RESEARCH ARTICLE

Non-toxic, high selectivity process for the extraction of precious metals from waste printed circuit boards
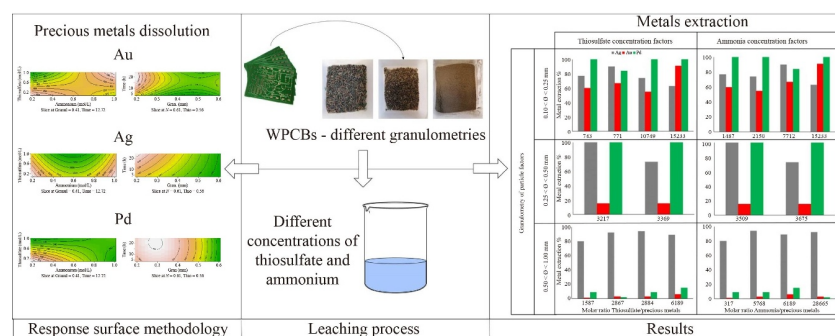
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GRAPHIC ABSTRACT

ABSTRACT

The work presented here focused on the extraction of gold (Au), silver (Ag) and palladium (Pd) from electronic waste using a solution of ammonium thiosulfate. Thiosulfate was used as a valid alternative to cyanide for precious metal extractions, due to its non-toxicity and high selectivity. The interactions between sodium thiosulfate, total ammonia/ammonium, precious metal concentrations and the particle size of the waste printed circuit boards (WPCBs) were studied by the response surface methodology (RSM) and the principal component analysis (PCA) to maximize precious metal mobilization. Au extraction reached a high efficiency with a granulometry of less than 0.25 mm, but the consumption of reagents was high. On the other hand, Ag extraction depended neither on thiosulfate/ammonia concentration nor granulometry of WPCBs and it showed efficiency of 90% also with the biggest particle size ($0.50 < \emptyset < 1.00$ mm). Pd extraction, similarly to Au, showed the best efficiency with the smallest and the medium WPCB sizes, but required less reagents compared to Au. The results showed that precious metal leaching is a complex process (mainly for Au, which requires more severe conditions in order to achieve high extraction efficiencies) correlated with reagent concentrations, precious metal concentrations and WPCB particle sizes. These results have great potentiality, suggesting the possibility of a more selective recovery of precious metals based on the different granulometry of the WPCBs. Furthermore, the high extraction efficiencies obtained for all the metals bode well in the perspective of large-scale applications.
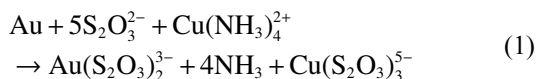
1 Introduction

A relevant fraction of the electronic industry waste consists of waste printed circuit boards (WPCBs), which represent around 5% of the whole electronic waste (e-waste) and they contain relevant amounts of strategic metals. These metals often exceed the concentration in natural minerals (Liu et al., 2016; Wu et al., 2017). This is the case of Au, which shows concentrations in WPCBs up to 70%, greater than that in the ores (Liu et al., 2016; Wu et al., 2017). Therefore, the recovery of strategic metals from e-waste bodes well for the conservation of resources since it delays the exhaustion of metals from ores and it avoids the environmental, economic and social issues of mining (Pham and Ting, 2009). Furthermore, the implementation of techniques to recover metals from

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this kind of waste is considered crucial for a more effective waste management (Cui and Zhang, 2008; Ha et al., 2014). Traditional methods for e-waste management, such as landfilling, incineration and exportation to underdeveloped countries (where safety standards are not complied), can cause relevant pollution with harmful effects for both the atmosphere, due to the gases resulting from thermal treatments, and for soil and water, due to the possible dissolution of heavy metals (Akcil et al., 2015; Islam et al., 2020). The proper management of e-waste can overcome these problems and preserve the health of both people and the environment (Islam et al., 2020) with a possible reduction of air and water pollution of up to 80% (Kaya, 2019).
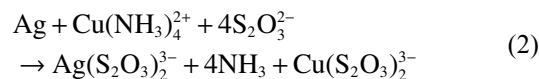
Hydrometallurgy is an approach used in the field of extractive metallurgy to obtain precious metals from ores and e-waste, performed by leaching using a variety of chemicals. Cyanide is one of the most common solutions for the leaching of precious metals and has been used for over a century in the mining industry due to its advantages, like high efficiency and low consumption rate (Komnitsas and Pooley, 1991; Kulandaisamy et al., 2003; Zhang et al., 2012). However, the main issue with cyanide use is its toxicity. Therefore, research focused on the identification of alternative lixiviants, such as thiourea, thiosulfate and halide. Among these, thiosulfate is very attractive for its high selectivity of precious metals and its properties of non-toxicity and non-corrosivity. Thiosulfate was used as a substitute to cyanide for the extraction of Au from both ores (Cui and Zhang, 2008) and e-waste (Senanayake, 2004; Ha et al., 2010; Li et al., 2012; Zhang et al., 2012; Petter et al., 2014; Camelino et al., 2015; Zhang and Senanayake, 2016). The dissolution of Au in ammonia thiosulfate solution is an electrochemical reaction catalyzed by the presence of cupric ions, which act as catalysts (Cui and Zhang, 2008). The leaching mechanism of thiosulfate in the presence of cupric ions is described by the Eq. (1):

$$
\begin{aligned}
& Au + 5S_2O_3^{2-} + Cu(NH_3)_4^{2+} \\
& \rightarrow Au(S_2O_3)_2^{3-} + 4NH_3 + Cu(S_2O_3)_3^{5-}
\end{aligned} \tag{1}
$$

The copper-ammonia complexes acquire the electrons on the cathodic portion of Au surface and then they are reduced. At the same time, ammonia or thiosulfate ions react with the Au ions on the anodic surface, forming the complexes $Au(NH_3)_4^{2-}$ or $Au(S_2O_3)_2^{3-}$. The dominant reaction depends on the concentration of the species in solution (Aylmore and Muir, 2001; Cui and Zhang, 2008) but the formation of the more stable $Au(S_2O_3)_2^{3-}$ complex is favoured (Zhang et al., 2012). The Au-thiosulfate complex is quite stable once formed. Nevertheless, both the presence of oxygen and the maintenance of the alkalinity conditions are necessary to avoid the thiosulfate decomposition and to guarantee the copper-ammonia complex stability (Cui and Zhang, 2008). Furthermore, in an alkaline environment the tetrathionate (which is easily

formed by thiosulphate oxidation) can be converted back into thiosulfate (Zhang et al., 2012).

