Synthesis of cuprous chloride and simultaneous recovery of Ag and Pd from waste printed circuit boards

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HIGHLIGHTS

- An environmentally friendly process was developed for high quality cuprous chloride synthesis from waste PCBs.
- Neither corrosive acid nor strong oxidant was used in the process.
- Ag and Pd were simultaneously recovered during cuprous chloride synthesis.
- A much faster reaction rate was achieved compared with other recovery methods.

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ABSTRACT

A benign and effective process for cuprous chloride synthesis and simultaneously recovery of Ag and Pd from waste printed circuit boards (PCBs) was developed in the present study. The main merit of the process is that neither corrosive acid nor strong oxidant was used. The PCBs were firstly pretreated by thermal shock process to obtain metallic particles (MPs), then cuprous chloride was synthesized by reacting MPs with cupric sulfate in the presence of sodium chloride. The optimum $V_{\text{NaCl}}/m_{\text{CuSO}_4}$ (mL/g) ratio, $[\text{Cu}]/[\text{Cu}^{2+}]$ mole ratio, treatment time and operation temperature were 6, 0.95, 30 min and 60 °C, respectively. Approximately 98.5% of Cu could be recovered from the PCBs through two synthesis circles. During the synthesis process, Ag and Pd could be simultaneously recovered by forming a stable chloride complex since Cu^{2+} played the role of oxidant in the system. The recovery percentages of Ag and Pd were 93.9% and 95.3%, respectively. Accordingly, it is believed that the process developed in the current study is benign and practical for copper and precious metal (Ag, Pd) recovery from waste PCBs.

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1. Introduction

Technological innovation and intense marketing strategies engender a rapid turnover of electrical and electronic equipment (EEE) [1,2]. Since the mid-1990s, e-waste has been recognized as the fastest-growing component of the solid-waste stream in the industrialized world [3,4]. Large amounts of waste EEE are constantly generated worldwide, posing an increasing global challenge for their disposal [4].

Printed circuit boards (PCBs), an essential part of almost all electric and electronic equipment, are widely subsistent in EEE [1]. In recent years, the average rate of worldwide PCBs manufacture increased by 8.7%, and this figure is much higher in Southeast Asia (10.8%) and mainland China (14.4%) [5]. Waste PCBs contain lots of valuable resources [6,7] together with plenty of hazardous materials [8,9], which are considered both an attractive secondary resource and an environmental contaminant [10]. Therefore,

recycling of the Waste PCBs is an important subject not only from the treatment for waste but also from the recovery of valuable materials [1,11].

Copper and precious metals make up more than 95% of the value for waste PCBs [11,12]. Hence, recovery of those metals is the inherent motivity in waste PCBs disposal. Many recycling techniques of copper from waste PCBs have been developed such as pyrometallurgy [13], hydrometallurgy [14–16], mechanical methods [17,18]. In the past two decades, the most active research area on recovery of metals from electronic scraps is recovering metals by hydrometallurgical techniques [11]. Separation of base metal and precious metal using environment-friendly, low corrosive leach reagents, such as $\text{NH}_3/\text{NH}_4\text{CO}_3$ for Cu [19], $\text{NH}_3\cdot\text{H}_2\text{O}/\text{KI}$ for Pd, Pt [20], thiourea and $(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{CuSO}_4/\text{NH}_4\text{OH}$ for Ag, Au [16,21,22], is widely investigated. However, the forgoing processes are either time-consuming or economically infeasible, and furthermore, leaching solution needs to be further treated by electrolytic winning or other method to recover metallic copper.

In recent years, new approaches for the recovery of waste PCBs has been developed, the aim of which are not to obtain high purity metallic copper from waste PCBs, but to produce Cu containing

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products, such as cupric sulfate [23], Cu_2O nanoparticles [24]. Those processes are general efficient for Cu recycling, but precious metals contained in waste PCBs could not be simultaneously recovered. Moreover, the compounds obtained usually contain many impurities and strongly corrosive acids of large quantity are employed.

Cuprous chloride is widely used in the manufacture of electrooptic modulators and optical filters, solid-state batteries, adsorbent and air purifying agents [25]. Especially, cuprous chloride is an important catalyst in organic synthesis industry and rubber industry. Its undemanding reaction conditions meet the current interest in developing more efficient and environmentally friendly methods for chemical synthesis, and thus it has attracted great attention over the years [26].

