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A Two-Step Leaching Process Using Thiourea for the Recovery of Precious Metals from Waste Printed Circuit Boards

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Abstract: The development of efficient recovery methods for waste printed circuit boards (WPCBs) not only tackles the environmental risks of disposal but also promotes the conservation of resources within the electronics industry. This study proposes a two-step leaching approach for recovering metals from WPCBs. Initially, transition metals are leached using nitric acid, followed by the recovery of precious metals with thiourea in the second stage. In the first stage, dissolution rates exceeding 90 wt% were achieved for transition metals, including Cu, Fe, Ni, Pb, and Sn. In this stage, the dissolution of precious metals (i.e., Au and Pd) was insignificant. In the second stage, the effect of four parameters was investigated, including the impact of temperature, concentrations of ferric ions, sulfuric media, and thiourea on the recovery of Au and Pd. Precise control over sulfate concentration played a vital role in achieving maximum Au recovery. The optimal acid concentration was 0.2 M, resulting in a recovery rate of ~50 wt%. Ferric ion concentration positively affects Au recovery, whereas, in extracting Pd, optimal conditions imposed the absence of ferric ions. Thiourea concentration positively impacted Au and Pd recovery rates, peaking at 49 wt% for Au at 1 M and 44 wt% for Pd at 1.5 M. Prolonged leaching resulted in declining Au recovery rates, indicating a decrease in reagent concentration. Temperature variation yielded similar outcomes, with 50 °C resulting in peak recovery rates of 53 wt% for Au and 54 wt% for Pd. Metal dissolution kinetics during leaching were analyzed using pseudo-first-order and pseudo-second-order models. The second-order model proved suitable for transition metals in the first stage, while only for Au and Pd in the second stage (with $R^2 = 0.99$).

Keywords: waste printed circuit boards (WPCBs); two-step leaching; precious metals recovery; thiourea

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1. Introduction

The quantity of electronic waste (e-waste), encompassing personal computers, cellular phones, tablet devices, and televisions, has experienced a notable upsurge in contemporary times. This occurrence can be ascribed to the expeditious growth of the economy conjoined with augmented rates of electronic production. Furthermore, the majority of electronic equipment has short usable lifetimes, which exacerbates this emerging problem [1]. When evaluating one of the most significant components within the spectrum of e-waste, waste printed circuit boards (WPCBs) are widely recognized as a highly significant secondary source, primarily due to their abundant supply of valuable base and precious metals [2]. WPCBs contribute significantly to the waste stream, comprising around 3–5% of all e-waste in the world [3]. The presence of materials such as Cu, Au, and Pd renders WPCBs particularly attractive for recovery. By extracting these metals from WPCBs, not only can we recover valuable resources, but also the adverse environmental consequences associated with mining and processing raw materials can be alleviated [4]. These WPCBs provide a substantial environmental concern due to the inclusion of toxic substances such as heavy metals, epoxy polymers, and brominated flame retardants. It is crucial to handle their disposal with utmost caution to mitigate any potential harm they may inflict [5].

Researchers from across the globe investigated different methods to recycle WPCBs. These methods include a few technological processes, namely physical and mechanical separation methods, pyrometallurgical procedures, hydrometallurgical processes, biotechnology applications, microwave treatments, and supercritical fluid technology) [6]. For pyrometallurgical procedures, a traditional method has been employed to reclaim valuable non-ferrous and precious metals from e-waste. This method involves using high-temperature techniques like incineration, plasma arc furnace, or blast furnace smelting, sintering, melting, and high-temperature gas-phase reactions [7]. In light of the need for significant upfront investment, low metal quality during partial extraction, the generation of harmful gases, and the substantial production of slag caused by ceramics in WPCBs, researchers are concentrating on a hybrid strategy that incorporates both hydrometallurgical and electrometallurgical techniques [8]. Hydrometallurgy involves the extraction of metallic elements from solid metal components in WPCBs by using specific leaching agents [9]. In hydrometallurgy, solid metals are dissolved into a liquid phase by employing chemical agents such as acidic solutions or complexing agents like sulfuric acid, aqua regia, and cyanide [10]. Nevertheless, a great deal of lixiviants used for metal recovery are toxic and detrimental to both human health and the environment. Furthermore, high recovery yields sometimes need the use of huge quantities of chemicals, which have additional requirements for safe disposal [11]. In comparison, thiourea is less harmful than strong chemical substances like cyanide, sulfuric acid, and aqua regia. The lesser toxicity of thiourea emphasizes its potential as a safer and more ecologically friendly alternative for procedures involving the dissolving of materials in aqueous phases, hence reducing health and ecological concerns [12]. Due to these promising attributes compared to other substances, thiourea is a suitable alternative for extracting valuable metals [13]. Furthermore, thiourea leaching offers notable economic benefits. It can reduce operational costs by lowering environmental compliance expenses and minimizing the need for stringent safety measures associated with more toxic reagents like cyanide [14]. The rapid extraction rates achieved with thiourea enhance productivity and overall profitability. Additionally, the ability to recycle thiourea contributes to its cost-effectiveness by decreasing the frequency of reagent replenishment [15].

Based on studies of Au recovery from leaching solutions, a variety of methods are documented in the literature. These methods include cementation, chemical precipitation, solvent extraction, ion exchange, adsorption, and electrowinning [16].

For extracting valuable metals using thiourea from complicated sources such as WPCBs, a multi-step leaching method has proven to be highly effective. This approach proves especially beneficial in tackling difficulties concerning Cu interference and the subsequent degradation of thiourea. Researchers presented a remedy to the problem of Cu, a prevalent component in e-waste, impeding the effectiveness of thiourea-based Au extraction [10]. A study by Torres and Lapidus underscores the significance of a multi-step leaching process [17]. Over 90 wt% of Cu was extracted during the first pre-treatment phases when peroxide, HCl, or citrate was employed effectively. Subsequently, in the phase dedicated to Au recovery, the solid residue originating from Cu extraction underwent treatment with thiourea solutions, leading to the successful removal of more than 90 wt% of Au within a brief one-hour period. In addition, Behnamfard et al. (2013) conducted a study that focused on an extensive leaching method for extracting elements from WPCBs [18]. This process involves three sequential leaching steps, including two oxidative sulfuric acid leaching stages and one acidic thiourea leaching stage. By utilizing these steps together, the researchers were able to enhance the dissolution of valuable metals like Au, with 84 wt% recovery rate. In the research undertaken by Birloaga et al. (2014) [19], similar findings were observed when extracting Au from Au-coated pins embedded in a WPCB that contained significant amounts of Cu using a multi-step leaching process. According to their study results, after a three-step thiourea leaching procedure, approximately 99% of the Cu in the solid WPCBs is successfully removed. In the case of Au, all of it is effectively leached into the solution after all stages of leaching. In another study conducted by Birloaga and

Vegliò (2016), their main goal was to enhance the efficiency of extracting Cu, Au, and Ag from WPCBs [20]. Their methodology involved a two-step leaching procedure: firstly, they employ an oxidative method that uses 2 M H_2SO_4 and 20 mL H_2O_2 for Cu extraction. This is followed by thiourea leaching on crushed WPCBs using a solution consisting of 20 g/L thiourea, 6 g/L ferric ion, and 10 g/L sulfuric acid, which led to 90 wt% of Au and 75 wt% of Ag extraction.

The primary aim of the present research is to offer a modified version of the two-step leaching approach, with a specific emphasis on enhancing the efficiency of valuable metal extraction, particularly utilizing ecologically friendly thiourea. This involves an initial step focused on effectively dissolving the majority of transition metals (>90 wt%), followed by a second step for the selective recovery of precious metals (Au and Pd), with a recovery rate of above 50 wt%. By integrating these elements, this study contributes novel insights into the complex dynamics of multistage, multi-elemental leaching processes. Meanwhile, the kinetics analysis revealed disparate behaviors between transition metals and precious metals when exposed to thiourea. Adopting this innovative method has the potential to enhance recovery initiatives, making more significant contributions to sustainability efforts.

2. Materials and Methods

2.1. Initial WPCB Powder

The e-waste material utilized throughout this research was dismantled multilayer WPCBs, specifically motherboards and modem boards of the FR-4 type, which were sourced from Reverse e-waste company, Sydney, Australia. The process involved in separating and improving the content of metallic and non-metallic parts within WPCBs is depicted in Figure 1, as demonstrated by Nekouei et al. (2018) [21]. It is worth mentioning that specific components such as the steel CPU case, capacitors, port locations, and plastic parts were dismantled from the boards manually. The initial step involved obtaining representative samples of WPCBs, which were then cut into pieces using a guillotine. The preparation process for the WPCB powder begins with coarse grinding in a knife mill. This is followed by further refinement of the coarse powder using a ring mill to achieve a finer and more consistent product. To classify the resulting PCB powder, it was divided into two categories based on sieve mesh sizes, i.e., green powder (<125 μ) and brown powder (between 212 and 125 μ). In this study, the green powder was chosen due to the significantly higher concentration of precious metals. In Table 1, the quantities of elements found in the green and brown powders are presented using inductively coupled plasma (ICP) analysis. Furthermore, the percentage of the recovered element represents the proportion relative to the initial concentration of that element in the waste solid material.

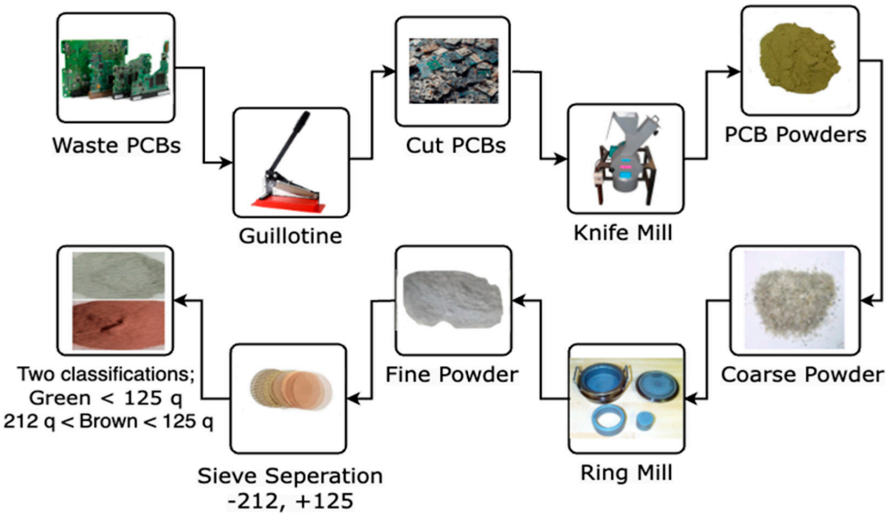

Figure 1. The preparation steps of waste printed circuit boards (WPCBs) as the initial secondary resource.

Table 1. The chemical composition of the WPCBs green and brown powder determined through ICP analysis.

Elements	**Cu (% wt)**	**Fe (% wt)**	**Ni (% wt)**	**Pb (% wt)**	**Sn (% wt)**	**Zn (% wt)**	**Au (mg/kg)**	**Pd (mg/kg)**
Green Powder	9.29	5.77	0.41	0.79	2.72	0.2	524	19.4
Brown Powder	42.93	1.28	0.41	1.11	6.48	2.15	44.6	34.1

2.2. The First Stage of Leaching

In the first stage, our goal was to gain insight into how varying concentrations of nitric acid (0.5, 1, 2, 3, and 4 M HNO_3 (70 v%), RCL Labscan (Distributed by Chem-Supply, Gillman, South Australiain laboratory grade) and changes in temperature (room temperature, 40, and 60 °C) affect the removal of transition metals. In all the experiments, the stirring speed (300 rpm), solid-to-liquid ratio (1:50), quantity of green powder (1 g), volume of the solution (50 mL), and duration (6 h) remained constant. In this study, the one-factor-at-a-time (OFAT) approach, a well-established method, was employed. With OFAT, only one factor changes at each stage while keeping other parameters constant. Consequently, the total number of experiments equals the sum of the levels for all factors [22]. Consequently, the total number of experiments equals the sum of the levels for all factors. Following every trial, vacuum filtering using cellulose-base filter papers (#41, Whatman) was performed. The residue was washed several times using deionized water, and the volume of fluid was measured for recovery calculations, followed by analysis of the solution by ICP.