The leaching mechanism for Ag by ammonia thiosulfate solution with cupric ions is comparable to that of Au (Oh et al., 2003) (Eq. (2)).

$$
\begin{aligned}
& Ag + Cu(NH_3)_4^{2+} + 4S_2O_3^{2-} \\
& \rightarrow Ag(S_2O_3)_2^{3-} + 4NH_3 + Cu(S_2O_3)_2^{3-}
\end{aligned} \tag{2}
$$

Although important, Pd has received less attention compared to other precious metals. It was demonstrated that Pd forms high stability complexes with thiosulfate ions (PdS_2O_3) which can be dissolved, as well as Au and Ag (Tyutyunnik et al., 2016).

The main issue linked to the thiosulfate use is the high consumption of reagents for metal mobilization, which makes this process neither economically, nor environmentally-friendly (Cui and Zhang, 2008; Zhang et al., 2012).

The present study assessed the effectiveness of ammonium thiosulfate for the mobilization of Au, Ag and Pd from end-of-life computer WPCBs, at different operative conditions. The response surface methodology (RSM) was selected to study the influence of several parameters, such as sodium thiosulfate concentration, total ammonia/ammonium concentration, granulometry of WPCBs and their interaction with the leaching time. The further optimization by RSM helped to understand the interaction among the parameters at various levels. Furthermore, this work considered three different WPCB particle sizes to verify the real effect of this parameter on metal mobilizations by thiosulfate.

The objectives of this study were:

1) The study of the influence and the interaction among sodium thiosulfate concentration, total ammonia/ammonium concentration and leaching time on Au, Ag and Pd mobilization.

2) The analysis of the effect of different WPCB particle sizes on the process efficiency.

3) The optimization of the leaching conditions for Au, Ag and Pd by RSM.

2   Materials and methods

2.1   Printed circuit boards from computers

The WPCBs for the leaching tests were pre-treated as reported by Becci et al. (2020). More precisely, the WPCBs were shredded, crushed, and washed by water saturated with NaCl for plastic removal. The plastic fraction can be re-used for bottle production or converted into energy through incineration, pyrolysis and gasification (Kaya, 2019; Islam et al., 2020). WPCBs were pre-treated by a chemical leaching with 50 g/L Fe^{3+} to avoid the interference between Cu and thiosulfate (Becci et al., 2019, 2020). After this step, Cu content decreased from 25% w/w to 5% w/w and precious metal

concentrations increased. The recovered Cu can be considered a secondary raw material for the current metal market (Kaya, 2019; Becci et al., 2020). The resulting WPCBs were crushed another time to obtain different dimensions: $0.1 < Ø < 0.25$ mm, $0.25 < Ø < 0.50$ mm and $0.50 < Ø < 1$ mm (Fig. 1).

2.2   Leaching test

Thiosulfate leaching experiments were performed following a full factorial plan to investigate the effects of sodium thiosulfate concentration (0.1, 1 mol/L), total ammonia/ammonium concentration (0.2, 1 mol/L) and WPCB particle sizes ($0.1 < Ø < 0.25$ mm; $0.50 < Ø < 1$ mm) on the Au, Ag and Pd mobilization. The reagents used were sodium thiosulfate ($Na_2S_2O_3$ anhydrous, 98%), ammonium hydroxide (NH_4OH, 30%), ammonium sulfate ((NH_4)$_2SO_4$, 99%) and copper sulfate ($CuSO_4$·$5H_2O$) obtained from Carlo Erba Srl, Italy. Furthermore, the central points of the factorial plan were analyzed (thiosulfate 0.55 mol/L, ammonia/ammonium 0.6 mol/L and WPCB particle sizes $0.25 < Ø < 0.50$ mm). $CuSO_4$ concentration was fixed at 10 mmol/L. All the leaching experiments were carried out by mixing 10 g/L of WPCBs and 0.5 L of ammonium thiosulfate solution. The pH was kept between 10 and 10.5 throughout the experiment by adding NaOH 10 mol/L. The experiments were performed at an agitation speed of 120 r/min at 25 °C for 24 h. The samples for chemical analysis were withdrawn every 4, 8, 16 and 24 h to determine the time effect.

2.3   Analytical determination and statistical analysis

Leaching solution samples (5 mL) and resulting solid samples (residues of leaching experiments) were analyzed to determine the metal concentrations by atomic absorption spectrophotometer (AAS) (Varian SpectrAA 220, Germany).

During the entire leaching experiment the pH was analyzed by a pH metro inoLab Multi 720 (Labexchange, Germany). The obtained results were optimized by central composite design (CCD) to assess the optimal experimental plan. The metal dissolutions, represented by the metal concentrations in the leach liquor (Y, μg/L), were taken as the response variables, while the initial ammonia/ammonium concentration (X_1, mol/L), the initial thiosulfate concentration (X_2, mol/L), and the granulometry of WPCBs (X_3, mm) were considered as independent variables (factors). The influence of the leaching time (X_4, hours) was also considered as a factor. Table 1 reports their levels (Table 1). The required experimental runs were 10 ($2^k + 2k + n_0$), where k is the number of the factorial points (= 2) and n_0 the central points (= 2). The CCD model allowed to obtain experimental results that can be expressed by Eq. (3):

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k-1} \sum_{j=1}^{k} b_{ij} X_i X_j + \sum_{i=1}^{k} b_{ii} X_i^2 + \varepsilon,$$
(3)

where b_0 is the constant coefficient, b_i, b_{ii}, and b_{ij} are the linear, second order, and interaction constants, respectively, and ε is random error.