In the present study, we attempted to develop a novel process for cuprous chloride synthesis and simultaneously recovery precious metals (Ag, Pd) from waste PCBs. High value-added cuprous chloride was obtained from solutions of cupric sulfate and sodium chloride using MPs as reducing agent. Different parameters such as $V_{\text{NaCl}}/m_{\text{CuSO}_4}$ (volume of saturated NaCl solution to mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, mL/g), $[\text{Cu}]/[\text{Cu}^{2+}]$ (mole ratio of Cu in MPs to Cu^{2+} in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) ratio, treatment time and temperature on cuprous chloride conversion were investigated. The effects of synthesis conditions on Ag and Pd recovery and the mechanism were discussed as well.

2. Materials and methods

2.1. Materials and sample preparation

Waste PCBs used in this work were supplied by XIAMEN OASIS Sources Co. Ltd. After the components (relays, capacitors, etc.) were disassembled, the PCBs were first cut into $10\text{ cm} \times 2\text{ cm}$ pieces and then pretreated by thermal shock process followed the methods of Li et al. [27] with minor modifications. Thermal shock process was carried out at 270°C for 30 min in a tubular type muffle furnace for the improvement of crushing performance. The vapor was trapped in a glass at low temperature and then passed through a bottle with alkaline solution to absorb off gas. After crushed in a hammer crusher, a centrifugal air separator was used to obtain the metallic components. The pictures were shown in Fig. 1. The weight percentage of metallic components was 21.2%. Thus, it favors the synthesis of cuprous chloride and recovery of Ag and Pd. Then, the 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 metallic particles (MPs) were measured by inductively coupled plasma optical emission spectrometer (ICP-OES, Prodigy, Leeman, USA) after $\text{HNO}_3\text{--HF--HClO}_4$ digestion. The results are given in Table 1. Cu, Ag and Pd contents in MPs were found to be 94.30%, 209 mg/kg and 307 mg/kg, respectively. All of the other chemicals were purchased from Chemical Reagent Company of Beijing in analytical grade.

2.2. Cuprous chloride synthesis and Ag, Pd recovery

Cuprous chloride synthesis experiments were carried out in a conical flask under magnetically stirring at certain temperatures. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was added to a stirred saturated solution of NaCl. When the solution reached the target temperature, MPs were added into the solution. The mixture became dark brown during reaction. Then, the mixture was carefully filtrated into deionized water by a suction filter after the reaction completed. The cuprous chloride settled readily in the filtering flask and the supernatant liquid was faintly green. The precipitate and supernatant liquid were stirred well and allowed to stand until all the cuprous chloride settled. Then, the precipitate was quickly washed onto a suction filter with 0.5–1% HCl solution. The cuprous chloride was then washed three times with 0.5–1% HCl solution. The washing was followed by absolute alcohol in exactly the same way. After the last portion of alcohol was removed fairly completely, the white solid was transferred quickly to a previously dried watch glass and placed in an oven (60°C) for 20–25 min. The obtained cuprous chloride sample was weighted and preserved in an airtight bottle for further analysis.

Theoretically, 2 mol cuprous chloride could be produced by reducing 1 mol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with 1 mol metallic copper. The conversion percentage of cuprous chloride is calculated as follows:

$$\text{Cuprous chloride conversion percentage (\%)} = \frac{m_1}{m_2} \times 100$$

where m_1 and m_2 are the actual and theoretical production of cuprous chloride, respectively.

Fig. 2 presents a reasonable process for Cu, Ag and Pd recovery. As it is shown in Fig. 2, Cu in filtrate II was transferred into next synthesis circle. Ag and Pd dissolved into filtrate II were detected to calculate the recovery percentages of Ag and Pd. Therefore, total Cu recovery could be expressed as the sum of Cu in filtrate II and in cuprous chloride. Ag and Pd recovery were expressed as the

Fig. 1. Pictures of thermal shock and mechanical separation.

Table 1
Metal contents in MPs obtained from waste PCBs (wt.%).

Elements	Al	Ni	Pb	Sn	Cr	Cu	Fe	Zn	Ag (mg/kg)	Pd (mg/kg)
Content	0.03	0.01	0.30	0.17	0.01	94.30	0.10	0.24	209	307

percentages of Ag and Pd extracted into filtrate II from MPs. The calculated formulas were listed below:

$$\text{Cu recovery(\%)} = \frac{\text{Cu in filtrate II} + \text{Cu in CuCl}}{\text{Total Cu in MPs}} \times 100$$

$$\text{Ag(Pd) recovery(\%)} = \frac{\text{Ag(Pd) in filtrate II}}{\text{Total Ag(Pd) in MPs}} \times 100$$

2.3. Characterization of the prepared cuprous chloride particles

The crystalline phases of the prepared cuprous chloride were characterized by X-ray diffraction spectroscopy (XRD, Philips PW1700) using Cu K α radiation ($\gamma = 1.5418 \text{ \AA}$) with 30 kV voltage and 30 mA current. Morphology and size information of the precipitates were observed on a JSM-7001F field emission scanning electron microscopy (FESEM). Cuprous chloride content and other characteristics (contents of cupric chloride, acid non-soluble substance, iron and sulfate) of the obtained product were measured according to Chinese chemical industry standard, cuprous chloride for industrial use (HG/T 2960-2000).

