Selective recovery of palladium from waste printed circuit boards by a novel non-acid process

Zhiyuan Zhang, Fu-Shen Zhang*

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China

HIGHLIGHTS

- An environmentally friendly process was developed for the selective recovery of palladium.
- Palladium was successfully separated from base metals.
- 96.9% of Pd was recovered during the dissolution–extraction–stripping process.
- Extractant (S201) can be regenerated and used repeatedly.
- Neither corrosive acid nor strong oxidant was used in the process.

ARTICLE INFO

Article history:

Received 27 March 2014

Received in revised form 6 June 2014

Accepted 21 June 2014

Available online 28 June 2014

Keywords:

Waste PCBs

Recovery

Palladium

Extraction

S201

ABSTRACT

An environmental benign, non-acid process was successfully developed for selective recovery of palladium from waste printed circuit boards (PCBs). In the process, palladium was firstly enriched during copper recovery procedure and dissolved in a special solution made of CuSO_4 and NaCl . The dissolved palladium was then extracted by diisoamyl sulfide (S201). It was found that 99.4% of Pd(II) could be extracted from the solution under the optimum conditions (10% S201, A/O ratio 5 and 2 min extraction). In the whole extraction process, the influence of base metals was negligible due to the relatively weak nucleophilic substitution of S201 with base metal ions and the strong steric hindrance of S201 molecular. Around 99.5% of the extracted Pd(II) could be stripped from S201/dodecane with 0.1 mol/L NH_3 after a two-stage stripping at A/O ratio of 1. The total recovery percentage of palladium was 96.9% during the dissolution–extraction–stripping process. Therefore, this study established a benign and effective process for selective recovery of palladium from waste printed circuit boards.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Copper and precious metals (mainly gold, silver and palladium) make up more than 95% of the economic value of waste PCBs [1]. Hence, the major economic driver in waste PCBs disposal is the recovery of copper and precious metals [2]. Silver and gold mostly exist in electronic components and contact materials while palladium is an essential material for the plated through hole (PTH) process during the manufacture of multilayer PCBs. It was reported that palladium contributes around 50% of the economic value of the bare waste personal computer PCBs after the components were disassembled [3].

In recent years, the most active research area on recovery of metals from waste PCBs is hydrometallurgical techniques [2,4–7].

However, most of those studies focused on the recovery of copper, silver, gold and other base metals [2,8–16]. Very few researches have been carried out on the recovery of palladium [6,17–19]. Besides, the forgoing methods developed for palladium recovery could not overcome the shortcomings of hydrometallurgy, such as time-consuming or economically infeasible, and series of acid or caustic leaching is necessary.

The key step for palladium recovery is the enrichment of palladium from base metals, especially copper. Copper content in waste PCBs is much higher than palladium. Besides, chemical properties of copper and palladium are similar [20]. The existing methods for selective dissolution of copper are inefficiency [6,8] and part of palladium will be lost in the leaching process of copper [21]. Hence, an economical, highly effective and environment-friendly method for the selective dissolution of copper is the key technology for palladium recovery.

After enrichment, separation of palladium from base metals is also a strategic challenge. Therefore, there is an increasing need

* Corresponding author. Tel.: +86 10 62849515; fax: +86 10 62849515.
E-mail address: fszhang@reccs.ac.cn (F.-S. Zhang).

to develop efficient technologies that ensure selective recovery of palladium from the leach liquor. Recently, solvent extraction has become a suitable method for the recovery of precious metals from low concentrated sources, because it offers a number of advantages such as: high selectivity, high metal purity obtained and more efficient recovery of metals by the use of multi-stage extraction. These have reduced the need for excessive recycling, shortened the refining times significantly and lowered production costs [21–24]. Many different extractants have been studied and proposed for the extraction of palladium, including dialkyl sulfides and sulphoxides, hydroxyoximes and ketoximes, alkyl derivatives of 8-hydroxyquinoline, hydrophobic amines, and organophosphorus extractants, etc. [24–26]. Among them, dialkyl sulfides attract more concern for their high selectivity and efficiency [26]. Diisoamyl sulfide (S201), one of those dialkyl sulfides extractants for Pd(II), has the additional advantages of high balancing speed, stable in property and easy stripping [26]. Hence, S201 was frequently employed for selective extraction of palladium.

In the present study, we attempted to develop a non-acid process for palladium recovery from waste PCBs. Palladium was primarily enriched during copper recovery process. Then, palladium was extracted by diisoamyl sulfide (S201) from the leach liquor. Various operation parameters including extractant concentration, aqueous to organic phase ratio (A:O) and extraction time were optimized. Palladium stripping from loaded organic phase was discussed as well.