Principal Component Analysis (PCA) was performed using the rsm package in RStudio software. The PCA led to detailed understanding as the molar ratio between ammonia or thiosulfate, the precious metal concentrations and the percentage of Au, Ag and Pd extraction (dependent variables) were correlated with the WPCB granulometry (independent variable).
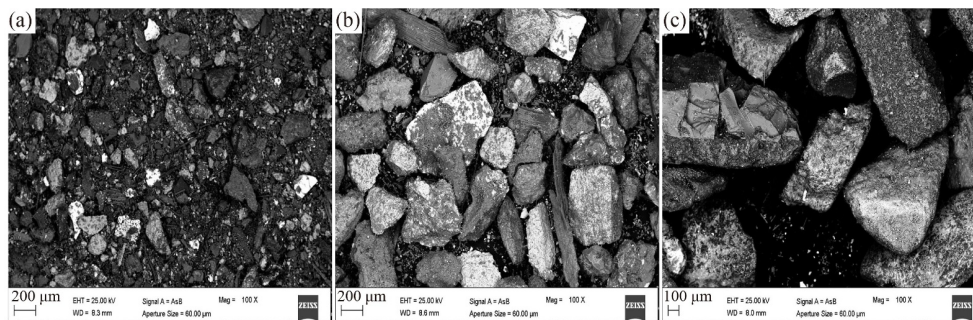

Fig. 1   WPCBs with different granulometries: lower than $0.10 < Ø < 0.25$ mm (a), $0.25 < Ø < 0.50$ mm (b) and $0.50 < Ø < 1.00$ mm (c) tested by SEM analysis.

Table 1   Factors and levels for the CCD-RSM

Code	Factors	−1	0	+ 1
X_1	[Ammonia/ammonium] (mol/L)	0.2	0.6	1
X_2	[Thiosulfate] (mol/L)	0.1	0.55	1
X_3	Granulometry (mm)	$0.1 < Ø < 0.25$	$0.25 < Ø < 0.50$	$0.50 < Ø < 1.00$

3   Results and discussion

3.1   Au leaching

The results in Fig. 2 show the Au mobilization profiles in the liquor, at different times, with three WPCB particle sizes (small: $0.10 < \emptyset < 0.25$ mm, medium: $0.25 < \emptyset < 0.50$ mm and large: $0.50 < \emptyset < 1$ mm) and different concentrations of thiosulfate and ammonia/ammonium. The highest Au mobilization (2 mg/L) was achieved after 16 h with the smallest WPCBs particle size and 0.2 mol/L ammonia/ammonium and 0.1 mol/L thiosulfate concentrations or 1 mol/L ammonia/ammonium and 1 mol/L thiosulfate concentrations (Fig. 2). Au dissolution was very low, less than 0.5 mg/L, using the medium and the biggest WPCB particle size, at all the tested conditions. Au extraction was limited by the increase in particle size dimension, which does not allow good material mixing, decreasing the contact between the precious metal and the leaching agent (Birloaga et al., 2013). It is evident that the reduction of WPCB size had a significant effect on the metal dissolution. The smallest particle size ensured the contact between the WPCBs and the thiosulfate, offering a large metal exposure area (Tripathi et al., 2012; Birloaga et al., 2013). The best operating conditions were obtained using the molar ratio 1:1 between thiosulfate and ammonia/ammonium concentrations. The increase in ammonia/ammonium concentration could improve Cu dissolution and the formation of high concentrations of copper-ammonia complexes which catalyze Au dissolution (Eq. (1)). The enhanced dissolution of Cu could also increase the dissolution of Au-bearing Cu particles, which is the most common form of Au in the WPCBs, growing the Au recovery (Jeon et al., 2020).

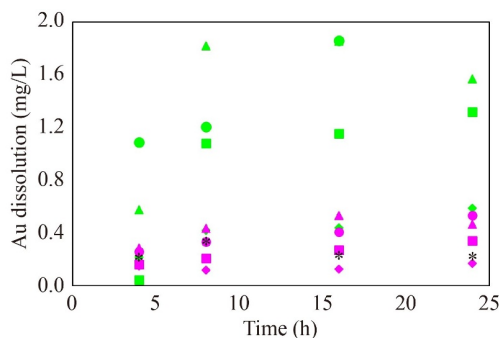The results were analyzed by CCD to optimize the considered factors. The Au concentration in the liquor was modeled as a function of initial ammonia/ammonium concentration, thiosulfate concentration, WPCB particle sizes and leaching time, and can be expressed by the following equation (Eq. (4)):

$$Au = 353.40 + 79.16X_1 - 57.66X_2 - 360.89X_3 + 98.69X_4 \\ + 247.15X_1X_2 - 47.91X_1X_3 + 25.00X_1X_4 + 47.40X_2X_3 \\ - 18.46X_2X_4 - 48.81X_3X_4 + 422.34X_3^2 - 34.75X_4^2. \tag{4}$$

Figure 3 shows the normal probability plot for the performed analysis of variances, indicating the normal distribution of residuals and the validity of analysis (R^2 of 0.92).

The ANOVA analysis highlighted that all the factors and their interactions affected Au mobilization (Table 2). More precisely, a negative effect was exerted by both thiosulfate concentration and granulometry while ammonia/ammonium concentration showed a positive effect (Eq. (5)).

The statistical analysis confirmed that the best operative condition for Au chemical leaching was 1:1 molar ratio between thiosulfate and ammonia/ammonium concentration (Fig. 4(a)). The granulometry increase reduced the Au dissolution in the liquor (Fig. 4(b)).

3.2   Ag leaching

Figure 5 reports the Ag mobilization profiles in the liquor with three WPCB particle sizes and different concentrations of thiosulfate and ammonia/ammonium. The highest Ag mobilization (around 15 mg/L) was achieved after 8 h, with the smallest WPCB particle size and 0.1 mol/L thiosulfate and 0.2 or 1 mol/L ammonia/ammonium concentrations (Fig. 5). With the largest WPCB particle size Ag dissolution increased during the leaching process with 0.1 mol/L thiosulfate and 0.2 or 1 mol/L ammonia/ammonium, but the values were lower, around 6.5 mg/L, compared to the smallest WPCB size. The medium size, with the central values of thiosulfate
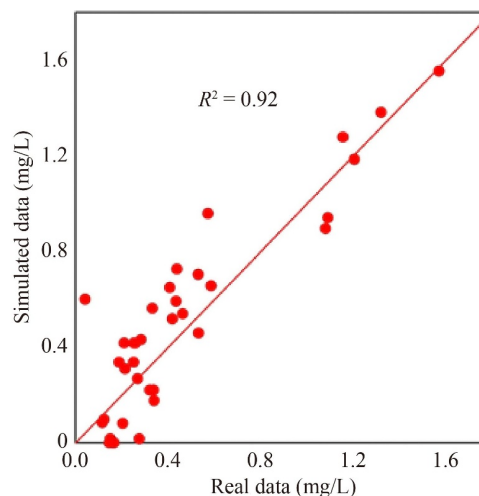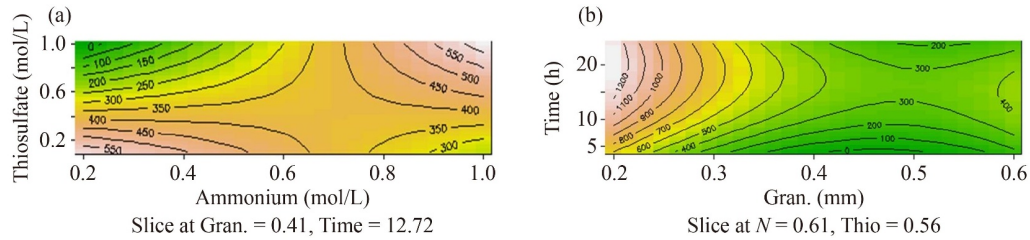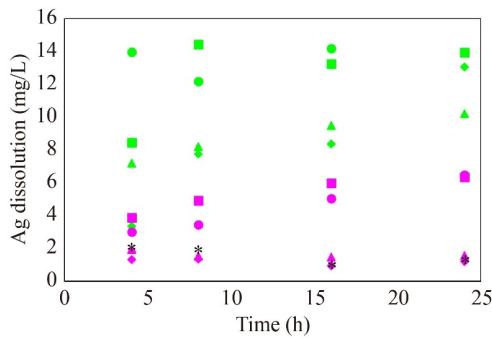