2.3. The Second Stage of Leaching

In this stage, the recovery efficiency of the rest of the transition metals, as well as Au and Pd, was evaluated by altering variables, including temperature, thiourea and ferric ions, and sulfuric acid concentrations, which are shown in Table 2. During the second phase of the leaching experiments, a 50 mL solution was prepared for each experiment. Similar to the initial phase, the stirring speed (200 rpm), solid-to-liquid ratio (1:50), quantity of powder (1 g from the residue of the first stage), and duration (24 h) remained unchanged. The chemicals used in this stage were thiourea (CN_4N_2S)−98 wt% and iron (III) Chloride ($FeCl_3$)−98 wt% (Chem-Supply in a laboratory grade), and the sulfuric acid (H_2SO_4)−98 v% (Sigma-Aldrich, St. Louis, MO, USA). Similarly, the one-factor-at-a-time (OFAT) approach was implemented across all experiments during the second stage of leaching, maintaining consistency with its application in the initial stage. The 50 mL solution under magnet stirring was placed in a glass water bath with a volume of 500 mL to reach the desired temperature. After each experiment, the solution underwent vacuum filtration, and the residue was washed continually with deionized water. The pH level was adjusted as needed through the addition of sulfuric acid. The pH of the solutions at the conclusion of the first and second stages of leaching predominantly fell below 1 and 1.5, respectively, indicating the unlikelihood of oxide and hydroxide precipitation.

Table 2. Differing temperature levels and varied thiourea, ferric ion, and sulfuric acid concentrations in the second stage of leaching.

Temperature (°C)	**H_2SO_4 Concentration (M)**	**Ferric Ion Concentration (g/L)**	**Thiourea Concentration (M)**
	0	0	0.2
25	0.05	3	0.5
50	0.1	6	1
70	0.2	9	1.5

Following every filtration procedure, the volume of the solution contained was measured for recovery calculations. Subsequently, the solutions underwent ICP analysis following a procedure similar to that in the first stage.

2.4. Kinetics of Leaching

2.4.1. First Stage of Leaching

The kinetic experiments were performed in a 500 mL glass laboratory beaker positioned on a magnetic stirrer. The experimental parameters consisted of a solid-to-liquid ratio of 1:50 g/mL, with a temperature set at 40 °C for 6 h while the stirrer ran at 300 rpm. In each trial, approximately 10 g of green powder underwent leaching using a nitric acidic solution with a concentration of 1 M. At different interval times, 5 mL syringes were utilized in conjunction with single-use syringe filters to collect samples from the solution for analysis. It is significant to consider that, as shown in Table 3, the studies commenced at the 2 min point and went on for the 6 h period, gathering data at predetermined intervals. After completing the vacuum filtration, the solid residue was carefully dried overnight in an oven to ensure it was ready for the second stage of kinetics testing procedures. The details of this table are shown in Table S-VIII-b and Table S-IX-b.

Table 3. The details of kinetics studies for both the first stage (1 M HNO_3, 40 °C, and 6 h) and second stage (6 g/L of ferric ion, 1 M thiourea, and 0.1 M H_2SO_4, 50 °C, and 24 h).

First Stage								
Elements Time (min)	Cu (ppm)	Fe (ppm)	Ni (ppm)	Pb (ppm)	Sn (ppm)	Zn (ppm)	Au (ppb)	Pd (ppb)
2 m	259	1008	63.1	148.7	251.6	12.9	0.65	29.5
5 m	309	1008	67.8	149.0	265.0	13.9	0.99	36.8
10 m	343	1013	70.6	149.7	269.2	14.4	1.12	42.5
15 m	351	1011	70.0	147.4	266.8	14.4	1.18	42.7
20 m	362	1002	72.2	149.9	276.8	14.8	1.61	42.4
30 m	366	1017	69.6	152.7	265.6	14.4	1.79	41.1
40 m	678	1032	75.0	157.2	273.8	17.6	1.98	62.7
50 m	774	1035	76.2	154.0	278.4	18.6	2.41	69.3
60 m	842	1034	75.4	158.2	274.2	18.8	2.67	80.3
75 m	952	1040	76.1	158.8	277.8	19.4	2.92	79.9
90 m	1040	1038	77.1	157.0	281.2	20.0	3.30	85.9
120 m	1222	1046	79.1	157.4	287.6	21.3	3.75	96.6
180 m	1440	1053	79.6	156.2	290.4	22.8	4.63	115
240 m	1660	1052	82.0	161.3	298.2	24.6	5.61	128
300 m	1716	1102	83.2	170.7	304.2	25.3	6.53	133
360 m	1769	1104	83.6	165.6	304.8	25.6	6.57	135
Second Stage								
Elements Time (min)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Sn (ppm)	Zn (ppm)	Au (ppb)	Pd (ppb)	
2 m	1.45	0.79	0.08	2.06	0.19	2408	322	
5 m	1.46	0.79	0.09	3.04	0.22	2494	318	
10 m	1.52	0.80	0.09	4.72	0.22	2511	310	
15 m	1.59	0.82	0.10	5.72	0.24	2629	323	
30 m	1.66	0.88	0.11	8.04	0.30	2602	314	
60 m	1.72	0.89	0.13	12.8	0.40	2620	317	
75 m	1.74	0.93	0.14	15.0	0.45	2626	317	
90 m	1.81	0.98	0.15	16.5	0.50	2665	325	
120 m	1.80	0.98	0.16	20.4	0.55	2687	329	
180 m	1.88	1.08	0.17	22.8	0.74	2746	334	
240 m	2.12	1.28	0.21	39.6	1.14	2889	355	
360 m	2.11	1.27	0.21	39.3	1.12	2823	349	
540 m	2.59	1.78	0.29	86.2	1.95	3331	411	
720 m	2.88	2.08	0.33	107.7	2.43	3284	410	
1080 m	3.04	2.48	0.37	132.7	2.90	3177	400	
1440 m	3.28	2.96	0.41	154.9	3.57	3283	415	

2.4.2. Second Stage of Leaching

The washed solid residue from the first leaching step was utilized in the following phase of leaching. The experimental conditions for this phase included utilizing 10 g of the first-stage solid residue and a solution comprised of 6 g/L of ferric ion, 1 M Thiourea, and 0.1 M H_2SO_4 in a glass beaker with a volume of 500 mL. The leaching procedure was carried out at a temperature of 50 °C for the duration of one day while maintaining continuous agitation at a rate of 300 rpm using a magnetic stirrer. During this stage, 5 mL syringes were utilized in conjunction with single-use syringe filters to collect samples from the solution for analysis. As in the first stage, samples were collected at various time intervals, as illustrated in Table 3, to monitor the progress of the leaching process. The metal concentrations in these solutions were then determined through ICP.

2.5. Characterization of Residue after the Leaching Process

In the process of quantitatively identifying metal contents within separated powders, microwave digestion was employed using an aqua regia solution. Following this digestion, the resultant solution underwent analysis via ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) and ICP-MS (Inductively Coupled Plasma Mass Spectrometry, Perkin Elmer, Waltham, MA, USA, Optima DV7300). Regarding the morphological investigation of the powder, samples were investigated using scanning electron microscopy (SEM, Hitachi S3400×, Tokyo, Japan) equipped with energy dispersive spectroscopy (EDS, Bruker, Billerica, MA, USA). By using a magnification level of 300× and an acceleration voltage of 15 kV, the SEM analysis aimed to uncover morphological changes that occur at various stages, offering valuable insights into the progression from raw material to multi-step leaching.

3. Results and Discussion

3.1. The First Stage of Leaching

3.1.1. Effects of Acid Concentration

As reported, there are different chemicals for the extraction of Cu and other base metals, but nitric acid is often chosen as a popular option, and by using a two-step leaching process, it is possible to dissolve almost 99% of Cu [23].

A promising performance was achieved at a nitric acid concentration of 0.5 M, with recovery rates exceeding 90 wt% for Cu, Fe, and Ni (Figure 2a). This concentration represented the highest level of recovery efficiency for these transition metals under different acid concentrations of 0.5, 1, 2, 3, and 4 M. However, when the nitric acid concentration ascended, recovery rates decreased noticeably for all elements, reaching a low point at 2 M concentration. At concentrations above 2 M concentration, all the elements showed an upward trend in recovery rates when the nitric acid concentration was increased to 3 M. The most dramatic rise was found during the transition from 2 to 3 M concentration in Sn recovery, eventually peaking at 67.7 wt% at a 4 M concentration. It is important to point out that Sn differs from the observed trends in other metals. The recovery rates for Sn demonstrated a marginal increase as the concentration of nitric acid increased, in contrast to the anticipated decline observed in other metals. Unlike the findings in Long Le et al.'s (2011) study, which showed little to no recovery rate for Sn, our study reveals a significant improvement in the recovery rate when higher concentrations of nitric acid were used. Specifically, after reaching a concentration of 3 M, the recovery rate of Sn experienced a notable increase [24].

Upon careful examination of precious metals, it is evident that Pd exhibits a recovery rate of 24 wt%, whereas Au, when subjected to a concentration of 0.5 M, only displays a recovery rate of 1.9 wt%. It is important to note that when the nitric acid concentration gradually increased, these values for both valuable metals gradually declined. A critical point in our analysis came at a 2 M nitric acid concentration, where recovery rates hit the lowest point of 12.1 wt% for Pd and 0.3 wt% for Au, as presented in Figure 2b. Subsequently, an obvious increase in recovery rates was seen as the nitric acid concentration climbed from

2 to 3 M. This shift resulted in the most noticeable rise in the recovery of Pd, culminating in the greatest recovery rate of 45.6 wt% within this experimental range. It is necessary to note, however, that this climb was followed by a subsequent decrease with further rises in nitric acid concentration. In addition, it was determined that there was not a substantial rise in Au, and the recovery value varied between 0.3 and 1.9 wt%.

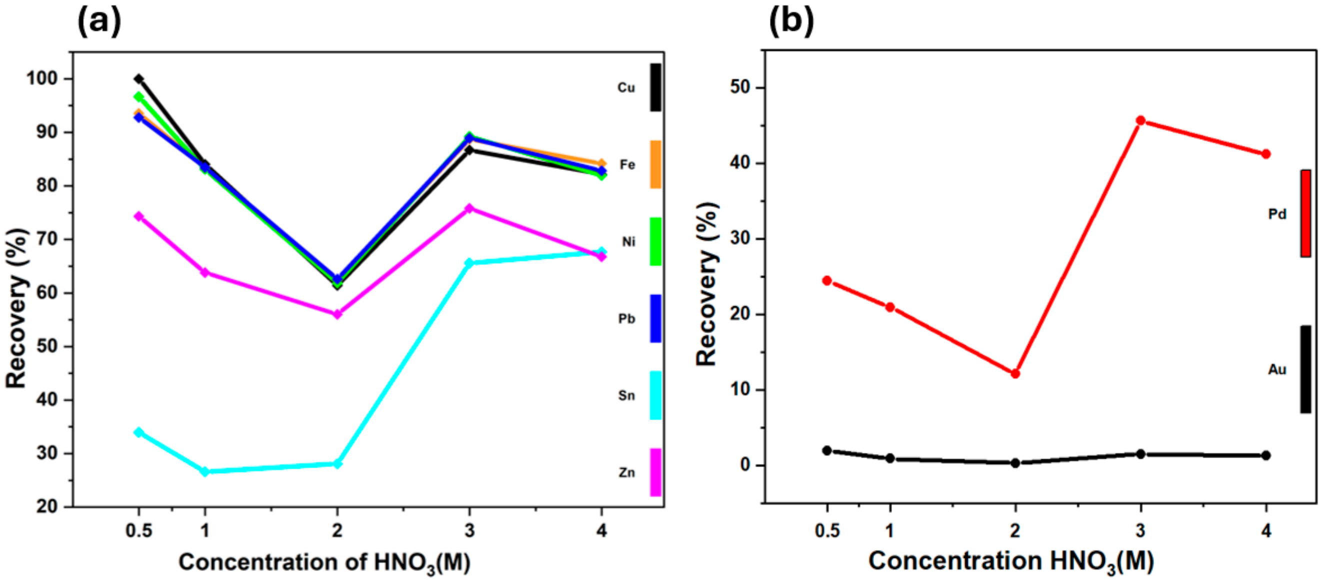

Figure 2. The effect of nitric acid concentration on (**a**) transition metals and (**b**) precious metals recovery rates in the first step of leaching (using 1 g of WPCB powder, from 0.5 to 4 M HNO_3, 40 °C, 6 h). The details of this figure are shown in Table S-II.

