentration increases both the organic loading capacity and the extraction efficiency for palladium. Isotherms serve as the foundational elements for a McCabe–Thiele analysis, which is used to design and evaluate extraction circuits.

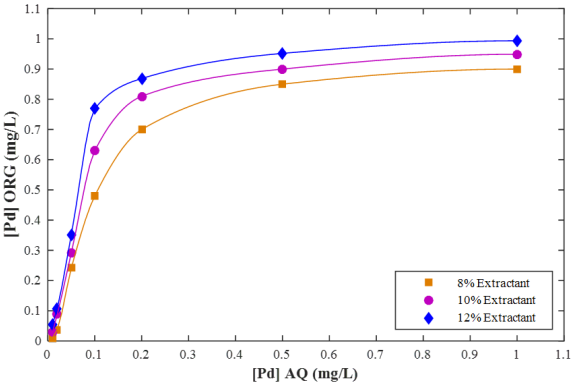

Figure 6. Effect of extractant concentration on palladium extraction isotherm.

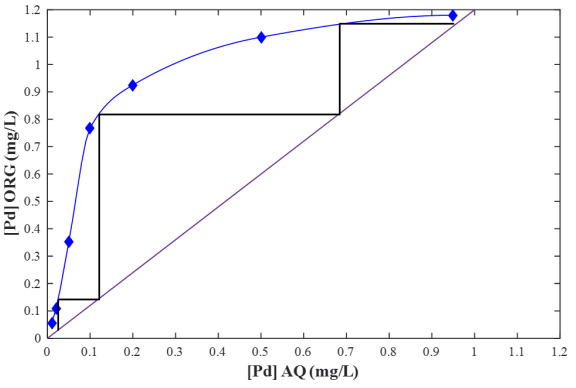

Figure 7. McCabe–Thiele diagram using 12% extractant v/v, a pH of 1.5, and a phase ratio of 1.2.

Using the isotherms obtained from batch experiments and working with an AQ:ORG ratio of 1:1.2 as the operating line, the effect of different extractant concentrations on the number of extraction stages can be analyzed through a McCabe–Thiele analysis. This information is then used to construct a typical McCabe–Thiele diagram. As shown in Figure 7, three theoretical stages are necessary to extract palladium ions. These data provide a reference for scaling up to a continuous system, which would determine the actual number of steps required.

3.4 *Selectivity of tertiary amine*

To calculate the Distribution Coefficients and the Selectivity for metal chlorides, we used aqueous solution containing Pd, Pt, Au, and Ag chlorides and, for the organic solvent it was used 12% extractant v/v, a phase ratio of 1.2:1. The distribution coefficients were calculated using the Equation 13.

$$D_M = \frac{[M]_{ORG}}{[M]_{AQ}} \tag{13}$$

Where D_M is the distribution coefficient of metal, $[M]_{ORG}$ concentration of the metal in the organic phase, and $[M]_{AQ}$ is the concentration of the metal in the aqueous phase.

Table 2. Extraction distribution coefficients and selectivity.

Metal	$[M]_{AQ}$ (mg/L)	$[M]_{ORG}$ (mg/L)	D_M	S_M^{Pd}
Pd	0.016	1.18	73.8	1
Pt	1.82	1.42	0.78	94.86
Au	2.79	8.65	3.10	23.8
Ag	3.55	7.74	2.18	33.85

The selectivity factors (S_M^{Pd}) for these metals chlorides using the Equation 14.

$$S_M^{Pd} = Selectivity = \frac{D_{Pd}}{D_M} \tag{14}$$

where D_{Pd} is the distribution coefficients of palladium, D_M is the coefficient of metal distribution that is compared to palladium. From these calculations, Table 2 summarizes the distribution coefficients.

The extractant exhibited the selectivity order as follows:

Pd > Au > Ag >Pt

Tertiary amines are commonly used in the extraction of palladium due to their ability to form stable complexes with metal ions. The extraction process operates through a mechanism known as ion pair formation. In this process, tertiary amines interact with palladium ions (Pd^{2+}). The positively charged palladium ions are attracted to the lone pair of electrons on the nitrogen atom of the amine, forming a coordination complex (Kislik, 2011).