Fig. 2   Au dissolution in the final liquor with small size WPCBs (0.10 $< \emptyset < 0.25$ mm, in green): ● 0.2 mol/L NH$_3$ 0.1 mol/L thiosulfate, ■ 1 mol/L NH$_3$ 0.1 mol/L thiosulfate, ◆ 0.2 mol/L NH$_3$ 1 mol/L thiosulfate, ▲ 1 mol/L NH$_3$ 1 mol/L thiosulfate; big size WPCBs (0.50 $< \emptyset < 1.00$ mm, in pink): ● 0.2 mol/L NH$_3$ 0.1 mol/L thiosulfate, ■ 1 mol/L NH$_3$ 0.1 mol/L thiosulfate, ◆ 0.2 mol/L NH$_3$ 1 mol/L thiosulfate, ▲ 1 mol/L NH$_3$ 1 mol/L thiosulfate; and medium size (0.25 $< \emptyset < 0.50$ mm, in black): * 0.6 mol/L ammonia/ammonium 0.55 mol/L thiosulfate.

Fig. 3   Simulated data *vs*. real data for Au mobilization.

Table 2   Summary of ANOVA results for RSM for Au mobilization

Sources	Sum of squares	df	Mean square	F-value	p-value
Linear (X_1, X_2, X_3, X_4)	4746626	4	1186656	15.67	****
Interaction (X_1, X_2, X_3, X_4)	2335806	6	389301	5.14	**
Quadratic (X_3, X_4)	1467480	2	733740	9.69	***
Residual	1968507	26	75712		
Lack of fit	1957804	22	88991	33.26	**
Pure error	10703	4	2676		

Fig. 4   Contours of thiosulfate *vs.* ammonium (a) and time *vs.* granulometry (b) for Au mobilization.

Fig. 5   Ag dissolution in the final liquor with small size WPCBs (0.10 < Ø < 0.25 mm, in green): ● 0.2 mol/L NH$_3$ 0.1 mol/L thiosulfate, ■ 1 mol/L NH$_3$ 0.1 mol/L thiosulfate, ♦ 0.2 mol/L NH$_3$ 1 mol/L thiosulfate, ▲ 1 mol/L NH$_3$ 1 mol/L thiosulfate; big size WPCBs (0.50 < Ø < 1.00 mm, in pink): ● 0.2 mol/L NH$_3$ 0.1 mol/L thiosulfate, ■ 1 mol/L NH$_3$ 0.1 mol/L thiosulfate, ♦ 0.2 mol/L NH$_3$ 1 mol/L thiosulfate, ▲ 1 mol/L NH$_3$ 1 mol/L thiosulfate; and medium size (0.25 < Ø < 0.50 mm, in black): * 0.6 mol/L ammonia/ammonium 0.55 mol/L thiosulfate.

and ammonia/ammonium concentrations (0.55 mol/L and 0.6 mol/L, respectively) gave low metal dissolution rate, as well as the largest WPCB particle size with 1 mol/L thiosulfate. This result could probably be correlated to an unfavorable ratio between thiosulfate and ammonia. The ammonia presence is fundamental for the metal mobilization, which occurred when the cupric ions in solution are fully complexed with ammonia, irrespective of its concentration. Previous work reported that Ag leaching was strictly dependent on pH values, a pH > 9.8 resulted in achieving the maximum cupric-tetraamine concentration, resulting in a high Ag dissolution (Ibarra-Galvan et al., 2014).

The dissolved Ag concentration in the liquor was modeled by statistical analysis as a function of initial ammonia/ammonium concentration, thiosulfate concentration, WPCB particle sizes and leaching time. The prediction model for Ag dissolution reflected the experimental data, with an R^2 of 0.97 (Fig. 6). The final predicted equation for Ag dissolution can be expressed as follows (Eq. (5)):

$$Ag = 1486.77 + 63.35X_1 - 2083.70X_2 - 3802.32X_3$$
$$+ 455.44X_4 + 247.27X_1X_2 + 282.45X_1X_3 - 152.46X_1X_4$$
$$+ 360.95X_2X_3 - 49.28X_2X_4 - 324.05X_3X_4$$
$$+ 5473.64X_3^2 - 13.77X_4^2,$$
(5)

The ANOVA analysis showed that all the factors considered influenced the predicted response at a significant level, while their interaction was not statistically significant (Table 3). As can be seen in Fig. 7(a),
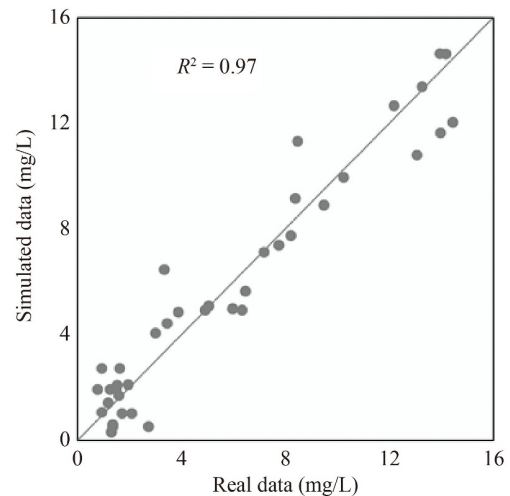

Fig. 6   Simulated data *vs.* real data for Ag mobilization.