Based on our findings, a substantial amount of base metals experience dissolution during the initial leaching phase, leading to a recovery rate of approximately 10% or lower in the second step of leaching (Figure 2a).

3.1.2. Effect of Temperature

To analyze the effect of temperature, it was set to three distinct levels: room temperature, 40, and 60 °C. According to Figure 3a, it is clear that a temperature of 25 °C is associated with the lowest recovery rates for most elements, apart from Sn. The temperature jumps from 25 to 40 °C had significant effects, with the greatest recovery rates for Cu, Fe, Ni, Pb, and Sn, ranging from 98.2 to 99.9 wt%. The rise in recovery efficiency emphasizes the temperature sensitivity inherent in the recovery process. However, when the temperature was raised to 60 °C, there was a decrease in recovery rates for all components. The most severe fall happened for Sn, where the recovery rate dropped from 98 to 59 wt%.

According to research conducted by Jeon et al. (2015), it was observed that the leaching efficiencies of Sn exhibited a pattern of initially increasing and then rapidly decreasing, except for 90 °C [25]. At this temperature, Sn was not detected during leaching. However, at 30 °C, the leaching efficiency reached 100% before rapidly decreasing to zero. These findings suggest that higher temperatures promote the precipitation of Sn as stannic acid, as depicted in Equation (1) [26].

$$3Sn + 4HNO_3 + H_2O \leftrightarrow 4NO + 3SnO_2.H_2O \quad (1)$$

$$Sn + 4HNO_3 + H_2O \leftrightarrow 4NO_2 + SnO_2.H_2O \quad (2)$$

Zn responded intriguingly to temperature modulation, with its recovery rate gradually surging with increasing temperature. In contrast to other metals, Zn displays a gradual increase in its recovery rate within the temperature range of 40 to 60 °C. According to

Mohammadzadeh et al. (2020), higher temperatures result in increased recovery of Zn. This can be explained by improved reaction kinetics and greater solubility of Zn-containing compounds in a solution with nitric acid [27]. The added energy from elevated temperature helps overcome activation barriers, enabling faster dissolution of Zn and breakdown of complex forms that hinder leaching at lower temperatures. As a result, higher temperatures promote favorable thermodynamics and enhance mass transfer, leading to more efficient recovery of Zn. Mecucci and Scott (2002) noted that the fluctuation in temperature has a favorable effect on the dissolution of Cu. This is because it facilitates the removal of epoxy coatings, enabling the nitric acid solution to access the underlying Cu layers. Their experiments highlight how necessary it is to consider the concentration of nitric acid for efficient metal recovery from scrap materials [28].

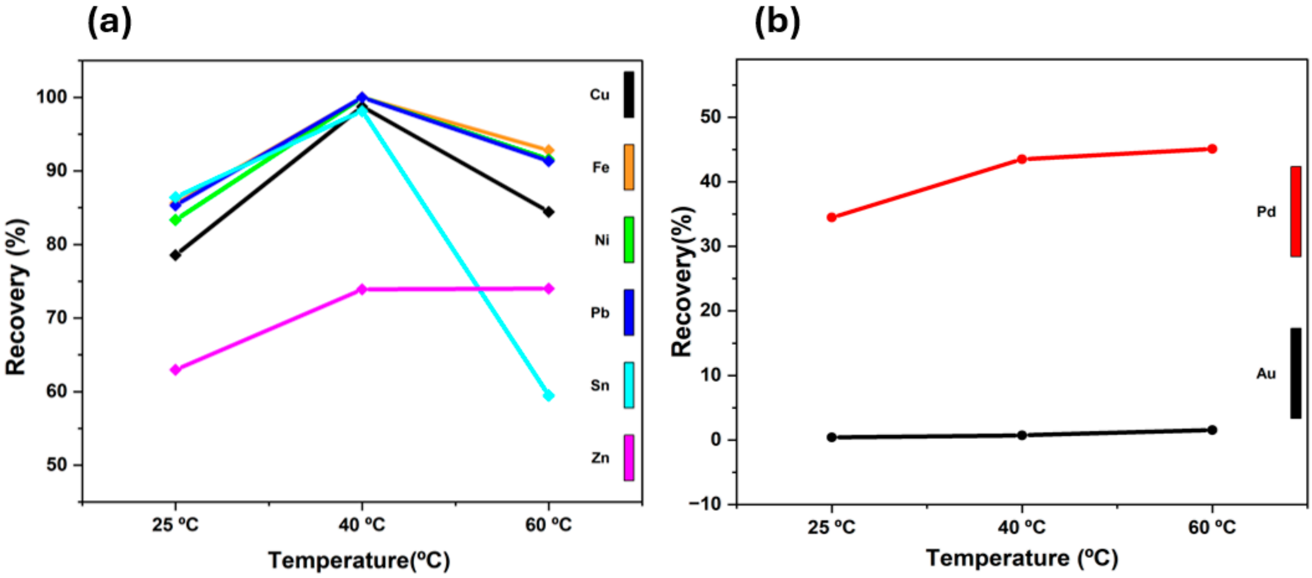

Figure 3. The influence of temperature levels on (**a**) transition metals and (**b**) precious metals recovery in the first step of leaching (using 1 g of WPCB powder, 1 M HNO_3, from 25 to 60 °C, 6 h). The details of this figure are shown in Table S-III.

In the analysis of precious metals, an initial examination indicated a comparatively restrained reaction to fluctuations in temperature. Pd, comparable to Au, initially demonstrated the lowest rate of recovery at room temperature. Nevertheless, as the temperature was elevated to 40 °C, a discernible enhancement in the efficiency of recovery became apparent. The recovery rate ascended from 34.5 to 43.5 wt% (Figure 3b). Subsequently, a marginal further increase was observed upon the temperature reaching 60 °C, culminating at 45 wt%. Results demonstrated that higher temperatures have a positive impact on Pd-leaching nitric acid. On the other hand, when examining Au, there was a gradual and minimal rise in recovery rates. The preliminary Au recovery rate, which started at 0.4%, experienced a slight increase to 1.5% when the temperature was raised to 40 °C, as shown in Figure 3b. However, it is important to note that this change was modest, indicating an insignificant response to temperature variation.

Overall, our findings align with previous research, as studies by Panda et al. (2020) demonstrate, which emphasizes that a higher temperature promotes improved kinetics during the leaching process, leading to a decrease in activation energy of leaching and an increase in Pd recovery rates [23].

3.2. The Second Stage of Leaching

3.2.1. Thiourea Concentration

According to the results of this study, thiourea has a positive effect on Au and Pd recovery up to a particular concentration threshold. The chosen range thiourea in this study was between 0.2 and 1.5 M. As shown in Figure 4a, initially, precious metal recovery rates were low, i.e., 27.2 wt% for Au and 35.9 wt% for Pd. In terms of Au recovery, an increase was found between 0.2 and 0.5 M, peaking at almost 50 wt% at 1 M and then falling to 41.9%. Pd, on the other hand, achieved the maximum recovery rate of 43.8 wt% at 1.5 M thiourea concentration.

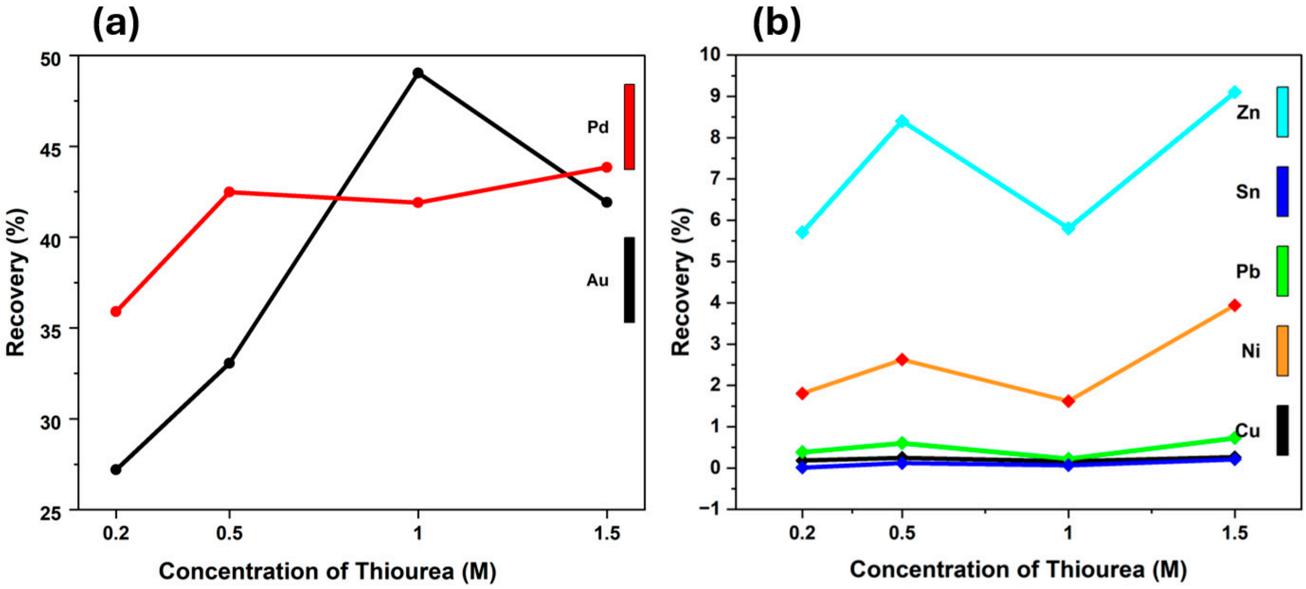

Figure 4. The effect of thiourea concentrations on the recovery efficiency of (**a**) precious metals and (**b**) transition metals (using 1 g of powder from the first stage of leaching, 6 g/L of ferric ion, and 0.1 M H_2SO_4, 50 °C, 24 h). The details of this figure are shown in Table S-IV.

A critical factor in the leaching of precious metals such as Au and Pd using thiourea is the possibility of decreasing reagent concentration. The concentration of active reagents, mainly thiourea, may gradually decrease as the leaching process continues due to their consumption in the dissolving reactions. This fall in reagent concentration has the potential to reduce leaching efficiency, resulting in the observed decrease in precious metal recovery rates in lower concentrations of thiourea [29].

Thiourea easily dissolves in acidic solutions and can efficiently solve precious metals, mainly Au, when paired with an oxidant. This chemical reaction can be illustrated by Equation (3) [10]. According to Kai et al. (1997), ferric ion is the most potent oxidant, and sulfuric acid outperforms nitric or hydrochloric acid during the leaching processes. The reaction with the ferric ion is presented in Equation (4) [30].

$$2CS(NH_2)_2 + Au \leftrightarrow Au\,[CS(NH_2)_2]_2{}^{+} + e^{-} \tag{3}$$

$$Fe^{3+} + Au + 2CS(NH_2)_2 \leftrightarrow Au\,[CS(NH_2)_2]_2{}^{+} + Fe^{2+} \tag{4}$$

The reversible transformation of thiourea into formamidine disulfide ($C_2H_8N_4S_2{}^{2+}$) is done using an oxidizing agent. This process is facilitated in the presence of iron (III), which causes the oxidation of thiourea to formamidine disulfide, as shown in Equation (5) [19].

$$2Fe^{3+} + 2CS(NH_2)_2 \leftrightarrow 2H^{+} + 2Fe^{2+} + (CS(NH_2)\,(NH))_2 \tag{5}$$

Production of formamidine disulfide might encourage the unintentional partial oxidation of formamidine disulfide to produce substances like elemental sulfur and cyanamide when there is a larger ambient electromotive force present, as shown in Equation (6) [30].

$$(CS(NH_2)\,(NH))_2 \leftrightarrow CS(NH_2)_2 + NH_2CN + S^0 \tag{6}$$

The presence of formamidine disulfide might cause competing reactions, diverting the leaching solution away from the desired precious metals) [12]. According to a study performed by Camelino et al. (2015), since elemental sulfur forms a barrier of protection on the Au surface, an additional breakdown of formamidine disulfide into sulfur has been proposed as a means of reducing the efficiency of Au leaching [31].