2. Materials and methods

2.1. Materials

Waste PCBs from personal computers used in this work were supplied by XIAMEN OASIS Sources Co., Ltd. All the components (relays, capacitors, etc.) were disassembled when we received these materials. The PCBs were pretreated by thermal shock process [27] and crushed in a hammer crusher. Then, a centrifugal air separator was used to obtain the metallic components. The obtained metallic components were sent to comminute in a cutting mill until the fraction reached particle size smaller than 0.25 mm. Metal contents in the raw materials and obtained metallic particles were measured by inductively coupled plasma optical emission spectrometer (ICP-OES, Prodigy, Leeman, USA) after HNO_3 -HF- HClO_4 digestion. The concentrations of major elements are shown in Table 1. The recovery rates of Cu and Pd after centrifugal air separation were 98.4% and 96.8%, respectively. Since palladium and copper contribute around 99% of the value of the bare PCBs employed in this experiment, the recovery of other metals was not considered.

Diisoamyl sulfide (S201, >98.5%), a palladium selective extractant, was provided by Beijing Ruilekang Separation Technology Corporation, Ltd. n-Dodecane was purchased from TCI (Shanghai, China) Development Co., Ltd. All of the other chemicals were purchased from Chemical Reagent Company of Beijing in analytical grade.

2.2. Recovery of palladium

The process of palladium recovery includes enrichment and dissolution of palladium from waste PCBs, extraction and

Fig. 1. Flow chart of palladium enrichment and recovery from waste PCBs.

stripping of Pd(II). The whole recovery process is shown in Fig. 1.

2.2.1. Enrichment and dissolution of palladium

Palladium was enriched during copper recovery process according to our previous study [27,28] with minor modification. The flow chart of the whole process was shown in Fig. 1. Briefly, metallic particles were reacted with mixed solution of CuSO_4 and NaCl at 60°C for 30 min. Then, the mixture was filtrated into deionized water by a suction filter. The filtrate was stirred and allowed to stand still until CuCl precipitated. Then, CuCl was obtained after filtration. $[\text{Cu}]/[\text{Cu}^{2+}]$ ratio varied in the mixture during the enrichment and dissolution steps. As shown in Fig. 1, over dosage of Cu ($[\text{Cu}]/[\text{Cu}^{2+}] \geq 1.4$) was used during the enrichment step while over dosage of Cu^{2+} ($[\text{Cu}]/[\text{Cu}^{2+}] \leq 0.9$) was employed during the dissolution step.

2.2.2. Extraction and stripping of Pd(II)

To determine the extraction percentage of Pd(II), a certain volume of aqueous and organic phases (S201 diluted in n-dodecane, S201/dodecane) were contacted in glass bottles for a stipulated time under vigorous shaking. After phase disengagement, the aqueous phase was separated and analyzed for metal concentrations by inductively coupled plasma optical emission spectrometer (ICP-OES, Prodigy, Leeman, USA). Extraction percentage (E) was calculated from concentration of palladium in the aqueous phase before $[M_i]$ and after $[M_a]$ extraction:

$$E(\%) = \frac{[M_i] - [M_a]}{[M_i]} \times 100$$

Table 1
Metal contents of the raw material and the obtained metallic particles.

Elements	Content (wt.%) Cu	Content (mg/kg)					
		Pd	Pb	Zn	Fe	Al	Ni
Raw material	19.7	64	684	554	194	82	61
Metallic particles	94.3	307	2988	2425	974	321	283

Distribution ratio (D_M) was defined as the ratio of the palladium concentration in the organic [M_o] and aqueous phase [M_a] after extraction.

$$D_M = \frac{[M_o]}{[M_a]}$$

Separation coefficient of Pd(II) with base metals (M) was expressed as:

$$S_M^{Pd} = \frac{D_{Pd}}{D_M}$$

Stripping of the loaded S201/dodecane was carried out using NH_3 solution. The stripping solution was analyzed for Pd(II) concentration by ICP-OES to determine the stripping efficiency.