Table 3   Summary of ANOVA results for RSM for Ag mobilization

| Sources	Sum of squares	df	Mean square	F-value	p-value
Linear (X_1, X_2, X_3, X_4)	551305110	4	137826277	60.98	****
Interaction (X_1, X_2, X_3, X_4)	12257716	6	2042953	0.90	0.51
Quadratic (X_3, X_4)	189728172	2	94864086	41.97	****
Residual	58764834	26	2260186		
Lack of fit	57380976	22	2608226	7.54	*
Pure error	1383858	4	345964		
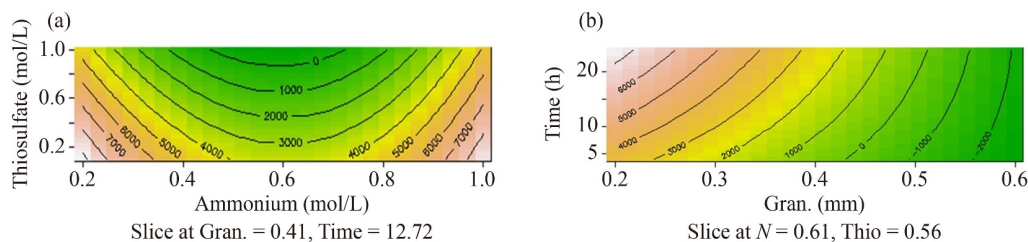
Fig. 7   Contours of thiosulfate *vs.* ammonium (a) and time vs granulometry (b) for Ag mobilization.

ammonia/ammonium concentration had a positive effect in low range (0.1–0.2 mol/L and 0.9–1 mol/L) and a negative effect in the central values at all the thiosulfate concentrations (Fig. 7(a)), granulometries and times tested (data not shown). Concerning the WPCB particle size, only the smallest size exerted a positive effect on Ag dissolution (Fig. 7(b)).

3.3   Pd leaching

Figure 8 reports the Pd mobilization profiles in the liquor during the leaching process. Pd mobilization was around 300–400 µg/L at all the tested concentrations of thiosulfate and ammonia/ammonium and using both the small and medium WPCB particle size (Fig. 8). Pd dissolution was very low (< 50 µg/L) in all the tests which used the largest WPCB particle size. As well as Au and Ag, Pd extraction was affected by particle dimension. However, Pd mobilization showed higher efficiencies, compared to both Au and Ag, using medium WPCBs. The achieved results were comparable to those observed with the smallest WPCB size.

Figure 8 shows that thiosulfate and ammonia/ammonium concentrations were not selective for metal dissolution and there were not any big differences in metal dissolution among the treatments. Overall, the rate of metal dissolution was high also in the central points of the factorial plan. It is possible that the low mobilization of Au and Ag using the medium WPCB particle size favoured a greater availability of thiosulfate for Pd, increasing its dissolution. Most previous work focused on Pd mobilization and used chloride solution as the leaching agent (Quinet et al., 2005; Viñals et al., 2006; Behnamfard et al., 2013) and they reported that Pd
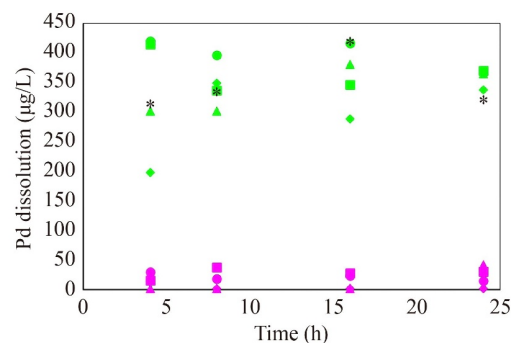
Fig. 8   Pd dissolution in the final liquor with small size WPCBs (0.10 < Ø < 0.25 mm, in green): ● 0.2 mol/L NH₃ 0.1 mol/L thiosulfate, ■ 1 mol/L NH₃ 0.1 mol/L thiosulfate, ♦ 0.2 mol/L NH₃ 1 mol/L thiosulfate, ▲ 1 mol/L NH₃ 1 mol/L thiosulfate; big size WPCBs (0.50 < Ø < 1.00 mm, in pink): ● 0.2 mol/L NH₃ 0.1 mol/L thiosulfate, ■ 1 mol/L NH₃ 0.1 mol/L thiosulfate, ♦ 0.2 mol/L NH₃ 1 mol/L thiosulfate, ▲ 1 mol/L NH₃ 1 mol/L thiosulfate; and medium size (0.25 < Ø < 0.50 mm, in black): * 0.6 mol/L ammonia/ammonium 0.55 mol/L thiosulfate.

leaching increases by increasing hydrogen chloride concentration from 2.5 to 5 mol/L at 60 °C (Behnamfard et al., 2013). The present paper demonstrated that the high Pd dissolution rate can also be obtained with thiosulfate, which is more environmentally-friendly than chloride, since it is not toxic or corrosive.

The results were statistically analysed to evaluate the effects of the considered factors on Pd mobilization. Thiosulfate and ammonia/ammonium concentrations had a negative effect on Pd concentration in the resulting liquor, while the interaction between the two factors was not statistically significant, as can be seen from the ANOVA analysis (Table 4). These effects are also

Table 4   Summary of ANOVA results for RSM for Pd mobilization

Sources	Sum of squares	df	Mean square	F-value	p-value
Linear (X_1, X_2, X_3, X_4)	919234	4	229809	22.63	****
Interaction (X_1, X_2, X_3, X_4)	103254	6	17209	1.69	0.16
Quadratic (X_3, X_4)	163732	2	81866	8.06	**
Residual	264071	26	10157		
Lack of fit	228562	22	10389	1.17	0.49
Pure error	35509	4	8877		

expressed by Eq. (6), which describes a quadratic model in agreement with the experimental data (Fig. 9):

$$Pd = 353.22 - 26.54X_1 - 26.50X_2 - 169.88X_3 + 6.33X_4 \\ + 35.72X_1X_2 + 26.24X_1X_3 + 14.33X_1X_4 + 16.64X_2X_3 \\ + 5.74X_2X_4 - 2.83X_3X_4 - 160.64X_3^2 - 2.01X_4^2. \quad (6)$$

As shown in Fig. 10, Pd dissolution was comparable at all the tested thiosulfate and ammonia/ammonium concentrations, ranging from 320 to 420 µg/L (Fig. 10(a)). On the other hand, the granulometry had the most significant effect on Pd mobilization. Taking this into consideration, the statistical analysis confirmed the greatest Pd dissolution at granulometry between 0.25 and 0.50 mm and the decrease in metal dissolution when the WPCB particle size increased above 0.50 mm (Fig. 10(b)).