In addition, the study carried out by Hiskey (1984) indicates that in the context of sulfuric acid systems using iron (III) as the oxidizing agent, thiourea undergoes a simultaneous reaction that results in the creation of an iron sulfate complex, as demonstrated in Equation (7) [32].

$$\mathrm{Fe^{3+} + {SO_4}^{2-} + CS(NH_2)_2 \leftrightarrow [FeSO_4(CS(NH_2)_2)]^+} \quad (7)$$

This reaction highlights the complex characteristics of thiourea that extend beyond simple breakdown and affect its application in precious metal leaching processes.

In this study, as presented in Figure 4a, recovery was observed in the presence of lower thiourea levels, perhaps due to competition with other ions present in the samples. Increased concentrations, on the other hand, could result in increased conversion of thiourea to formamidine disulfide and an irreversible transformation into cyanamide and elemental sulfur, which in turn decreased the recovery of Au (Equations (5) and (6)).

According to another study conducted by Groenewald (1976), the reaction between thiourea and ferric ions, often considered slow due to the formation of stable complexes in acid sulfate solutions, proves beneficial in the context of Au leaching, as seen in Equation (7) [33]. While thiourea consumption is reduced, there is still significant potential for fast Au dissolution due to this delayed reaction. His study also suggests that iron ions and thiourea may combine to create rather stable complexes in acidic conditions, which is advantageous for the leaching of Au. However, in the majority of Au leaching applications, there is a significant thiourea consumption and, finally, a passivated Au surface, leading to relatively poor Au leaching kinetics and low extraction, as shown in Equations (4) and (5).

Regarding transition metals, a study by Ray et al. (2022) indicates that the presence of iron (III) and sulfuric acid (H_2SO_4) can result in thiourea forming complexes with transition metals and reducing their ability to form compounds with Au [10]. This creates complications for the decomposition of thiourea, especially in relation to e-waste containing transition metals such as Cu, which can be found in a substantial majority of WPCBs. When iron (III) is present, Cu can undergo leaching through the redox mechanism illustrated in Equation (8). Following this, elevated concentrations of Cu can lead to higher thiourea decomposition into $[(\mathrm{CS(NH_2)(NH)})_2]$ and the creation of a copper (I) complex in Equation (9)) [34].

$$\mathrm{2Fe^{3+} + Cu \leftrightarrow 2Fe^{2+} + Cu^{2+}} \quad (8)$$

$$(n + 1)\ \mathrm{CS(NH_2)_2 + Cu^2 \leftrightarrow (CS(NH_2)(NH_2)^+)_2 + Cu(CS(NH_2)_2)^+}{}_n \quad (9)$$

Therefore, to deal with this situation, using a pre-leaching process to dissolve Cu and other transition metals before recovering precious metals with thiourea is a viable strategy [31]. This is demonstrated in Figure 4b, where the recovery efficiency for all base metals is almost complete due to their dissolution in the first stage.

Leaching time also plays a crucial role in ensuring the completion of the dissolution process in this study. The extended leaching duration allows for sufficient time for thiourea to diffuse into the material and interact with the metal species. Additionally, thiourea may form stable complexes with the target metal ions, but the formation kinetics of these complexes can be relatively slow [16]. Therefore, prolonged contact time is required for thorough complexation and subsequent extraction, especially in the case of Au leaching.

3.2.2. Ferric Ion Concentration

Numerous studies have shown that the ferric ion can accelerate reactions and have a positive effect on the extraction of precious metals [35]. According to Figure 5a, it becomes evident that at 0 g/L ferric ion concentration, the Au recovery rate was 44.8 wt%. However, it appears that without ferric ions as oxidants, the oxidation of thiourea to its active complexing state (thiourea dioxide) is not effective enough in enhancing Au solubility [29]. Consequently, this leads to a low rate of Au recovery. In this study, when 3 g/L of ferric ions were added to the solution, there was an improvement in the Au recovery rate, which reached 48.4 wt%. However, when the ferric ion concentration was further increased to 9 g/L, the Au recovery rate decreased to 45.1 wt%. To justify this information, a study showed that once the concentration exceeds a certain range, the recovery rate of Au decreases [36]. When both oxidizing agents (ferric ion and sulfuric acid) reach high concentrations, and ferric ions concentration exceeds 5 g/L, the leaching rate of Au goes down. This decrease in the Au leaching rate is linked to many reasons, such as longer reaction times and passivation.

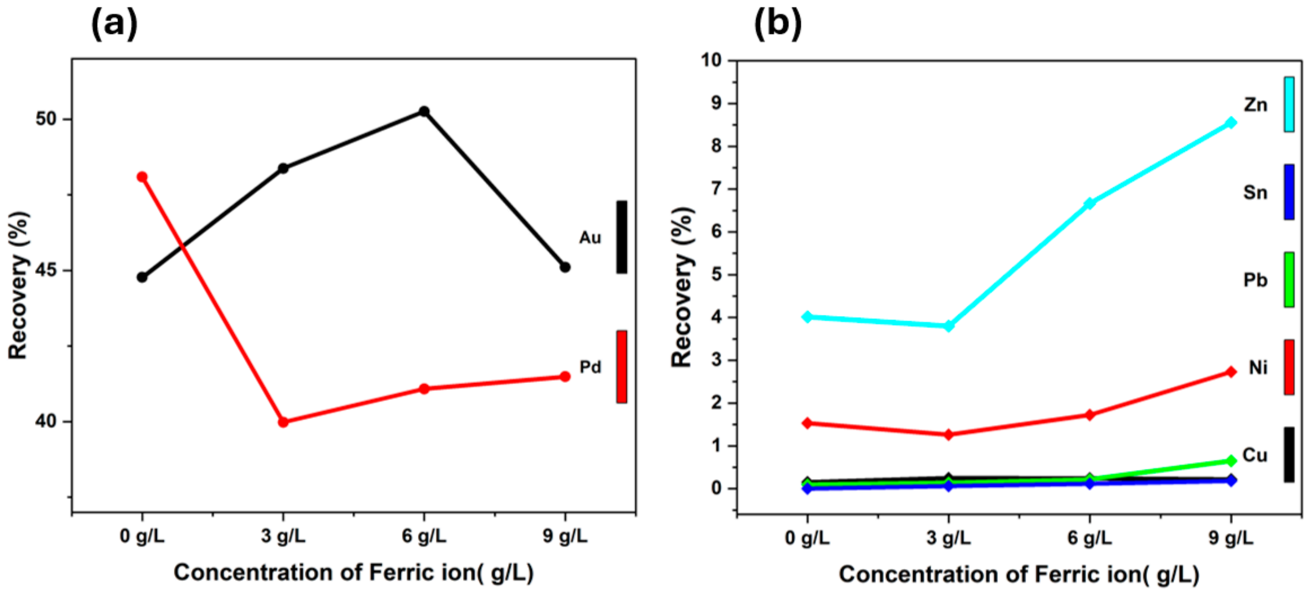

Figure 5. The influence of ferric ion on the recovery rate of (**a**) precious metals and (**b**) transition metals (using 1 g of powder from the first stage of leaching, 1 M thiourea, and 0.1 M H_2SO_4, 50 °C, 24 h). The details of this figure are shown in Table S-V.

According to Figure 5a, the recovery rate for Pd is the highest (at 48.1 wt%) when ferric ions are not added. As the concentrations of ferric ions increased from 0 to 3 g/L, there was a clear pattern of decreasing Pd recovery rate. After this point, it increases slightly until reaching 41.4 wt% in 9 g/L ferric ion concentration. The reason for the low efficiency after a certain point for Pd is that excessive ferric ions will speed up the oxidation of thiourea. In this case, the decomposition of thiourea can result in the creation of iron–thiourea complexes, which may hinder Pd leaching, as presented in Equation (5).

Regarding the effect of ferric ions in the dissolution of transition metals in the second stage of leaching, ferric ions may not show immediate effects. A study conducted by Arslan et al. (2004) suggests a positive impact of ferric ions on Cu leaching recovery, whereas the leaching recoveries of metals like Pb, Zn, and Ni remain largely unaffected [37]. It becomes evident that in this study, the interaction with ferric ions yields a minor positive effect on transition metals, primarily attributed to their dissolution in the first stage of the leaching process, as presented in Figure 5b.

3.2.3. Sulfuric Acid Concentration

The acid concentration tests included four levels (i.e., 0, 0.05, 0.1, and 0.2 M). According to the results, increasing the concentration of sulfuric acid has a positive impact on Au and Pd recovery, as illustrated in Figure 6a. Higher acid contents, in general, result in a faster leaching rate. As a result, at 0.2 M acid concentration, Au dissolution resulted in a greater Au recovery rate of 50.3 wt%. Considering the notable recovery of Pd (i.e., 47 wt%) using nitric acid in the initial stage, it becomes apparent that 42.3 wt% of Pd undergoes dissolution in the second stage. Although the rate of change may not demonstrate the same level as seen for Au, it still surpasses 40 wt%.

Sulfuric acid plays an important role in various studies, whether it involves adjusting the pH in solutions or facilitating the dissolution of ferric ions. Regarding pH, which is a critical factor in working with thiourea and in this study, sulfuric acid is utilized to regulate the acidity of the leaching solution. A study carried out by Syed (2012) indicates that leaching of Au using thiourea typically takes place within the pH range of 1–2 [16], which was maintained within the specified range in this study. Additionally, his study also highlighted the effectiveness of ferric ions in sulfuric acid solutions, recognizing them as potent oxidizing agents that prove highly efficient in the Au leaching process. According to another study by Pyper and Hendrix (1981), the thiourea and oxidant concentrations, as well as the pH values, have an impact on how quickly Au leaches [38]. These studies illustrate the important role of sulfuric acid in maintaining a specific pH level and creating an acidic environment, which, in turn, enhances the interaction between Au and thiourea in the leaching process, as demonstrated in our findings in Figure 6a.

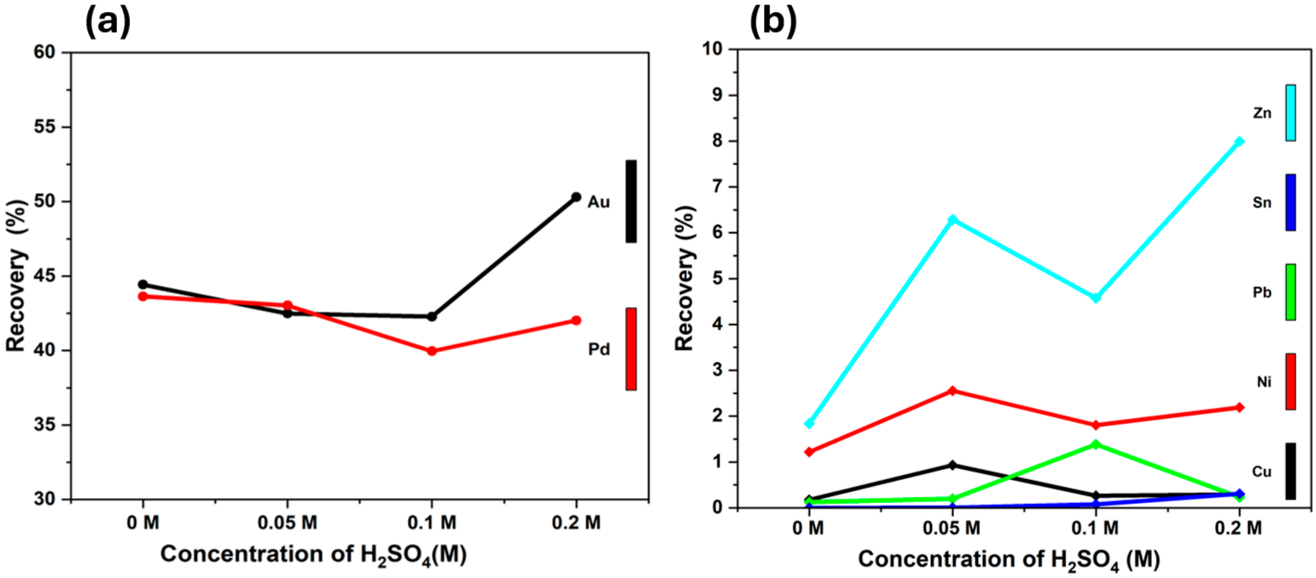

Figure 6. The influence of varied sulfuric acid concentrations on (**a**) precious metals and (**b**) transition metals (using 1 g of powder from the first stage of leaching, 6 g/L of ferric ion, 1 M thiourea, 50 °C, 24 h). The details of this figure are shown in Table S-VI.