The hydrophobic nature of the alkyl chain can influence the solubility and partitioning behavior of the amine compound in aqueous and organic phases. This can be applied in solvent extraction processes for the selective recovery of metal ions. The alkyl chain in a tertiary amine can significantly influence its solubility in solvents such as kerosene. This is because the physical and chemical properties of the alkyl chain affect amine's affinity for kerosene and its ability to dissolve in this solvent (Ritcey & Ashbrook, 1984).

The AQ:ORG ratio and pH significantly impacted platinum ion extraction. At an AQ:ORG ratio of 1.2 and a pH of 2, the extraction percentage was less than 50% across all extractant concentrations in the organic phase. A contact time of three minutes of stirring was sufficient for the extraction process, as equilibrium was reached for platinum and palladium within this time, while gold and silver reached equilibrium after just one minute of stirring.

The AQ:ORG phase ratio and pH did not significantly affect palladium ion extraction, as the extraction percentage remained greater than 90% at all ratios and pH levels. However, these parameters did impact the other chloride ions in the solution, benefiting the purification of palladium by keeping ions such as $AgCl_3^{2-}$, $AuCl_4^-$, and $PtCl_6^{2-}$ in the aqueous phase. Therefore, the phase ratio can be adjusted for selective palladium extraction.

Tertiary amines can effectively interact with positively charged metal ions through ion pairing interactions, facilitating their extraction into the organic phase. The amine acts as a counterion to balance the charge of the metal ion, thereby enhancing its solubility in the organic phase. At higher HCl concentrations, acidic conditions suppress the hydrolysis of metal ions, which would otherwise compete with complexation reactions. This suppression allows for more efficient complexation of metal ions by the tertiary amine (Swain *et al*., 2010).

The size and shape of the alkyl chain can influence the accessibility of the amine group to the metal ions. Larger alkyl chains may hinder the approach of certain metal ions while allowing others to interact more readily. The alkyl chain can act as a spacer, positioning the amine group at an optimal distance for chelation with specific metal ions. Chelation enhances the selectivity of metal ion binding by providing multiple points of attachment (Ritcey & Ashbrook, 1984).

Based on the extraction isotherms, a higher loading capacity was achieved using an extractant concentration of 12%. With this information, a McCabe–Thiele diagram was constructed, determining that three theoretical stages were required for effective extraction.

3.5 *Stripping*

Figure 8 shows the kinetics of metal stripping. After 3 minutes, the stripping percentage of gold remained constant, reaching above 98%. In contrast, the other chlorides studied achieved equilibrium after 5 minutes, with stripping percentages also exceeding 98%. This equilibrium time was used for all subsequent re-extraction experiments.

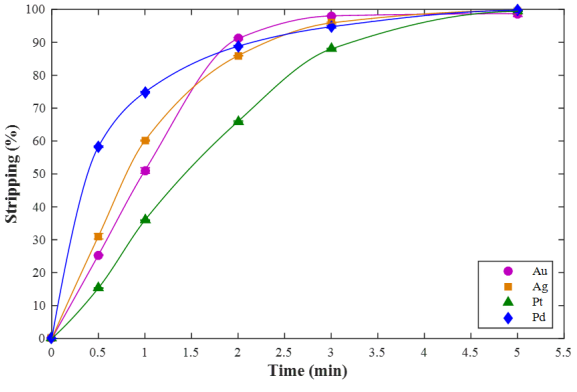

Figure 8. Metal stripping kinetics using 1 M thiourea and AQ:ORG phase ratio of 2.