3.4   PCA analysis

The previous models fit very well with the metal concentrations in the leach liquor. An additional statistical analysis was carried out to further understand how much each factor affected the leaching efficiency. The PCA analysis considered the efficiency (and not the metal
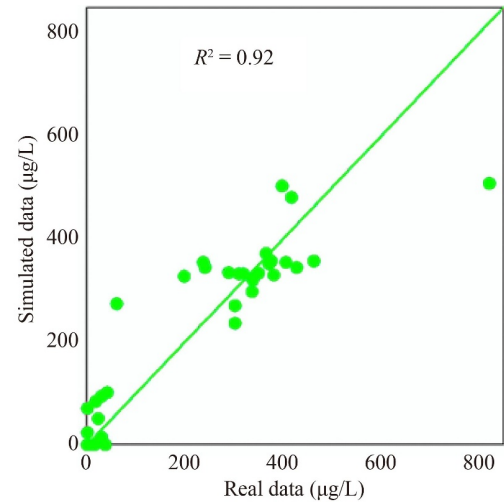
Fig. 9   Simulated data *vs.* real data for Pd mobilization.

concentrations) since the metal concentration in the leach liquor is affected by both thiosulfate and ammonia starting concentrations and the metal concentration in the initial sample. The metal contents were different in the three particle sizes (Table 5). Au showed a concentration 6 times lower in the smallest particles than in the largest
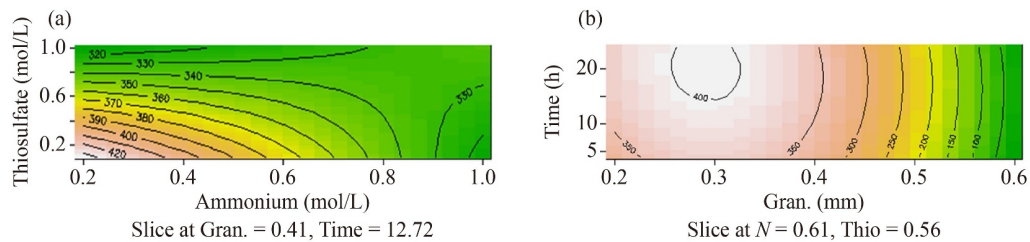
Fig. 10   Contours of thiosulfate *vs.* ammonium (a) and time *vs.* granulometry (b) for Pd mobilization.

Table 5   Metal concentrations in the different particle sizes (mg/kg)

Metal	Granulometry					
	0.10 < Ø < 0.25 mm		0.25 < Ø < 0.50 mm		0.50 < Ø < 1.00 mm	
	Mean	St.dev.	Mean	St.dev.	Mean	St.dev.
Au	170	± 30	212	± 6	1100	± 200
Ag	1690	± 50	220	± 3	400	± 100
Pd	42	± 4	32	± 8	30	± 6

one. On the other hand, Ag showed the opposite trend, the smallest particles had an Ag concentration 3 times higher than the largest one. Pd showed a constant concentration in the three particle sizes.

Considering the sample heterogeneity, the selected variables for PCA were the molar ratio between thiosulfate and precious metal concentrations in the starting sample, the molar ratio between ammonia and precious metal concentrations in the starting sample, the granulometry and the percentage of Au, Ag and Pd extraction. More precisely, the ratio between thiosulfate and precious metal concentrations increased around 15 times increasing the thiosulfate concentration from 0.1 to 1 mol/L with the smallest particle size. On the other hand, when the largest particle sizes were used, the molar ratio between thiosulfate and precious metal concentrations was quite constant, despite the initial thiosulfate concentration (Fig. 11(a)). Furthermore, the ratio between ammonia and the precious metal concentrations increased 6 times changing the ammonia concentration from 0.2 to 1 mol/L, with the smallest particle size. The ammonia concentration ranged between 300 and 30000 times higher than the precious metal concentrations with the largest particle size (Fig. 11(b)). On the contrary, the medium particle size showed a constant thiosulfate and ammonia concentration, around 3500 times higher than the precious metals with initial concentrations of 0.55 and 0.6 mol/L, respectively (Fig. 11). The data confirmed that as the ratio between the reagents and the initial metal concentrations was more fluctuating, these variables are more suitable, than the initial molar reagent concentrations, to understand the chemical leaching mechanism.

The results of the PCA analysis highlighted that the Au extraction is correlated with the ratio between thiosulfate and the precious metal concentrations, especially for the smallest particle size. The Au mobilization increased by decreasing the particle size from 0.50 to less than 0.25 mm and by increasing the molar ratio between thiosulfate/ammonia and precious metal concentrations. On the contrary, the Ag extraction efficiency was correlated more with the largest particle size and wasn't correlated with the ratio between thiosulfate and precious metal concentrations, or to the ratio between the ammonia and the precious metal concentrations (Fig. 12). The Ag extraction was between 70% and 90% for all the tested conditions, reaching the highest efficiency with the largest particle size, irrespective of the ammonia and thiosulfate concentrations. These results are more evident in Fig. 13. The Pd extraction showed the same trend of Au: the efficiency increased by decreasing the particle size, but it was around 100%, also with the medium particles (Fig. 13). Pd did not show any correlation with the thiosulfate and ammonia concentration, consistent with Ag.