Concerning the recycling of transition metals, similar to my study findings, as indicated in the research conducted by Batnasan et al. (2018), the dissolution of transition metals from the residue sample using thiourea solutions with varying concentrations of sulfuric acid did not adversely impact the leaching of precious metals [1].

It can be seen that a significant portion of the metal is dissolved after the first stage. Consequently, there is a minimal amount of transition metals remaining to be dissolved in the second stage, as demonstrated in Figure 6b. Therefore, the dissolution of metals in the thiourea solutions under varied conditions was not further investigated in these studies, with the primary focus remaining on the leaching behavior of precious metals.

3.2.4. Effect of Temperature

In the temperature analysis, as shown in Figure 7, three different temperatures (25, 50, and 70 °C) were investigated. The leaching procedure yielded a satisfactory Pd recovery rate, but Au extraction was relatively limited, with only 1.5wt% recovery at a temperature of 25 °C, as depicted in Figure 7. Temperature is a critical factor in Au leaching with thiourea [6,29]. Elevated temperatures increase system energy, leading to the breaking of bonds and improving Au dissolution compared to lower temperatures [29]. Additionally, complex formation improves up to certain temperature levels, resulting in increased Au recovery [6]. Au and Pd recovery rates (Figure 7a) were highest at 50 °C, with values of 52.9 and 54.4 wt%, respectively. However, above 50 °C, there was a minor decline in recovery rates, with values of 42.3 for Au and 53.6 wt% for Pd. It has been reported that in the two-step leaching method, higher temperatures have advantages for improving the recovery rates of valuable metals like Au) [39]. However, thiourea decomposition becomes more likely at higher temperatures, such as 70 °C. This can result in the degradation of thiourea and a decrease in its effectiveness as a complexing agent for Au and Pd ions. Consequently, the dissolution and recovery of precious metals may be hindered) [40].

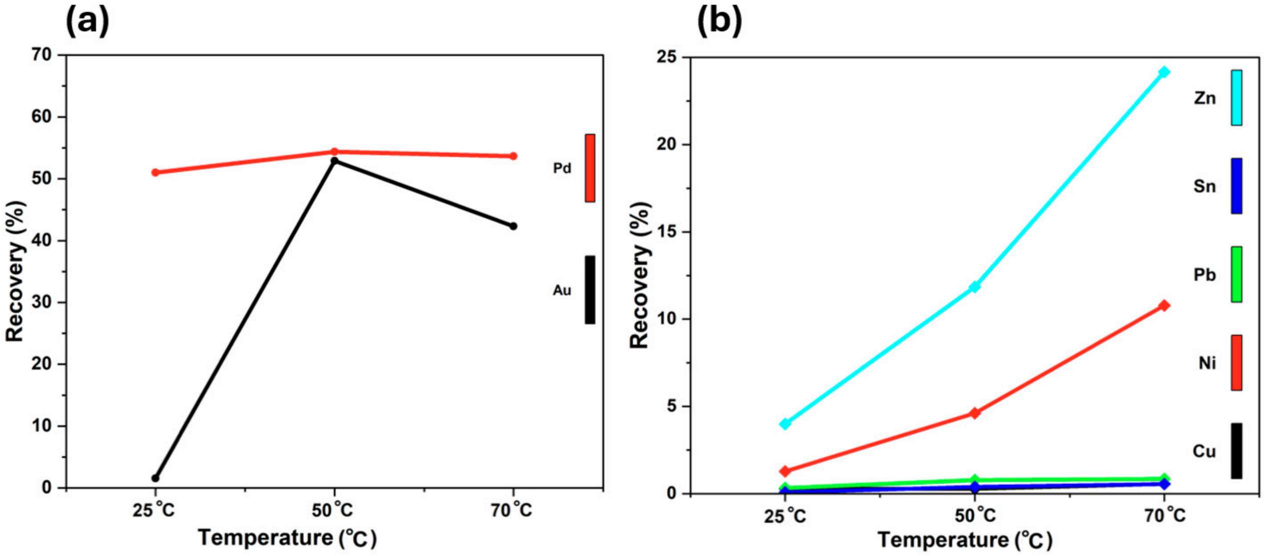

Figure 7. The impact of different temperature levels on recovery rates in the second stage for (**a**) precious metals and (**b**) transition metals (using 1 g of powder from the first stage of leaching, 6 g/L of ferric ion, 1 M thiourea, and 0.1 M H_2SO_4, from 25 to 70 °C, 24 h). The details of this figure are shown in Table S-VII.

Additionally, when the temperature reaches 70 °C, there is an increased probability of certain impurities or unwanted compounds (iron (II) sulfate) precipitating, as demonstrated in Equation (7). These precipitates can interfere with the leaching process and reduce both Au and Pd efficiency. Moreover, although an increase in temperature enhances the solubility of Au and Pd, excessively elevated temperatures can lead to reduced solubility due to the formation of less stable metal–thiourea complex formations. The decline in effectiveness could be ascribed to the disintegration of thiourea at elevated temperatures above 60 °C, leading to negative implications for the leaching procedure of Au [41]. Likewise, the empirical evidence presented by Ubaldini et al. (1998) supports the notion that the reduction in the extraction of Au at 60 °C can be ascribed to the thermal decomposition of thiourea [40], which produces sulfur compounds, as shown in Equation (6). This decomposition reduces its capacity to combine with Au to create complexes. Higher temperatures also cause thiourea to oxidize, which results in the formation of a barrier of protection on the surface of Au. These two elements impede the leaching process, which affects the total Au dissolution efficiency.

In addition, Figure 8 illustrates the recovery rates of precious and transition metals from both leaching stages under optimal conditions. The plot distinctly demonstrates the efficient extraction of Au and Pd in the second stage.

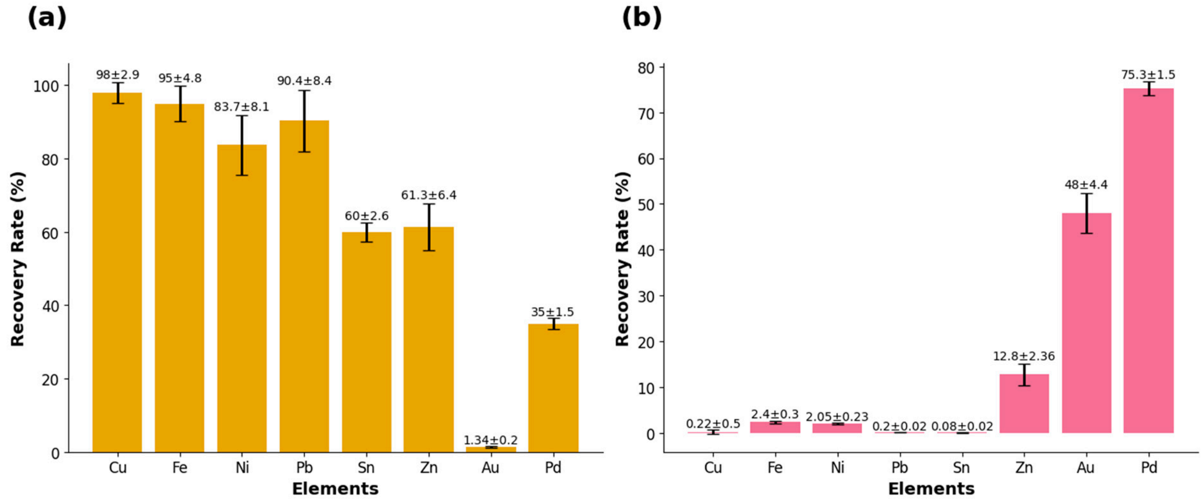

Figure 8. Elemental recovery rates of the (**a**) first and (**b**) second stages of the leaching process under the optimized conditions.

3.3. Kinetics of Leaching Processes

The pseudo-first-order and pseudo-second-order models are frequently employed to explain the rate of dissolution in different chemical and environmental systems [42]. Researchers often utilize these models, such as the ones described by Blanchard et al. (1984), to investigate processes like solute adsorption on solid surfaces, the leaching of elements from solid materials, and reactions occurring in solution [43]. Additionally, in academic papers, researchers commonly employ these two order models, as highlighted by Simonin (2016), to describe the dynamics of a particular phenomenon in detail [44]. The first-order model pertains to processes influenced by diffusion and is known as the intraparticle diffusion equation. Recent studies have introduced more sophisticated methods for analyzing this equation [45].

The second order, on the other hand, involves assuming that an adsorption reaction occurring at the interface between the liquid and solid phases within the adsorbent material is the main driving force behind the process [46]. When modeling the leaching behavior of metals from solid materials, particularly e-waste materials, the pseudo-second-order kinetics model has been applied thoroughly. The leaching rate and the concentration of leachate metal ions on the solid surface are assumed to be identical in this model. Most of the dissolution systems examined in the literature review are compatible with the pseudo-second-order kinetics model, which demonstrated the best degree of agreement with experimental data. This is the reason for the widespread utilization of this order [47].

In this study, in order to improve the understanding of leaching kinetics, rate constants needed to be determined for the adsorption process of each individual element. Afterward, mathematical models were used effectively to analyze these sets of data and compare them with experimental results. To assess the kinetics of leaching, two widely recognized models, the Largergen pseudo-first-order (a) and the pseudo-second-order (b) models by Nekouei et al. (2019) were used, represented by Equations (10) and (11) [48].

$$ln(q_{max} - q_t) = ln(q_{max}) - k_1 t \tag{10}$$

$$\frac{t}{q_{max}} + \frac{1}{k_2 \cdot q_{max}^2} = t/q_t \tag{11}$$

where k_1 (min^{-1}) is the rate constant per minute, k_2 (g/mg.min), t is the time, q_{max} is the maximum adsorption capacity, and q_t is the amount of adsorbate absorbed at time t.

According to the study conducted by Wang and Guo (2023), researchers frequently employ linearized versions of the pseudo-first-order and pseudo-second-order equations [49]. In this study, the usual method for estimating dissolution kinetic parameters and modeling the adsorption process involves using linearized versions of the models. This requires plotting ln $[q_e - q(t)]$ vs. t and $t/_{(t)}$ for the pseudo-first-order and pseudo-second-order models, respectively, in accordance with the provided Equations (10) and (11).

As presented in Table 4 and Figure 9, in all transition metals, the R-squared value aligns with the second-order model during the initial stage. However, for Cu, this value is 0.98 for the first-order model and 0.93 for the second-order model. Ho and McKay (1999) suggest that the pseudo-first-order model is more applicable in the early stages of the process [42], which is consistent with the early-stage dissolution behavior of Cu that has been observed. On the other hand, the behavior of the other base metals under investigation seems to support the idea that the pseudo-second-order model is more appropriate for describing dissolution kinetics over a longer leaching time.