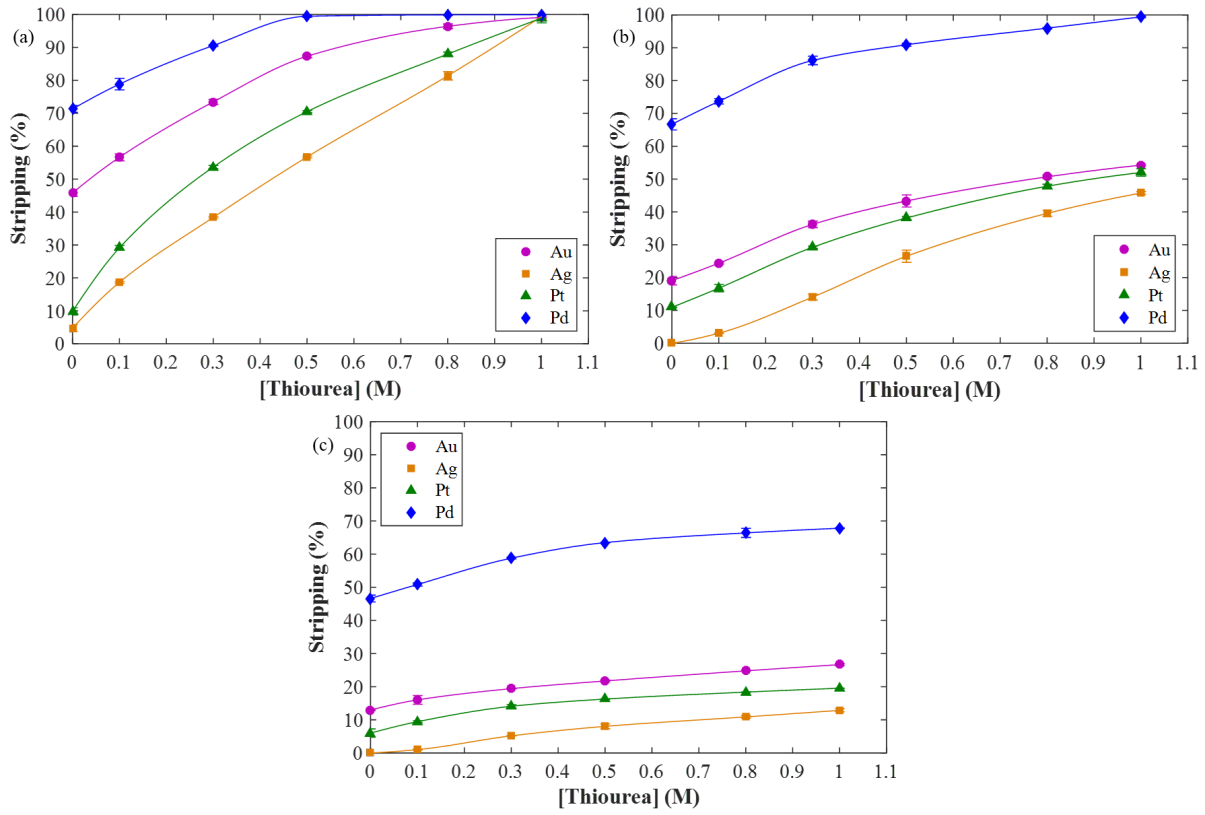

Figure 9. Metal stripping (%) as a function of thiourea concentration. (a) AQ:ORG = 2, (b) AQ:ORG = 5, and (c) AQ:ORG = 10.

Figure 9 illustrate the effect of varying thiourea ($CS(NH_2)_2$) concentrations on the stripping of different metals from the organic phase after 5 minutes of stirring. Figure 9(a) shows the extraction of isotherms when using an AQ:ORG ratio of 2:1, in which, as the thiourea concentrations higher, the stripping percentage increases, obtaining re-extraction percentages greater than 95% when a 1 M thiourea was used. Figure 9(b) presents the stripping graph when an AQ:ORG ratio of 5:1 is used, it demonstrated that higher thiourea concentrations lead to increased, stripping percentage, with re-extraction percentages exceeded 95% for $PdCl_6^{2-}$ while less than 60% is obtained for other chloride ions. Figure 9(c) depicts the stripping results when an AQ:ORG ratio of 10:1 is used, this graph shows that, as the thiourea concentration increases the stripping percentage for palladium exceeds 60%, whereas the stripping percentage for other chloride while, for the other chloride ions present remain below 30%. In this research the best results are obtained when an AQ:ORG ratio of 5 and a concentration of 1 M thiourea are used, under these conditions, stripping percentages greater than 98% for $PdCl_6^{2-}$, 51 % for $PtCl_6^{2-}$, 53% for $AuCl_4^-$, and 44% for $AgCl_3^{2-}$ were obtained.