4 Conclusions

The results showed that Au, Ag and Pd leaching is a complex process correlated with thiosulfate, ammonia and precious metal concentrations and WPCB particle sizes. The metal concentrations changed depending on the granulometry. The Au concentration decreased with decreasing particle size, while the Ag increased its concentration in the smallest particle size. On the other hand, the Pd concentration was constant regardless of the considered granulometry. The results highlighted that Au leaching took place only with a granulometry less than 0.25 mm. The percentage of extraction grew by increasing the molar ratio between thiosulfate/ammonia and precious metal concentrations and with a ratio between thiosulfate and ammonia concentration 1. These results emphasized a very high consumption of reagents. The Pd leaching showed the same Au dependence to granulometry. A granulometry lower than 0.50 mm was necessary to achieve extraction efficiencies higher than 90%. Concerning Ag, the extraction efficiencies were constant regardless of the considered granulometry. The results also showed that Ag and Pd leaching depended less on thiosulfate and ammonia concentrations. In both cases, the lowest reagent concentrations ensured high
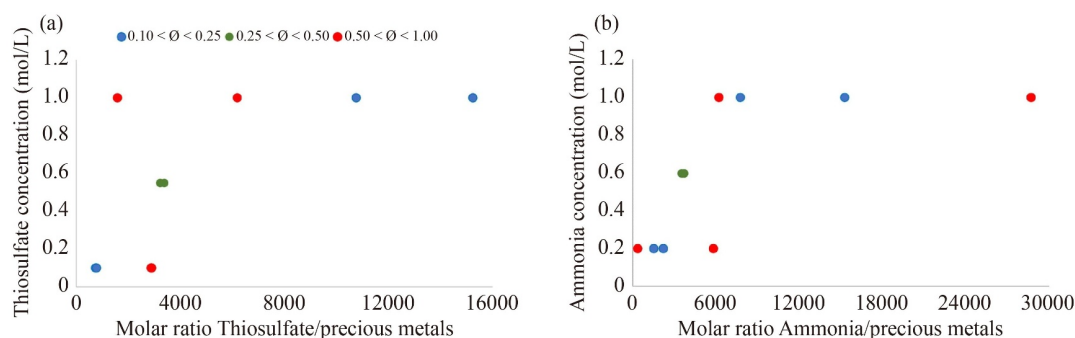

Fig. 11 Changing in the molar ratio between thiosulfate (a) or ammonia (b) and the precious metal concentrations in the different experimental plans.
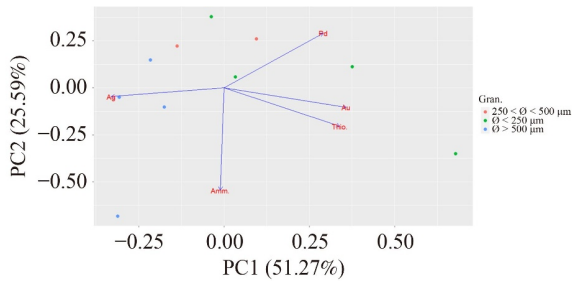
Fig. 12 Principal component analysis (PCA) results.

extraction efficiencies. These results suggest the possibility of a more selective recovery of precious metals based on the different granulometry of the WPCBs. Furthermore, the increase in selectivity can reduce the reagent consumptions, making the leaching process more sustainable and attractive for large-scale applications.

Further studies are needed to:

1) Optimize the WPCB grinding processes, since the particle size has proved to be crucial for the leaching of

Au but not for the other precious metals. A grinding circuit can be evaluated to decrease costs and increase efficiencies,

2) Verify the possibility of a leaching process in series. The combination of two chemical processes, or a chemical approach with a bacterial leaching, can focus, more selectively, on the single target metals by a better control of the experimental conditions.

The development of innovative and more sustainable hydrometallurgical techniques leads to safe e-waste recycling with a decrease of environmental issues.
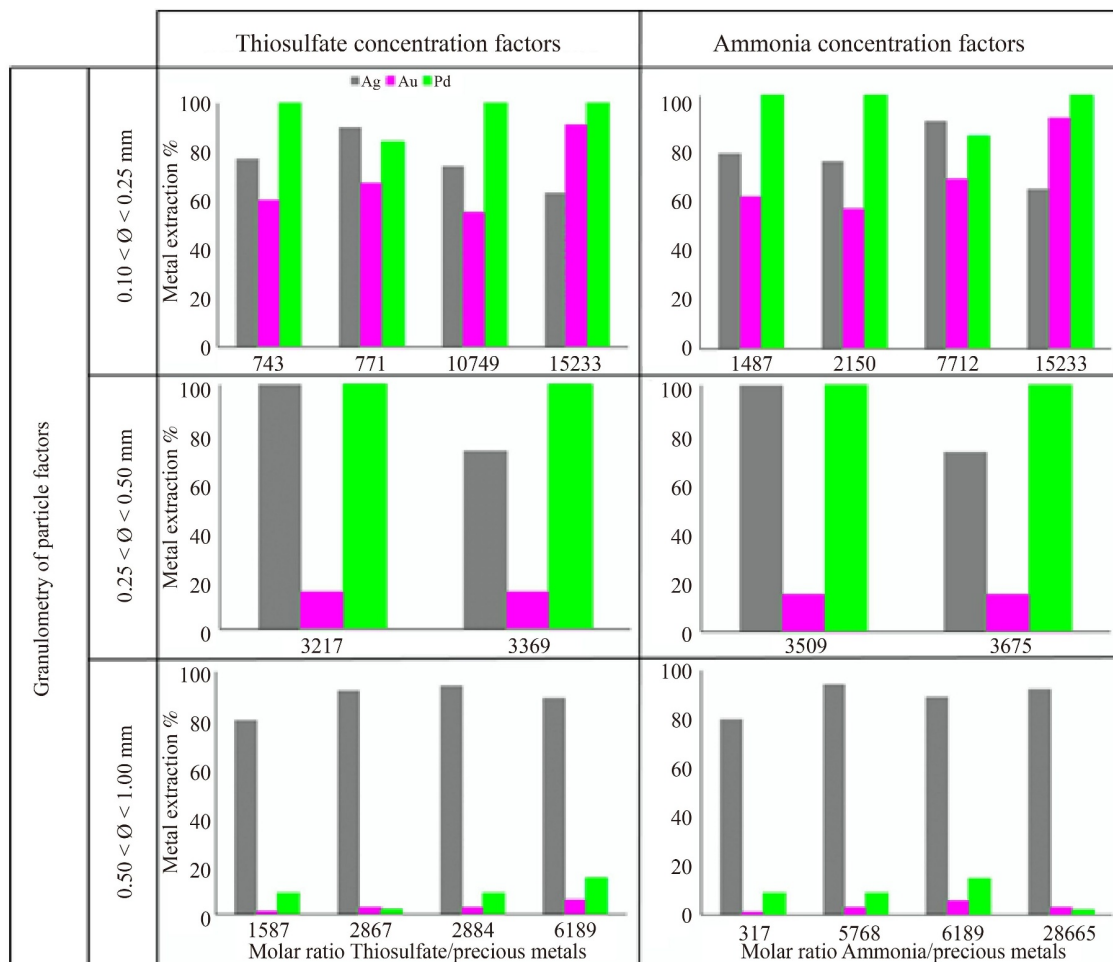
Fig. 13 Au, Ag and Pd extraction efficiencies (%) in the different experiments.

