Journal of Hazardous Materials 279 (2014) 46–51

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

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

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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 irons 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.

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

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http://dx.doi.org/10.1016/j.jhazmat.2014.06.045
0304-3894/

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

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

Elements	Content (wt.%)	Content (mg/kg)					
	Cu	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

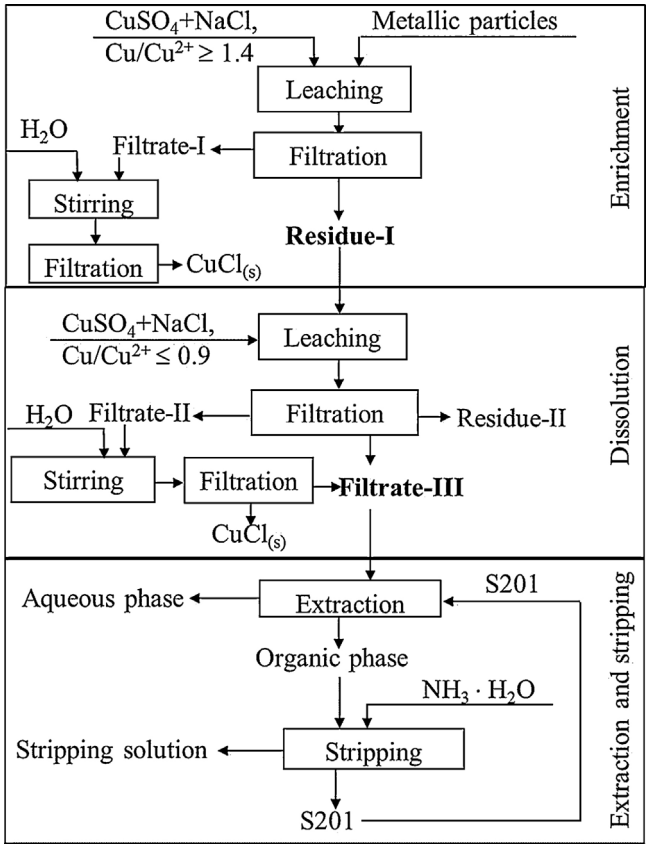

Fig. 1. Flow chart of palladium enrichment and recovery from waste PCBs.

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. $[Cu]/[Cu^{2+}]$ ratio varied in the mixture during the enrichment and dissolution steps. As shown in Fig. 1, over dosage of Cu ($[Cu]/[Cu^{2+}] \geq 1.4$) was used during the enrichment step while over dosage of Cu^{2+} ($[Cu]/[Cu^{2+}] \leq 0.9$) 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:

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