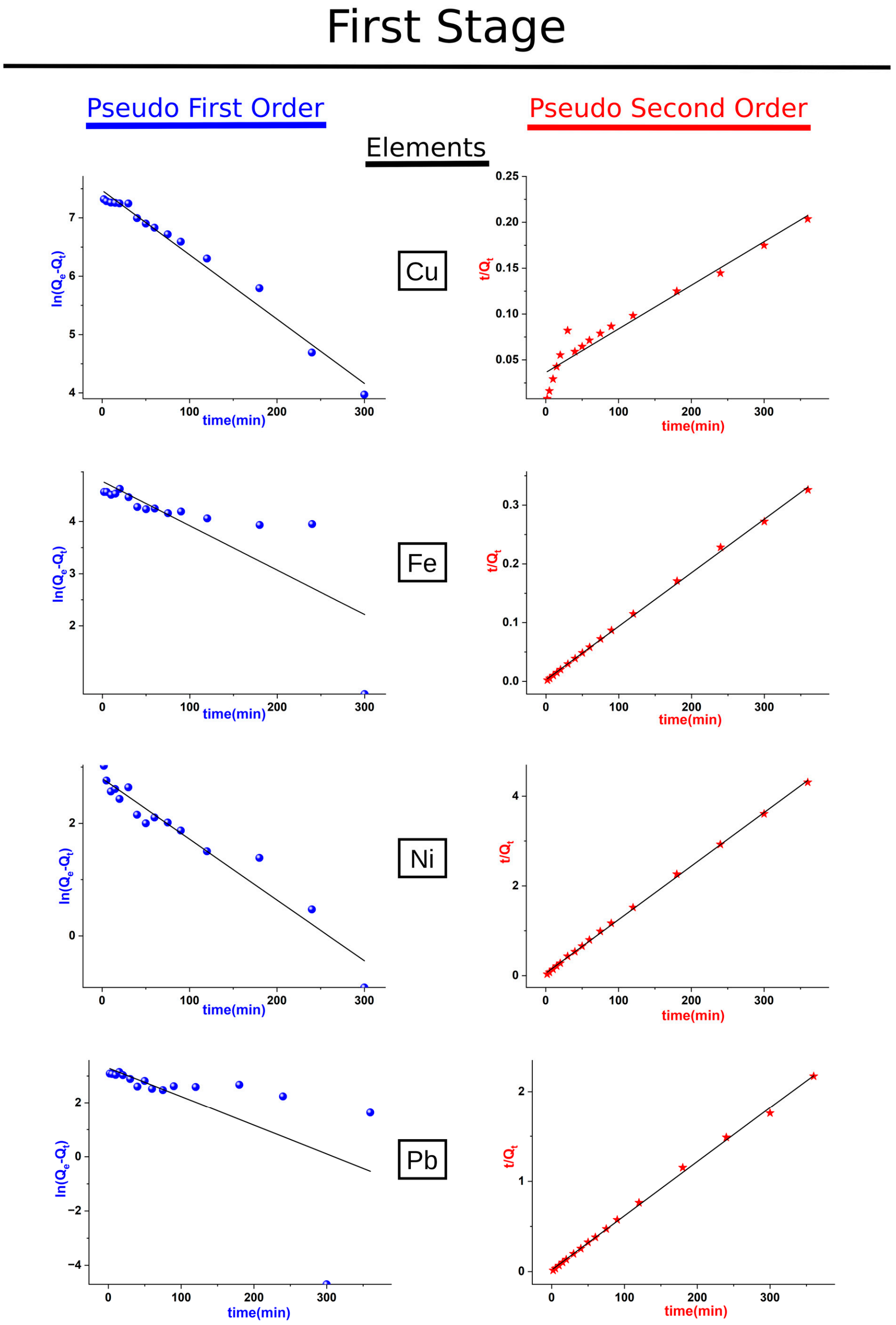

Figure 9. *Cont.*

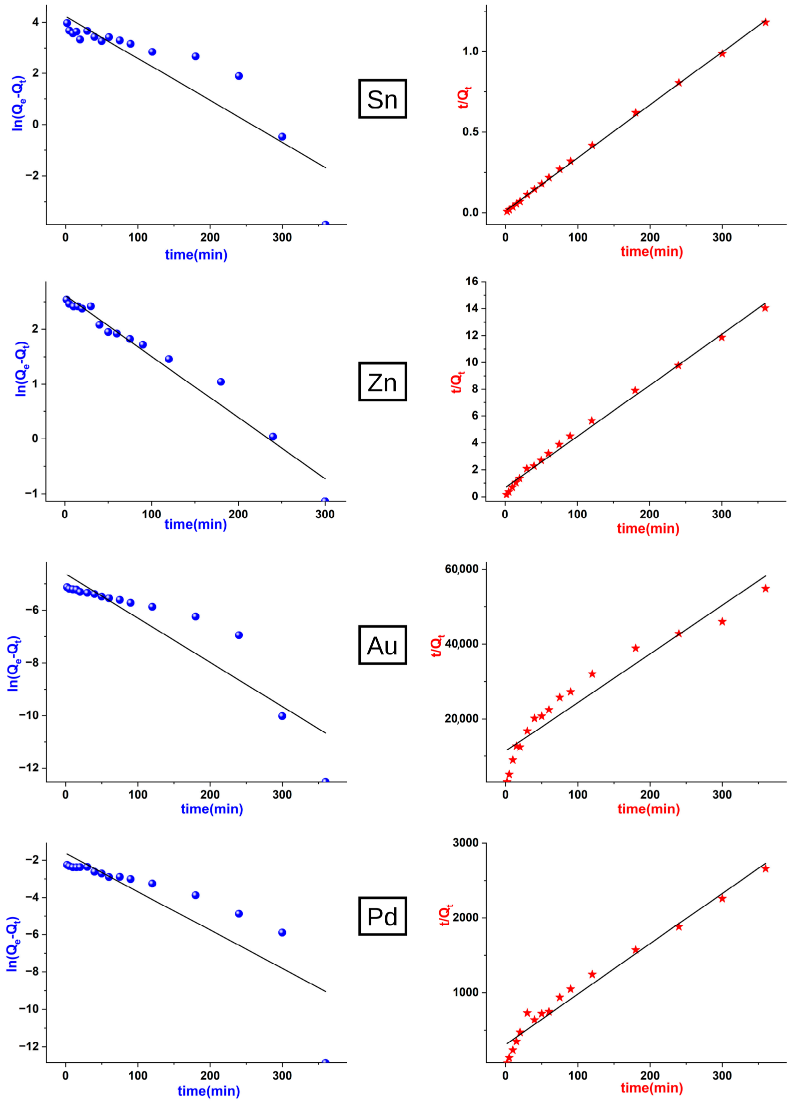

Figure 9. The model data-fitting of dissolution of different metals after the first stage of leaching under these conditions: 10 g of powder, 1 M HNO_3, 40 °C for 6 h, 300 rpm.

Table 4. The kinetics information obtained from Equations (10) and (11) for the first stage of leaching (using 10 g powder, 1 M HNO3, 40 °C for 6 h, 300 rpm).

Elements Recovered	**(1) Pseudo-First-Order**			**(2) Pseudo-Second-Order**			**(3) q_{max} Experimental (mg/g)**	**Error (%) between (1) and (3)**	**Error (%) between (2) and (3)**
	q_{max} (mg/g)	k_1 ($min^{-1)}$	Adjusted R-square	q_{max} (mg/g)	k_2 (g/mg·min)	Adjusted R-square			
Cu	1755.6	−0.01102	0.98	2104.0	4.75124×10^1	0.93	1769.0	0.79	−18.9
Fe	117.7	−0.0085	0.61	1096.4	9.12059×10^{-4}	0.99	1104.0	89.4	0.7
Ni	16.4	−0.0108	0.93	83.8	0.01193	0.99	83.6	80.3	−0.2
Pb	27.0	−0.01065	0.35	166.7	0.006	0.99	170.7	−5.6	0.2
Sn	68.9	−0.01643	0.81	304.9	0.00328	0.99	304.8	77.3	0.0
Zn	13.8	−0.01116	0.97	26.23	0.03813	0.99	25.6	46.2	−2.4
Au	0.0098	−0.01676	0.83	0.0077	129.88199	0.911	0.0066	−49.1	−17.2
Pd	0.1967	−0.02061	0.74	0.1487	6.72189	0.97	0.1354	−45.3	−9.82

In the second stage of leaching and with a focus on Au and Pd, it is apparent that the adjusted R-squared values differ significantly, as presented in Table 5. The R-square values show a significant alignment with the pseudo-second-order model, with values of 0.99 for both Au and Pd. In contrast, the adjusted R-squared values in the pseudo-first-order model for Au and Pd are 0.12 and 0.82, respectively, indicating a less accurate fit with this model. Consequently, these two precious metals demonstrate a significant correlation to the second-order model, as showcased in Figure 10. However, this level of consistency is not observed among transition metals.