The contact time for the stripping stage was found to be five minutes, achieving a stripping percentage of over 95% for the chloride ions in the organic phase. Since the extractant in the extraction stage removed other chloride ions, selective stripping was possible.

This research also discusses the stripping stage. Varying the concentration of thiourea can facilitate selective stripping, as noted by other authors. The use of a mixture of HCl and thiourea significantly enhances the stripping power. In a study by Sun *et al.* (2011), most of the palladium was stripped from the loaded tertiary amines using 0.5 M HCl and 0.1 M thiourea. Under these conditions, the stripping percentage of platinum was below 20% (Sun & Lee, 2011).

For stripping gold, silver, and platinum, an AQ:ORG ratio of 2:1 and a 1 M thiourea were used. Under these conditions, a stripping percentage greater than 97% was obtained for these ions.

Conclusion

Tertiary amines are effective in extracting metal ions at higher HCl concentrations due to their ability to form stable complexes with metal ions, interact efficiently with positively charged species, suppress hydrolysis reactions, and maintain complex stability in acidic environments.

The extraction of the leaching solution from waste electronic cards using a tertiary amine resulted in the selective extraction of palladium. The raffinate contained chlorides of silver, gold, palladium and platinum. The tertiary amine effectively extracted most of the palladium from a hydrochloric acid solution, achieving an extraction efficiency of over 98%. Subsequently, most of the palladium was separated from the loaded organic phase using thiourea as the stripping reagent. From this experimentation, it was possible to establish the best conditions for palladium extraction, reaching an efficiency of more than 98%.

The extraction of free palladium raffinate with a tertiary amine resulted in the coextraction of silver, gold, and platinum. Due to the similar extraction behavior of these metals by the tertiary amine, selective stripping was attempted using thiourea. Selective extraction was achievable because the extractant also removed other chloride ions during the extraction stage. In this research, the best conditions for palladium stripping were established, achieving more than 98% extraction at this stage.

This research demonstrated the feasibility of palladium extraction from the leachate of waste electronic cards. Furthermore, selective stripping and regeneration of the organic extractant were successfully achieved. To enhance the recovery of other metals, such as gold, silver, and platinum from the chloride solution, it is crucial to investigate the chemical reactions and explore alternative solvent extraction reagents. Additionally, varying the concentration of thiourea and incorporating other reagents should be explored for more effective stripping. Future studies should focus on analyzing the process in a continuous system to establish a complete workflow for extraction and re-extraction.

A process flow diagram was proposed to treat hydrochloric acid leaching solutions from waste electronic cards, which mainly contain silver, gold, platinum, and palladium. A McCabe-Thiele diagram was developed to determine the number of stages required for the solvent extraction process.

Acknowledgements

Thanks to the Chemical Engineering and Metallurgy Department of the University of Sonora, LANGEM, National Laboratory of Geochemistry and Mineralogy in México and CONAHCYT (National Council of Humanities, Science and Technology) for the postdoctoral scholarship for one author (G.M.B.).

References

Aguayo, S., Valenzuela, J. L., Parga, J. R., Lewis, R. G. & Cruz, M. (2007). Continuous laboratory gold solvent extraction from cyanide solutions using LIX 79 reagent. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, *30*(11), 1532-1536.

Alguacil, F. J., Cobo, A., Coedo, A. G., Dorado, M. T. & Sastre, A. (1997). Extraction of platinum (IV) from hydrochloric acid solutions by amine alamine 304 in xylene. Estimation of the interaction coefficient between $PtCl_6^{2-}$ and H^+. *Hydrometallurgy*, *44*(1-2), 203-212.

Bandekar, S. V. & Dhadke, P. M. (1998). Solvent extraction separation of platinum (IV) and palladium (II) by 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A). *separation and purification Technology*, *13*(2), 129-135.