3. Results and discussion

3.1. Enrichment and dissolution of palladium

Previous studies [28] indicated that $[Cu]/[Cu^{2+}]$ in the leaching solution significantly affected the dissolution percentage of palladium. Dissolution percentage of palladium reached 98% when $[Cu]/[Cu^{2+}] \leq 0.9$ while more than 98.5% of palladium remained in Residue-I when $[Cu]/[Cu^{2+}] \geq 1.4$. The main reaction can be expressed by the following Eq. (1) [27]:

As shown in Fig. 1, $Na[CuCl_2]$ reacted with deionized water as follows:

The total reaction could be written as:

According to Fritz [29], the solubility of CuCl is significantly affected by the concentration of Cl^- in the solution. This solubility decreases markedly with decreasing total Cl^- concentration in solution. Solubility of CuCl decreased from 2.4 to 0.04 mol/L as the concentration of Cl^- decreased from 6.0 to 0.5 mol/L after deionized water added. Hence, cuprous chloride was separated from palladium after filtration. Therefore, through the enrichment step, copper in metallic particles was recovered as CuCl and palladium was concentrated in Residue-I under the condition of $[Cu]/[Cu^{2+}] \geq 1.4$ (Fig. 1). The main components of the Residue-I were glass fiber, resin and unreacted metals. It was calculated that the weight ratio of Residue-I to the feed material was 0.19. Dissolution of palladium was achieved with over dosage of Cu^{2+} ($[Cu]/[Cu^{2+}] \leq 0.9$) in the leaching solution. As shown in Fig. 1, more than 98% of palladium was dissolved in Filtrate-III by forming a stable chloride complex as Cu^{2+} played the role of oxidant according to the following reaction:

3.2. Extraction of palladium from the multi-metal solution

As discussed above, more than 98% of palladium was dissolved in Filtrate-III. Recovery of palladium was carried out using this leach liquor by liquid–liquid extraction. Table 2 presents the metal

Table 2
Metal concentrations in Filtrate-III.

Elements	Pd	Cu	Pb	Zn	Fe	Al	Ni
Concentration (mg/L)	19.82	7259.87	8.93	0.86	0.35	0.06	0.38

Fig. 2. Effect of S201 concentration (10–50%) on Pd(II) extraction.

concentrations in Filtrate-III. As can be seen, the concentrations of Pd(II) and Cu(II) in the solution were 19.82 and 7259.87 mg/L, respectively.

The extraction of Pd(II) was firstly carried out with S201 varied from 10% to 50% (vol.%) in n-dodecane. The results are shown in Fig. 2. As can be seen from Fig. 2, more than 99% of Pd(II) was extracted into S201 and Pd(II) extraction percentages had no significant change with S201 concentration increasing from 10% to 50%. But the amount of Cu(II) extracted into the organic phase exhibited a significant increase as S201 concentration varied from 10% to 50%. Nevertheless, Cu(II) extracted was negligible when 10% S201 was used. When S201 concentration increased to 50%, Cu(II) in the organic phase increased 20 times to 2.3 mg/L after extraction. Therefore, 10% S201 was chosen for the subsequent extraction experiments considering the separation of palladium from copper.

Accordingly, McCabe–Thiele plot was obtained for the extraction of Pd(II) with 10% S201 at O:A ratios from 1:1 to 1:10 (Fig. 3). The plot shows that quantitative Pd(II) extraction was achievable in two stages at A/O ratio of 5, thereby showing possible enrichment of palladium concentration during extraction stage by 5 times. Under this condition, less than 0.01% of Cu(II) was extracted. Cu(II) in the organic phase was 0.42 mg/L after extraction and other base metal ions extracted were negligible.

Based on the above results, experiments were carried out to study the effect of time on extraction of Pd(II) using the optimum condition: 10% S201 and A/O of 5. It can be seen from Fig. 4 that the extraction of Pd(II) with S201 was rapid and equilibrium was

Fig. 3. McCabe–Thiele diagram for Pd(II) extraction by S201.

Table 3
Metal concentrations in different phases after Pd extraction.

Elements	Pd	Cu	Pb	Zn	Fe	Al	Ni
$[M_o]$ (mg/L)	98.50	0.18	0.16	0.09	0.05	0.04	0.07
$[M_a]$ (mg/L)	0.12	7259.8	8.90	0.84	0.34	ND	0.37
D_M	820.83	0.00	0.02	0.10	0.13	–	0.20
S_M^{Pd}	–	44431	44476	7987	6136	–	4108

$[M_o]$: organic phase; $[M_a]$: aqueous phase; D_M : distribution ratio; S_M^{Pd} : separation coefficient.

Fig. 4. Effect of time on Pd(II) extraction under optimum condition: 10% S201 and A/O of 5.

achieved in 2 min. Phase separation after extraction was fast and no formation of emulsions was observed.