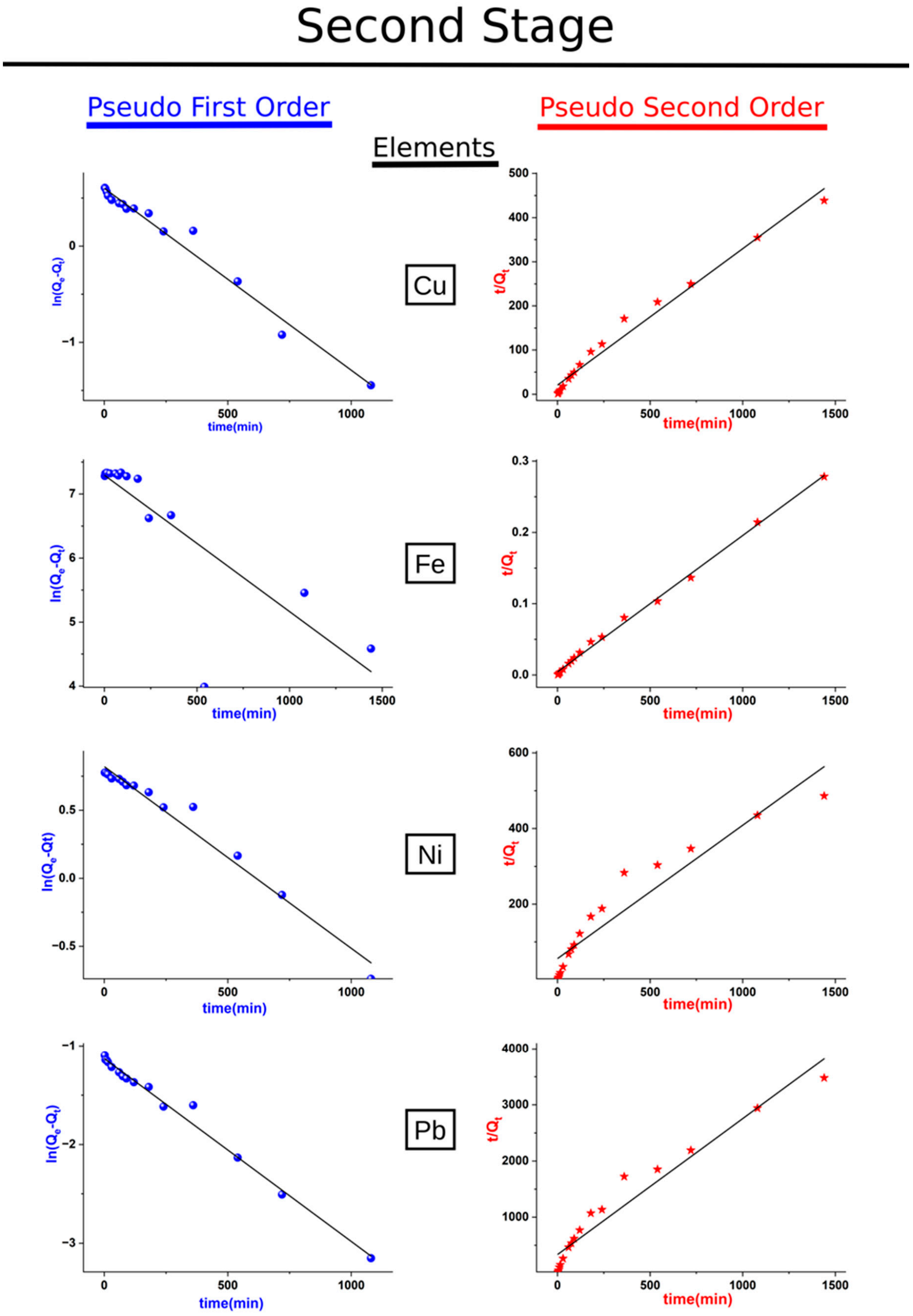

Figure 10. *Cont.*

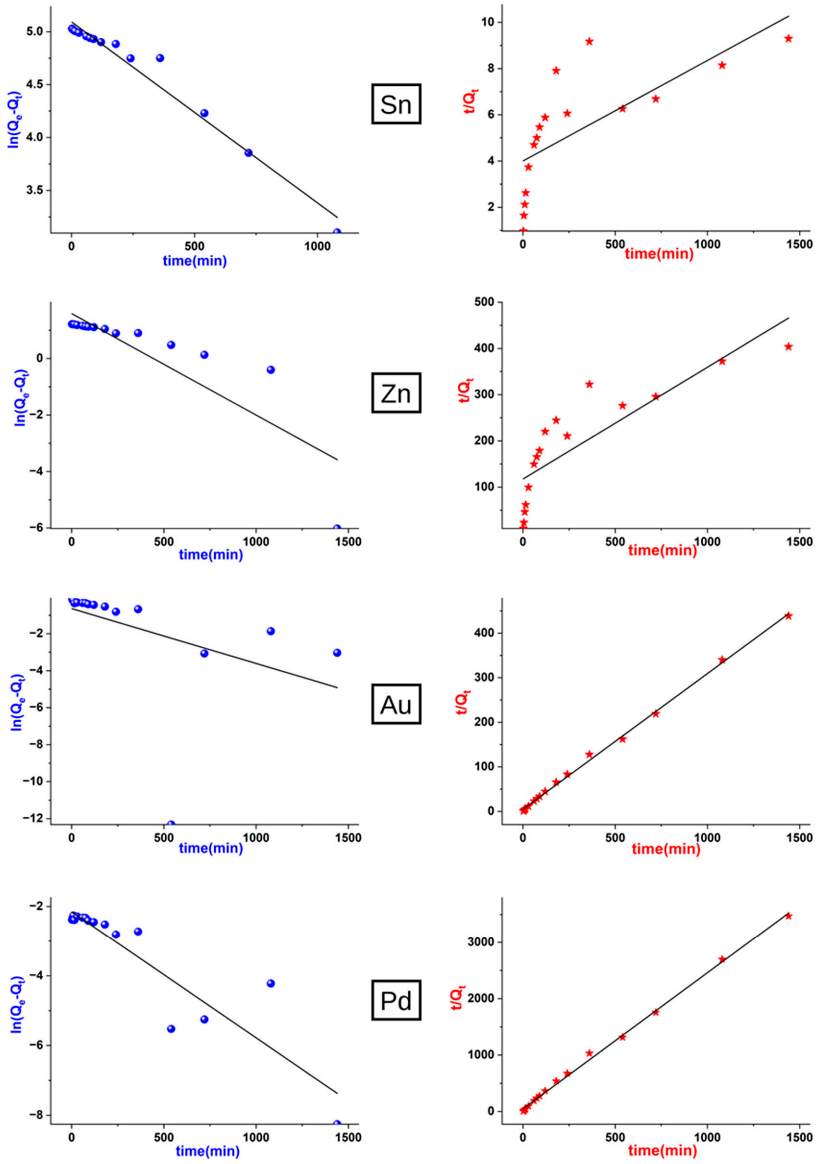

Figure 10. The data-fitting of dissolution of different metals during the second leaching stage under these conditions: 6 g/L ferric ions, 1 M thiourea, and 0.1 M H_2SO_4, at 50 °C for 24 h, 300 rpm.

Table 5. The kinetic insights derived from Equations (10) and (11) for the second stage of leaching (using 10 g of powder from the first stage of leaching, 6 g/L ferric ions, 1 M thiourea, and 0.1 M H_2SO_4, at 50 °C for 24 h, 300 rpm.).

Elements Recovered	**(1) Pseudo-First-Order**			**(2) Pseudo-Second-Order**			**(3) q_{max} Experimental (mg/g)**	**Error (%) between (1) and (3)**	**Error (%) between (2) and (3)**
	q_{max} (mg/g)	k_1 (min^{-1})	Adjusted R-square	q_{max} (mg/g)	k_2 (g/mg. min)	Adjusted R-square			
Cu	1.823	−0.00189	0.97816	3.23	0.30889	0.98004	3.28	44.40	1.52%
Fe	1471	−0.00213	0.66411	5224	1.91416×10^1	0.99723	5273	72.13	0.9%
Ni	2.271	−0.00134	0.97276	2.83	0.35281	0.89712	2.96	23.31	4.39%
Pb	0.3229	−0.00185	0.98894	0.4131	2.42034	0.94234	0.41	21.24	0.14%
Sn	162.846	−0.00171	0.96612	229.8	0.00435	0.47715	154.9	5.29	−48.35%
Zn	4.886	−0.00359	0.72107	4.13	0.24203	0.69214	3.57	36.86	−15.68%
Au	0.526	−0.00297	0.11806	3.28374	0.30453	0.99809	3.28253	83.97	−0.12%
Pd	0.115	−0.00362	0.82173	0.414	2.41319	0.99775	0.415	31.03	0.24%

3.4. Morphological Analysis

WPCBs consist of a variety of components, which can be categorized into plastics (30 wt%), ceramics (34 wt%), and metals (36 wt%)) [50]. Among the metallic components are transition metals and precious metals, forming complex mixtures and multi-element alloys dispersed throughout the metal layers and joining materials of PCBs [51]. According to Estrada-Ruiz et al. (2016), it is crucial to evaluate the presence of precious materials and harmful substances in WPCBs in order to create recovery systems that are both economically feasible and environmentally sustainable [52].

After examining the EDS map analysis of the original green powder, which represents the unprocessed material obtained from WPCBs, a variety of base metals such as Al, Cu, Ni, Pb, and Sn, and precious metal (i.e., Au) was observed, as demonstrated in Figure 11. This examination underscores the distribution of these metals within the WPCB powders.

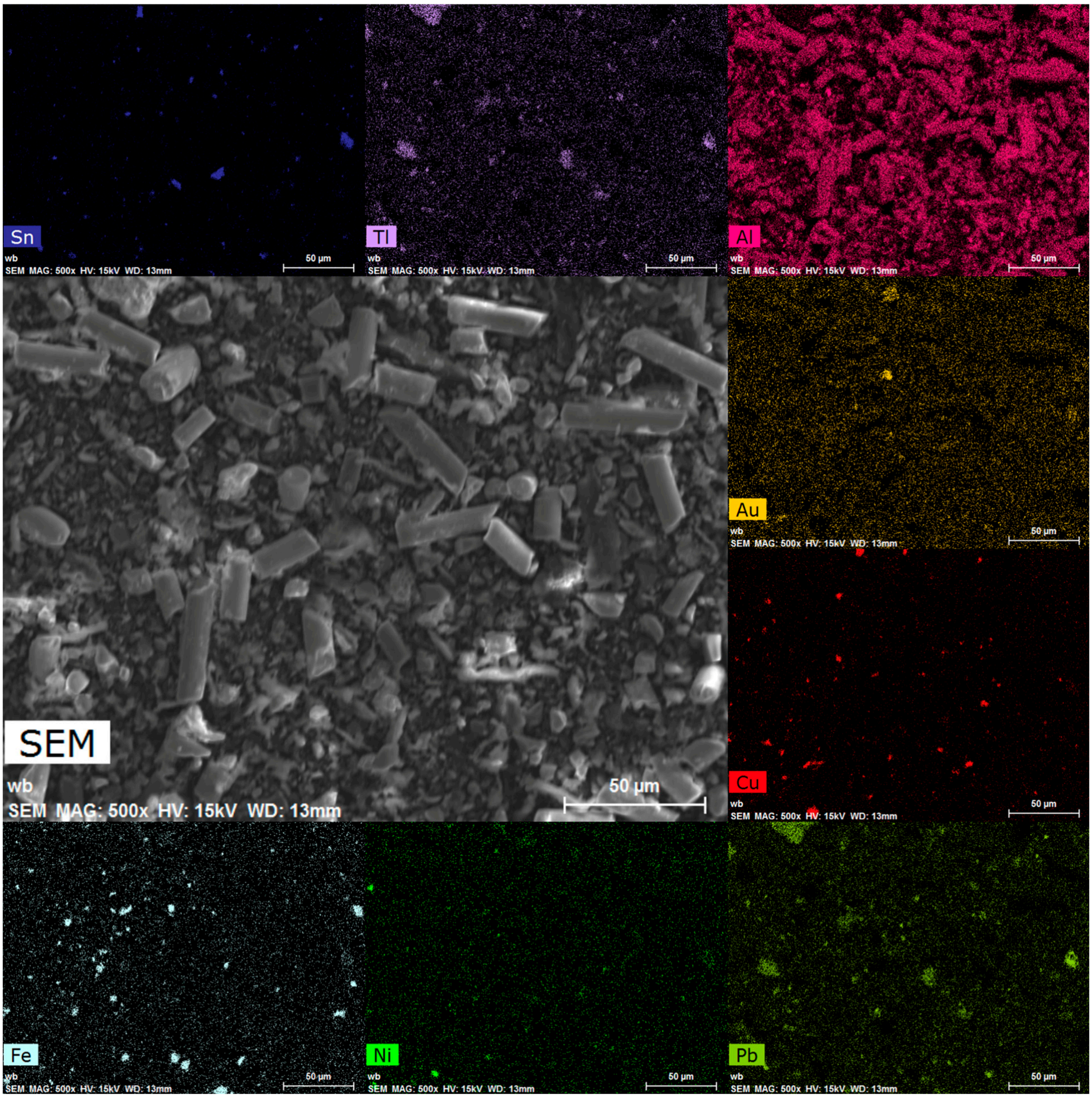

Figure 11. SEM images of the green powder from WPCBs and EDS map analysis of elements (yellow: Au, red: Cu, purple: Ti, pink: Al, dark blue: Sn, light blue: Fe, dark green: Pb, light green: Ni).

After the first stage of leaching, there is a significant dissolution of most transition metals. This poses difficulties in detecting the aforementioned transition metals. However, small amounts of Sn remained in the leaching residue. In contrast to other materials, Sn exhibited an initial dissolution rate of 40 wt%, which progressively increased to approximately 70 wt% with varying concentrations of HNO_3. This unique behavior highlights the distinctive challenge posed by Sn in the leaching process, which will be discussed later. Apart from base metals, the precious metals that were not dissolved, such as Au, remained mostly unaffected, as shown in the EDS analysis shown in Figure 12.