Barakat, M. A., Mahmoud, M. H. H. & Mahrous, Y. S. (2006). Recovery and separation of palladium from spent catalyst. *Applied Catalysis A: General*, *301*(2), 182-186.

Calla-Choque, D. & Nava-Alonso, F. (2020). Thiourea determination for the precious metals leaching process by iodate titration. *Revista Mexicana de Ingeniería Química*, *19*(1), 275-284.

Doidge, E. D., Kinsman, L. M. M., Ji, Y., Carson, I., Duffy, A. J., Kordas, I. A., Shao, E., Tasker, P. A., Ngwenya, B. T. & Morrison, C. A. (2019). Evaluation of simple amides in the selective recovery of gold from secondary sources by solvent extraction. *ACS Sustainable Chemistry & Engineering*, *7*(17), 15019-15029.

Duan, H., Li, J., Liu, Y., Yamazaki, N. & Jiang, W. (2012). Characterizing the emission of chlorinated/brominated dibenzo-p-dioxins and furans from low-temperature thermal processing of waste printed circuit board. *Environmental pollution*, *161*, 185-191.

Faye, G. H. & Inman, W. R. (1963). A Scheme for the Separation of Platinum, Palladium, Rhodium, and Iridium by Solvent Extraction. *Analytical Chemistry*, *35*(8), 985-988.

Fontana, D., Pietrantonio, M., Pucciarmati, S., Torelli, G. N., Bonomi, C. & Masi, F. (2018). Palladium recovery from monolithic ceramic capacitors by leaching, solvent extraction and reduction. *Journal of Material Cycles and Waste Management*, *20*, 1199-1206.

Forti, V., Balde, C. P., Kuehr, R. & Bel, G. (2020). The Global E-waste Monitor 2020: Quantities, flows and the circular economy potential.

Islam, A., Roy, S., Teo, S. H., Khandaker, S., Taufiq-Yap, Y. H., Abd Aziz, A., Monir, M. U., Rashid, U., Vo, D.-V. N. & Ibrahim, M. L. (2022). Functional novel ligand based palladium (II) separation and recovery from e-waste using solvent-ligand approach. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *632*, 127767.

Jackson, E. (1998). The solvent extraction behaviour of platinum (II) with P-50 oxime in aqueous chloride solutions. *Minerals engineering*, *11*(7), 651-656.

Jin, C., Chen, M., Fan, M., Luo, G., Shao, M., Huang, Z. & Xie, X. (2021). Hydrophobic phosphonium-based ionic liquids as novel extractants for palladium (II) recovery from alkaline cyanide solutions. *Journal of Molecular Liquids*, *336*, 116358.

Kislik, V. S. (2011). *Solvent extraction: classical and novel approaches*. Elsevier.

Lee, J.-Y., Kumar, J. R., Kim, J.-S., Kim, D.-J. & Yoon, H.-S. (2009). Extraction and separation of Pt (IV)/Rh (III) from acidic chloride solutions using Aliquat 336. *Journal of Industrial and Engineering Chemistry*, *15*(3), 359-364.

Lee, J. Y., Raju, B., Kumar, B. N., Kumar, J. R., Park, H. K. & Reddy, B. R. (2010). Solvent extraction separation and recovery of palladium and platinum from chloride leach liquors of spent automobile catalyst. *Separation and Purification Technology*, *73*(2), 213-218.

Marsden, J. & House, I. (2006). *The chemistry of gold extraction*. SME.

Martinez-Ballesteros, G., Valenzuela-Garcia, J. L., Gomez-Alvarez, A., Encinas-Romero, M. A., Mejia-Zamudio, F. A. & Rosas-Durazo, A. d. J. (2023). Base Metals Extraction from Printed Circuit Boards by Pressure Acid Leaching. *Minerals*, *13*(1), 98.

Martinez-Ballesteros, G., Valenzuela-García, J. L., Gómez-Alvarez, A., Encinas-Romero, M. A., Mejía-Zamudio, F. A., Rosas-Durazo, A. d. J. & Valenzuela-Frisby, R. (2021). Recovery of Ag, Au, and Pt from printed circuit boards by pressure leaching. *Recycling*, *6*(4), 67.