Therefore, the optimum conditions of Pd(II) extraction using S201 from the leach liquor were: 10% S201 in n-dodecane, two-stage extraction at A/O ratio of 5 and the extraction time was 2 min. Under the above condition, loaded organic phase contained 98.5 mg/L palladium. The concentration of Pd(II) in raffinate was 0.12 mg/L corresponding to 99.4% Pd(II) extraction efficiency. As shown in Table 3, the separation coefficient S_M^{Pd} ($M = Cu, Pb, Zn, Fe, Al, Ni, Mg$) were more than 4000.

According to the hard and soft acid–base (HSAB) theory, S201 is a soft Lewis base and Pd(II) is a soft Lewis acid, which leads to a favorable mutual affinity [30]. In addition, Cl^- in the solution results in the transformation of $Pd(H_2O)_4^{2+}$ to $PdCl_4^{2-}$, and consequently the promotion of Pd(II) extraction from aqueous solutions [31]. The extraction of $PdCl_4^{2-}$ from aqueous solutions to the organic phase can be described according to the following equation [26]:

where R_2S represents S201.

Base metal ions (such as Cu(II), Pb(II), Zn(II), Fe(III), Al(III), etc.) are hydrated to form various multi-ligand species expressed as $M(H_2O)_m^{n+}$ [30]. The relatively weak electron-donating ability of $-S-$ atom of S201 and stronger steric hindrance of S201 molecular prohibit the combine of S201 with the hydrated $M(H_2O)_m^{n+}$ species [30]. Besides, those base metal ions are borderline Lewis acids and the interactions with S201 are predicted to be weak [20]. Therefore, much stronger nucleophilic substitution between S201 and $PdCl_4^{2-}$ promotes Pd(II) to selectively transfer from the aqueous phase to the S201 organic phase. Thus, base metal ions and Pd(II) are separated from each other.

3.3. Stripping of palladium from the loaded organic phase

The stripping of palladium from organic phase can be achieved by different reagents, such as thiourea, thiocyanate,

Fig. 5. Effect of different NH_3 concentrations (0.01–1 mol/L) on the stripping of Pd(II) from the loaded S201 phase (s1: first stage stripping, s2: second stage stripping, s3: third stage stripping).

dimethylamine, NH_3 , etc. Among them, NH_3 has many advantages as fast phase separation, low cost and facilitating the subsequent refining. Therefore, stripping of Pd(II) was carried out using NH_3 solutions at different concentrations and A/O ratios. The aqueous phase was separated and analyzed. Fig. 5 shows the effect of different NH_3 concentration (0.01–1 mol/L) on the stripping of Pd(II) from the loaded S201 phase. Generally, stripping efficiency was enhanced with the increase of NH_3 concentration. However, the stripping efficiency was less than 98% with 1 mol/L NH_3 by single-stage stripping while 99.5% of Pd(II) could be removed from the loaded S201 phase by two-stage stripping with 0.1 mol/L NH_3 . Therefore, 0.1 mol/L solution of NH_3 was chosen as the suitable concentration for Pd(II) stripping.

In order to find out the extent of enrichment possibility, effect of O/A ratio on the stripping of Pd(II) was studied using the proposed concentration of NH_3 . The results are shown in Fig. 6. It was observed that two-stage stripping of Pd(II) at A/O ratio of 1 gave a stripping efficiency of 99.5%. Under this condition, the equilibrium of Pd(II) stripping was achieved in 2 min. Moreover, there were no problems with emulsion or precipitation, both phases were transparent and separated immediately.

It is well known that Pd(II) can form more stable complexes with NH_3 than S201 [31]. The stripping reaction using NH_3 can be represented as follows:

Metal concentrations in the obtained stripping solution are presented in Table 4. As indicated in Table 4, Pd(II) concentration

Table 4
Metal concentrations in the obtained stripping solution.

Elements	Pd	Cu	Pb	Zn	Fe	Al	Ni
Concentration (mg/L)	98.52	0.09	0.08	0.04	ND	ND	ND

Fig. 6. Effect of different A/O ratio on the stripping of Pd(II) from the loaded S201 phase with NH_3 (s1: first stage stripping, s2: second stage stripping, s3: third stage stripping).

was 98.52 mg/L while other metals were negligible. Accordingly, recovery of Pd(II) with S201/dodecane from the leach liquor was selective and the total recovery percentage of Pd was 96.9% during the dissolution–extraction–stripping process.