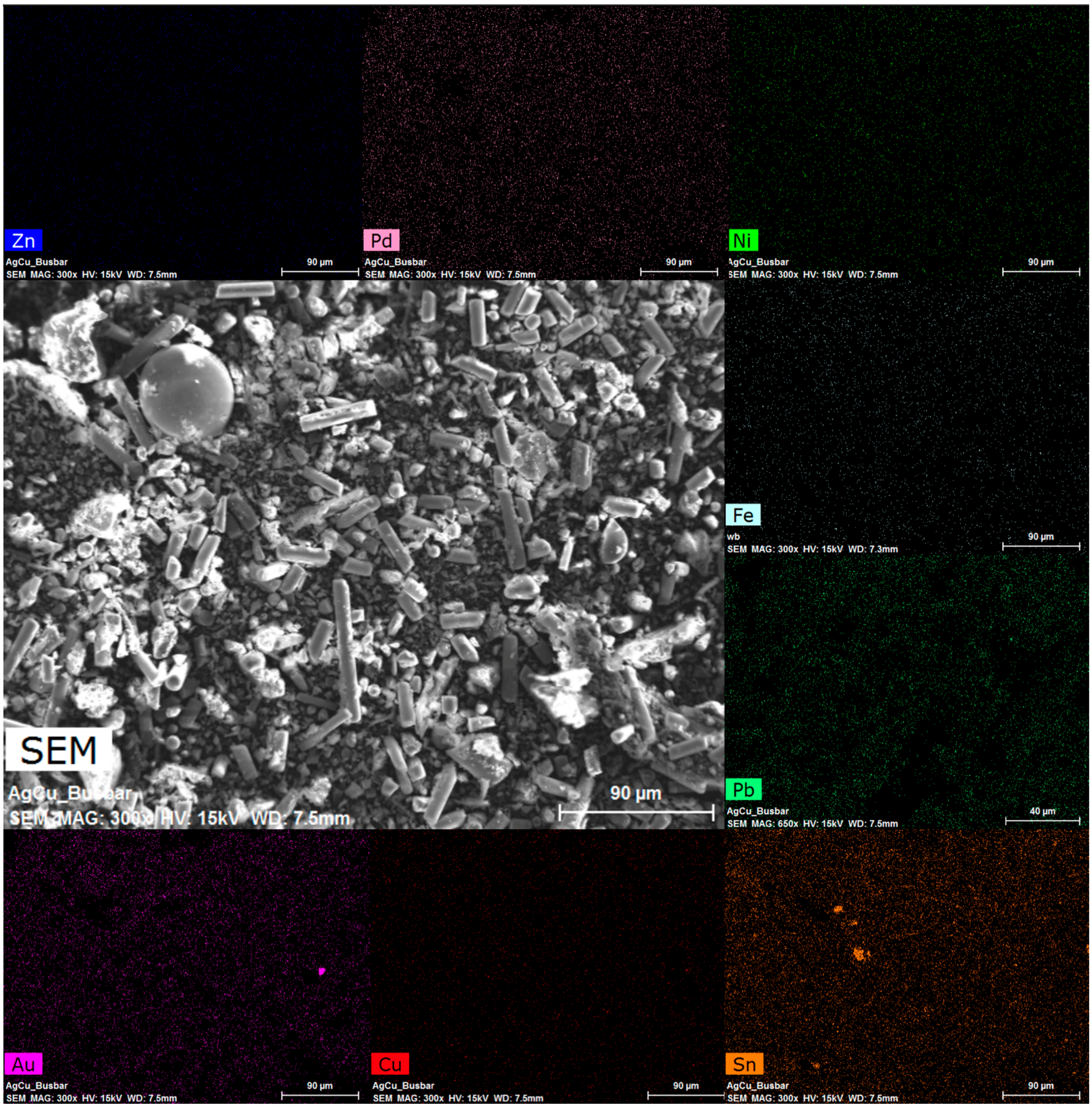

Figure 12. SEM images of residue of the green powder after the first stage of leaching and EDS map analysis of elements (purple: Au, red: Cu, orange: Sn, seafoam green: Pb, light green: Ni, pink: Pd, light blue: Fe, dark blue: Zn). Leaching conditions: 1 g of WPCB powder, 1 M HNO_3, 40 °C, 6 h.

In the second stage of leaching using thiourea, detecting any residual transition and precious metals was challenging. The combined effect of both leaching stages is evident as there are no traces of base or precious metals left, highlighting the achievement of extracting almost all metals from the WPCBs through two leaching stages, as presented in Figure 13.

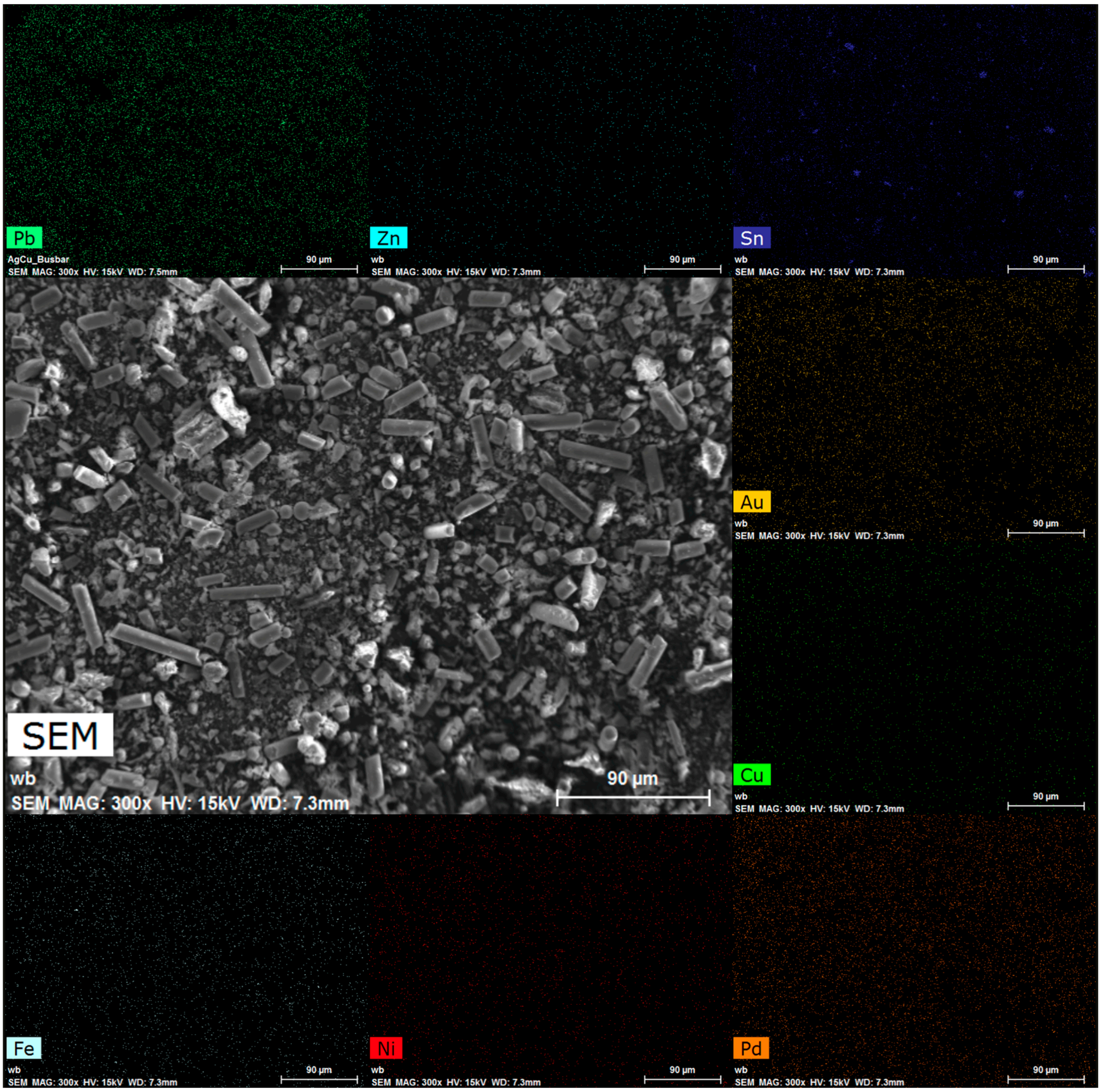

Figure 13. SEM images of residue after the second stage of leaching and EDS map analysis of elements (light blue: Fe, red: Ni, orange: Pd, seafoam green: Pb, yellow: Au, dark blue: Zn, aqua blue: Zn, light green: Cu). Under the conditions of 6 g/L of ferric ion, 1 M thiourea, and 0.1 M H_2SO_4, 50 °C, and for 24 h.

3.5. Economic Consideration

To evaluate the commercial potential of thiourea leaching and its global applicability, a comprehensive analysis is crucial. Studies show thiourea offers advantages like rapid Au extraction and low human and environmental toxicity compared to traditional methods like cyanide leaching [5,14,15]. However, current challenges include cost and reagent consumption due to a process still under development [5,53]. Similar to other leaching reagents, careful techno-economic evaluation is essential for thiourea systems. This evaluation examines the balance between environmental benefits and economic feasibility of using thiourea. Key aspects include reducing toxic byproducts, comparing costs with alternative reagents, and assessing Au recovery efficiency. Considerations include potential cost fluctuations and recycling feasibility. The impact of technological advancements on cost reduction is also evaluated, aiming to balance environmental and economic factors in using thiourea for Au recovery. Research can focus on methods to enhance Au recovery efficiency and minimize thiourea oxidation (the process that breaks down the reagent, increasing cost). Aligning with global environmental regulations and investing in research can make thiourea leaching economically viable. By addressing these challenges and leveraging its environmental benefits, thiourea leaching has the potential to become a competitive and eco-friendly alternative in the Au extraction industry. It offers a win-win scenario for both financial gain and environmental responsibility. Based on the literature studies [14,54] Table 6 compares cyanidation, thiourea, and thiosulfate leaching techniques to provide some suggestions for the analysis of different reagents. Cyanidation is effective and well researched but poses high environmental risks. Thiourea provides a balanced approach with moderate financial and environmental scores, offering reduced toxicity. Thiosulfate is the most environmentally friendly but less efficient and researched. Overall, thiourea emerges as a promising alternative, balancing efficiency and sustainability.

Table 6. The basic evaluation index scores for various leaching techniques.

Financial Sustainability		Effect on Environment		Level of Research	
Rate of Leaching	**Reagent Cost**	**Corrosive**	**Toxicity**	**Reliability**	**Leaching Technique**
3	5	5	0	5	Cyanidation
4	4	4	4	4	Thiourea
2	2	5	4	2	Thiosulfate

4. Conclusions

This study implemented a two-step leaching strategy using thiourea to selectively dissolve transition and precious metals. In the first stage, over 90 wt% of transition metals (Cu, Fe, Ni, Pb, and Sn) and 78% of Zn were dissolved under optimal conditions of 1 M HNO_3 and 40 °C. In the second leaching stage, optimal conditions were found to be 6 g/L ferric ions, 1 M thiourea, 0.1 M sulfuric acid, and 50 °C. Ferric ions enhance Au recovery by promoting thiourea oxidation; however, excessive amounts (>6 g/L) lead to iron sulfate precipitates, which may reduce recovery. Pd recovery was highest without ferric ions, as concentrations exceeding 3 g/L accelerated thiourea oxidation, thus hindering Pd recovery. Additionally, increasing sulfuric acid concentration improved both Au and Pd recoveries, peaking at 50.3 wt% with 0.2 M acid. Thiourea was beneficial up to 1 M for Au (49.0 wt%) and 1.5 M for Pd (43.8 wt%), though prolonged leaching decreased Au recovery due to reagent depletion. The highest recoveries were obtained at 50 °C, with Au at 52.9 wt% and Pd at 54.4 wt%. However, temperatures exceeding 70 °C caused thiourea to decompose and resulted in impurity precipitation, which hindered the dissolution of the metals. Moreover, the pseudo-second-order kinetic model was most suitable for both leaching stages. EDS analysis confirmed substantial transition metal dissolution after the first stage and effective extraction of both transition and precious metals after the second stage. Consequently, this two-step leaching process significantly enhances metal recovery and contributes to sustainability efforts.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/waste2030018/s1, **Table S-I:** The replicates of recovery rate of chemical applications alongside their respective standard deviations, conducted as preliminary steps prior to the selection of nitric acid leaching with metals presented. **Table S-II:** The replicate tests of recovery rates of varying nitric acid concentrations (M) in Figure 2, alongside their associated standard deviations of shown metals in the first stage of leaching. **Table S-III:** The replicate tests of recovery rates of different temperature levels of Figure 3, alongside their associated standard deviations of shown metals in the first stage of leaching. **Table S-IV:** The duplicate tests of varied concentrations of thiourea (M) in Figure 4 with their corresponding standard deviations after the second stage of leaching. **Table S-V:** The duplicate trials with recovery rates for the different concentration of ferric ion (g/L) in Figure 5 with their corresponding standard deviations following the second stage of leaching. **Table S-VI:** The replicate tests of recovery rate of the varied concentration of sulfuric acid (M) in Figure 6 with their corresponding standard deviations following the second stage of leaching. **Table S-VII:** The replicate tests with minimum recovery rates and their respective standard deviations following the second stage of leaching, where temperature levels were varied in Figure 7. **Table S-VIII-a:** The tests for the kinetics of leaching were conducted within a 6-h timeline in the first stage of leaching in manuscript in Table 3. **Table S-VIII-b:** The Standard deviations of duplicate tests for the kinetics of leaching were conducted within a 6-h timeline in the first stage of leaching in Table 3. **Table S-IX-a:** The tests for the kinetics of leaching were conducted within a 24-h timeline in the second stage of leaching in manuscript in Table 3. **Table S-IX-b:** The Standard deviations of duplicate tests for the kinetics of leaching were conducted within a 24-h timeline in the second stage of leaching in Table 3.

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