Nguyen, T. H., Sonu, C. H. & Lee, M. S. (2015). Separation of platinum (IV) and palladium (II) from concentrated hydrochloric acid solutions by mixtures of amines with neutral extractants. *Journal of Industrial and Engineering Chemistry*, *32*, 238-245.

Radzyminska-Lenarcik, E., Pyszka, I. & Kosciuszko, A. (2021). Separation and recovery of Gold (III), Palladium (II) and Platinum (IV) by solvent extraction using a new β-Diketone derivative from Acidic solutions. *Materials*, *14*(16), 4436.

Rane, M. V. (2019). PGM ore processing: LIX reagents for palladium extraction & platinum stripping from Alamine 336 using NaOH-NaCl. *Minerals Engineering*, *138*, 119-124.

Rane, M. V. & Venugopal, V. (2006). Study on the extraction of palladium (II) and platinum (IV) using LIX 84I. *Hydrometallurgy*, *84*(1-2), 54-59.

Ritcey, G. M. & Ashbrook, A. W. (1984). *Solvent Extraction: Principles and Applications to Process Metallurgy. Vol. 1*. Elsevier.

Rovira, M., Cortina, J. L. & Sastre, A. M. (1999). Selective liquid-liquid extraction of palladium (II) from hydrochloric acid media by di-(2-ethylhexyl) thiophosphoric acid (DEHTPA). *Solvent extraction and ion exchange*, *17*(2), 333-349.

Segura-Bailón, B. & Lapidus-Lavine, G. (2023). Importance of chemical pretreatment for base metals remotion and its effect on the selective extraction of gold from Printed Circuits Boards (PCBs) Importancia del pretratamiento químico para la remoción de metales base y su efecto en la extracción selectiva de oro de tarjetas de circuito impreso (PCBs). *Revista Mexicana de Ingeniería Química*, *22*(2), 1-17.

Shittu, O. S., Williams, I. D. & Shaw, P. J. (2021). Global E-waste management: Can WEEE make a difference? A review of e-waste trends, legislation, contemporary issues and future challenges. *Waste Management*, *120*, 549-563.

Sun, P. P. & Lee, M. S. (2011). Separation of Pt (IV) and Pd (II) from the loaded Alamine 336 by stripping. *Hydrometallurgy*, *109*(1-2), 181-184.

Swain, B., Jeong, J., Kim, S.-k. & Lee, J.-c. (2010). Separation of platinum and palladium from chloride solution by solvent extraction using Alamine 300. *Hydrometallurgy*, *104*(1), 1-7.

Tang, N., Liu, L., Yin, C., Zhu, G., Huang, Q., Dong, J., Yang, X. & Wang, S. (2021). Environmentally benign hydrophobic deep eutectic solvents for palladium (II) extraction from hydrochloric acid solution. *Journal of the Taiwan Institute of Chemical Engineers*, *121*, 92-100.

Uheida, A., Zhang, Y. & Muhammed, M. (2002). Selective extraction of palladium (II) from chloride solutions with nonylthiourea dissolved in chloroform. *Solvent extraction and ion exchange*, *20*(6), 717-733.

Wang, J., Xu, W., Liu, H., Yu, F. & Wang, H. (2021). Extractant structures and their performance for palladium extraction and separation from chloride media: A review. *Minerals Engineering*, *163*, 106798.

Wang, J.-l., Lu, L. I. U., Xu, G.-d., Wang, P.-l., Huang, G.-y. & Yu, F.-s. (2023). New compound N-methyl-N-isopropyl octanthioamide for palladium selective extraction and separation from HCl media. *Transactions of Nonferrous Metals Society of China*, *33*(5), 1609-1618.

Zheng, H., Ding, Y., Wen, Q., Liu, B. & Zhang, S. (2021). Separation and purification of platinum group metals from aqueous solution: Recent developments and industrial applications. *Resources, Conservation and Recycling*, *167*, 105417.