3.4. Regeneration of S201

The possibility of regeneration of spent organic phases and their reuse in subsequent extraction is an important economic and ecological issue. After stripping of Pd(II) with 0.1 M NH_3 , the S201/dodecane organic phase was regenerated for subsequent use by washing with NaCl (O:A=2:1) aqueous solution. Regenerated S201/dodecane was used again for Pd(II) extraction (2nd cycle) and then stripped twice with 0.1 M NH_3 . The procedure of extraction–stripping–regeneration was repeated 5 times. Extraction percentage of Pd(II) with regenerated S201/dodecane was comparable with fresh S201/dodecane as more than 99% of Pd(II) could be transported to the organic phase in the 5th cycle. FT-IR and ^{13}C NMR spectra of fresh S201/dodecane and S201/dodecane used 5 times are shown in Fig. 7. Both spectra are the same, which indicates that the chemical properties of the S201/dodecane did not change. Hence, S201 is a stable extractant that can be regenerated and used repeatedly for Pd(II) extraction.

4. Conclusions

A novel process was successfully developed for selective recovery of palladium from waste PCBs without corrosive acid or strong oxidant utilization. In the process, palladium was firstly enriched during copper recovery process and dissolved in cupric sulfate and sodium chloride solution in the form of PdCl_4^{2-} , which was then recovered by S201 extraction. In the extraction process, the influence of base metals was negligible due to the relatively weak nucleophilic substitution of S201 with the base metal ions and stronger steric hindrance of S201 molecular, and S201 could be regenerated and used repeatedly for Pd(II) extraction. The total recovery percentage of palladium reached 96.9% during the dissolution–extraction–stripping process.

Acknowledgements

This research was financially supported by the National Natural Science Foundation of China (51278485), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB05050200) and the Science Promotion Program of Research Center for Eco-Environmental Sciences, CAS (YSW2013B05).

References

- [1] P. Chancerel, C.E.M. Meskers, C. Hagelüken, V.S. Rotter, Assessment of precious metal flows during preprocessing of waste electrical and electronic equipment, *J. Ind. Ecol.* 13 (2009) 791–810.
- [2] J. Cui, L. Zhang, Metallurgical recovery of metals from electronic waste: a review, *J. Hazard. Mater.* 158 (2008) 228–256.
- [3] A. Tuncuk, V. Stazi, A. Akcil, E.Y. Yazici, H. Deveci, Aqueous metal recovery techniques from e-scraps: hydrometallurgy in recycling, *Miner. Eng.* 25 (2012) 28–37.
- [4] O. Herreros, R. Quiroz, A. Restovic, J. Viñals, Dissolution kinetics of metallic copper with $\text{CuSO}_4\text{--NaCl--HCl}$, *Hydrometallurgy* 77 (2005) 183–190.
- [5] Z. Ping, F. ZeYun, L. Jie, L. Qiang, Q. GuangRen, Z. Ming, Enhancement of leaching copper by electro-oxidation from metal powders of waste printed circuit board, *J. Hazard. Mater.* 166 (2009) 746–750.
- [6] A. Behnamfard, M.M. Salarirad, F. Veglio, Process development for recovery of copper and precious metals from waste printed circuit boards with emphasize on palladium and gold leaching and precipitation, *Waste Manage.* 33 (2013) 2354–2363.
- [7] E.Y. Kim, M.S. Kim, J.C. Lee, B.D. Pandey, Selective recovery of gold from waste mobile phone PCBs by hydrometallurgical process, *J. Hazard. Mater.* 198 (2011) 206–215.
- [8] C.J. Oh, S.O. Lee, H.S. Yang, T.J. Ha, M.J. Kim, Selective leaching of valuable metals from waste printed circuit boards, *J. Air Waste Manage.* 53 (2003) 897–902.
- [9] E.-y. Kim, M.-s. Kim, J.-c. Lee, B. Pandey, Selective recovery of gold from waste mobile phone PCBs by hydrometallurgical process, *J. Hazard. Mater.* 198 (2011) 206–215.
- [10] W.J. Hall, P.T. Williams, Separation and recovery of materials from scrap printed circuit boards, *Resour. Conserv. Recycl.* 51 (2007) 691–709.

Fig. 7. FT-IR and ^{13}C NMR spectra of fresh and regenerated S201 in n-dodecane (a: fresh S201, b: regenerated S201).