References

Akcil A, Erust C, Gahan C S, Ozgun M, Sahin M, Tuncuk A (2015). Precious metal recovery from waste printed circuit boards using cyanide and non-cyanide lixiviants: a review. Waste Management (New York, N.Y.), 45: 258–271

Aylmore M G, Muir D M (2001). Thiosulfate leaching of gold: a review. Minerals Engineering, 14(2): 135–174

Becci A, Amato A, Fonti V, Karaj D, Beolchini F (2020). An innovative biotechnology for metal recovery from printed circuit boards. Resources, Conservation and Recycling, 153: 104549

Becci A, Amato A, Rodríguez Maroto J M, Beolchini F (2019). Prediction model for Cu chemical leaching from printed circuit boards. Industrial & Engineering Chemistry Research, 58(45): 20585–20591

Behnamfard A, Salarirad M M, Veglio F (2013). Process development for recovery of copper and precious metals from waste printed circuit boards with emphasize on palladium and gold leaching and precipitation. Waste Management (New York, N.Y.), 33(11): 2354–2363

Birloaga I, De Michelis I, Ferella F, Buzatu M, Vegliò F (2013). Study on the influence of various factors in the hydrometallurgical processing of waste printed circuit boards for copper and gold recovery. Waste Management (New York, N.Y.), 33(4): 935–941

Camelino S, Rao J, Padilla R L, Lucci R (2015). Initial studies about gold leaching from printed circuit boards (PCB's) of waste cell phones. Procedia Materials Science, 9: 105–112

Cui J, Zhang L (2008). Metallurgical recovery of metals from electronic waste: a review. Journal of Hazardous Materials, 158(2–3): 228–256

Ha V H, Lee J C, Huynh T H, Jeong J, Pandey B D (2014). Optimizing the thiosulfate leaching of gold from printed circuit boards of discarded mobile phone. Hydrometallurgy, 149: 118–126

Ha V H, Lee J C, Jeong J, Hai H T, Jha M K (2010). Thiosulfate leaching of gold from waste mobile phones. Journal of Hazardous Materials, 178(1–3): 1115–1119

Ibarra-Galvan V, López-Valdivieso A, Tong X, Cui Y Q (2014). Role of oxygen and ammonium ions in silver leaching with thiosulfate-ammonia-cupric ions. Rare Metals, 33(2): 225–229

Islam A, Ahmed T, Awual M R, Rahman A, Sultana M, Aziz A A, Monir M U, Teo S H, Hasan M (2020). Advances in sustainable approaches to recover metals from e-waste: a review. Journal of Cleaner Production, 244: 118815

Jeon S, Tabelin C B, Park I, Nagata Y, Ito M, Hiroyoshi N (2020). Ammonium thiosulfate extraction of gold from printed circuit boards (PCBs) of end-of-life mobile phones and its recovery from pregnant leach solution by cementation. Hydrometallurgy, 191: 105214

Kaya M (2019). Electronic Waste and Printed Circuit Board Recycling Technologies. Berlin, Germany: Springer

Komnitsas C, Pooley F D (1991). Optimization of the bacterial okidation of an arsenical gold sulphide concentrate from Olympias, Greece. Minerals Engineering, 4(12): 1297–1303

Kulandaisamy S, Rethinaraj J P, Adaikkalam P, Srinivasan G N, Raghavan M (2003). The aqueous recovery of gold from electronic scrap. Journal of the Minerals Metals & Materials Society, 55(8): 35–38

Li J Y, Xu X L, Liu W Q (2012). Thiourea leaching gold and silver from the printed circuit boards of waste mobile phones. Waste Management (New York, N.Y.), 32(6): 1209–1212

Liu R, Li J, Ge Z (2016). Review on *Chromobacterium violaceum* for gold bioleaching from e-waste. Procedia Environmental Sciences, 31: 947–953

Oh C J, Lee S O, Yang H S, Ha T J, Kim M J (2003). Selective leaching of valuable metals from waste printed circuit boards. Journal of the Air & Waste Management Association, 53(7): 897–902

Petter P M H, Veit H M, Bernardes A M (2014). Evaluation of gold and silver leaching from printed circuit board of cellphones. Waste Management (New York, N.Y.), 34(2): 475–482

Pham V A, Ting Y P (2009). Gold bioleaching of electronic waste by cyanogenic bacteria and its enhancement with bio-oxidation. Advanced Materials Research, 71–73: 661–664

Quinet P, Proost J, Van Lierde A (2005). Recovery of precious metals from electronic scrap by hydrometallurgical processing routes. Minerals & Metallurgical Processing, 22(01): 17–22

Senanayake G (2004). Analysis of reaction kinetics, speciation and mechanism of gold leaching and thiosulfate oxidation by ammoniacal copper(II) solutions. Hydrometallurgy, 75(1–4): 55–75

Tripathi A, Kumar M, Sau D C, Agrawal A, Chakravarty S, Mankhand T (2012). Leaching of gold from the waste mobile phone printed circuit boards (PCBs) with ammonium thiosulphate. International Journal of Metallurgical Engineering, 1(2): 17–21

Tyutyunnik O A, Kubrakova I V, Pryazhnikov D V (2016). Formation and sorption behavior of the palladium thiosulfate complexes under natural conditions (model experiments). Geochemistry International, 54(1): 85–91

Viñals J, Juan E, Ruiz M, Ferrando E, Cruells M, Roca A, Casado J (2006). Leaching of gold and palladium with aqueous ozone in dilute chloride media. Hydrometallurgy, 81(2): 142–151

Wu Z, Yuan W, Li J, Wang X, Liu L, Wang J (2017). A critical review on the recycling of copper and precious metals from waste printed circuit boards using hydrometallurgy. Frontiers of Environmental Science & Engineering, 11(5): 8

Zhang X M, Senanayake G (2016). A review of ammoniacal thiosulfate leaching of gold: an update useful for further research in non-cyanide gold lixiviants. Mineral Processing and Extractive Metallurgy Review, 37(6): 385–411

Zhang Y, Liu S, Xie H, Zeng X, Li J (2012). Current status on leaching precious metals from waste printed circuit boards. Procedia Environmental Sciences, 16: 560–568