- [11] M. Gurung, B.B. Adhikari, H. Kawakita, K. Ohto, K. Inoue, S. Alam, Recovery of gold and silver from spent mobile phones by means of acidothiurea leaching followed by adsorption using biosorbent prepared from persimmon tannin, *Hydrometallurgy* 133 (2013) 84–93.
- [12] P. Zhu, Y. Chen, Z. Fen, G. Qian, Y. Chu, Y. Lei, M. Zhou, Preparation of ultrafine copper oxide using metal powders recovered from waste printed circuit boards, *J. Hazard. Tox. Rad. Waste* 17 (2013) 175–180.
- [13] E. Yazici, H. Deveci, Extraction of metals from waste printed circuit boards (WPCBs) in H_2SO_4 – CuSO_4 – NaCl solutions, *Hydrometallurgy* 139 (2013) 30–38.
- [14] J. Yang, Y. Wu, J. Li, Recovery of ultrafine copper particles from metal components of waste printed circuit boards, *Hydrometallurgy* 121–124 (2012) 1–6.
- [15] F.R. Xiu, F.S. Zhang, Size-controlled preparation of Cu_2O nanoparticles from waste printed circuit boards by supercritical water combined with electrokinetic process, *J. Hazard. Mater.* 233–234 (2012) 200–206.
- [16] E.-y. Kim, M.-s. Kim, J.-c. Lee, J. Jeong, B. Pandey, Leaching kinetics of copper from waste printed circuit boards by electro-generated chlorine in HCl solution, *Hydrometallurgy* 107 (2011) 124–132.
- [17] B.-S. Kim, J.-c. Lee, S.-P. Seo, Y.-K. Park, H.Y. Sohn, A process for extracting precious metals from spent printed circuit boards and automobile catalysts, *JOM* 56 (2004) 55–58.
- [18] N.J. Creamer, V.S. Baxter-Plant, J. Henderson, M. Potter, L.E. Macaskie, Palladium and gold removal and recovery from precious metal solutions and electronic scrap leachates by *Desulfovibrio desulfuricans*, *Biotechnol. Lett.* 28 (2006) 1475–1484.
- [19] Y.J. Park, D.J. Fray, Recovery of high purity precious metals from printed circuit boards, *J. Hazard. Mater.* 164 (2009) 1152–1158.
- [20] J.A. Dean, *Lange's Handbook of Chemistry*, Science Press, Beijing, 2003.
- [21] F.L. Bernardis, R.A. Grant, D.C. Sherrington, A review of methods of separation of the platinum-group metals through their chloro-complexes, *React. Funct. Polym.* 65 (2005) 205–217.
- [22] A. Cieszyńska, M. Wiśniewski, Extractive recovery of palladium (II) from hydrochloric acid solutions with Cyphos®IL 104, *Hydrometallurgy* 113–114 (2012) 79–85.
- [23] P. Quinet, J. Proost, A. Van Lierde, Recovery of precious metals from electronic scrap by hydrometallurgical processing routes, *Miner. Metall. Proc.* 22 (2005) 17–22.
- [24] E. Mowafy, H. Aly, Extraction and separation of Pd (II), Pt (IV), Fe (III), Zn (II), Cu (II) and Ag (I) from hydrochloric acid solutions with selected cyanamides as novel extractants, *J. Hazard. Mater.* 149 (2007) 465–470.
- [25] A. Cieszyńska, M. Wisniewski, Extraction of palladium (II) from chloride solutions with Cyphos®IL 101/toluene mixtures as novel extractant, *Sep. Purif. Technol.* 73 (2010) 202–207.
- [26] J. Yu, *Solvent Extraction Chemistry of Precious Metals*, Chemical Industry Press, Beijing, 2005.
- [27] Z. Zhang, F.-S. Zhang, Synthesis of cuprous chloride and simultaneous recovery of Ag and Pd from waste printed circuit boards, *J. Hazard. Mater.* 39 (2013) 8–40, 4.
- [28] Z. Zhang, F.-S. Zhang, A green process for copper recovery from waste printed circuit boards, *Adv. Mater. Res.* 878 (2014) 374–379.
- [29] J.J. Fritz, Solubility of cuprous chloride in various soluble aqueous chlorides, *J. Chem. Eng. Data* 27 (1982) 188–193.
- [30] T. Zhu, Z. Li, *Solvent Extraction*, Chemical Industry Press, Beijing, 2007.
- [31] P. Yu, K. Huang, C. Zhang, K. Xie, X. He, H. Liu, One-step separation of platinum, palladium, and rhodium: a three-liquid-phase extraction approach, *Ind. Eng. Chem. Res.* 50 (2011) 9368–9376.