Fig. 2. Flowchart of CuCl synthesis and Ag, Pd recovery from waste PCBs.

3. Results and discussion

3.1. Thermal shock process

Thermal shock process changed the physical property of the board. The appearance and layer spacing of the basal plane changed clearly when the temperature reached 270 °C, and the bulging, cracking, and delaminating of the board apparent was observed. Therefore, the crushing efficiency was improved. Previous studies showed that PCBs began to pyrolyze at >295 °C and the decomposition of PCBs did not take place under the conditions of the current study (270 °C). The average percentage of weight loss was 0.79%, which was mainly attributed to the dehydration reaction of PCBs. Hence, the environmental impact was negligible during the thermal shock process.

3.2. Effects of different parameters on cuprous chloride synthesis

There are many factors affecting the reaction rate of copper and cuprous chloride conversion percentage such as $V_{\text{NaCl}}/m_{\text{CuSO}_4}$ (volume of saturated NaCl solution to mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, mL/g), $[\text{Cu}]/[\text{Cu}^{2+}]$ ratio, reaction time and temperature. In the synthesis process of cuprous chloride, the reaction can be expressed by the following Eqs. (1) and (2) [28]:

The total reaction could be written as:

Fig. 3a shows the effect of $V_{\text{NaCl}}/m_{\text{CuSO}_4}$ on cuprous chloride synthesis (experiment condition: $[\text{Cu}]/[\text{Cu}^{2+}] = 1.3$, treatment time 1 h, operation temperature 60 °C). The conversion percentage of cuprous chloride increased with the increase of $V_{\text{NaCl}}/m_{\text{CuSO}_4}$. When $V_{\text{NaCl}}/m_{\text{CuSO}_4}$ was 6, the conversion reached maximum, i.e., 61.2% of Cu was converted into cuprous chloride. It is known that solubility of cuprous chloride in water is extremely low, e.g., the solubility is approximately 2×10^{-7} at 25 °C [29]. The solubility increases markedly with increasing total chloride ion concentration in the solution, which is attributed to the formation of cuprous chloro complexes as expressed by the general reaction (4) [30]:

when $V_{\text{NaCl}}/m_{\text{CuSO}_4}$ was less than 4.8, the reaction of metallic copper was inhibited due to the formation of a superficial layer of solid cuprous chloride [28]. Consequently, cuprous chloride conversion percentage was remarkably decreased. When $V_{\text{NaCl}}/m_{\text{CuSO}_4}$ exceeded 6, more cuprous chloride was dissolved into filtrate II. Therefore, cuprous chloride conversion percentage decreased with $V_{\text{NaCl}}/m_{\text{CuSO}_4} = 6.4$.

Fig. 3b demonstrates the effect of $[\text{Cu}]/[\text{Cu}^{2+}]$ ratio on cuprous chloride synthesis (experiment condition: $V_{\text{NaCl}}/m_{\text{CuSO}_4} = 6$, treatment time 1 h, operation temperature 60 °C). $[\text{Cu}]/[\text{Cu}^{2+}]$ ratio affected not only the conversion of cuprous chloride, but also the recovery of Pd and Ag (discussing in Section 3.3). It can be seen that the conversion percentage of cuprous chloride was influenced significantly with the increase of $[\text{Cu}]/[\text{Cu}^{2+}]$. The highest conversion percentage could be obtained at the ratio of 1.05 (74.7%).

Fig. 3. Effects of different parameters on cuprous chloride synthesis. (a) $V_{\text{NaCl}}/m_{\text{CuSO}_4} = 4.8 - 6.4$, $[\text{Cu}]/[\text{Cu}^{2+}] = 1.3$, treatment time 1 h, temperature 60 °C, (b) $[\text{Cu}]/[\text{Cu}^{2+}] = 0.85 - 1.3$, $V_{\text{NaCl}}/m_{\text{CuSO}_4} = 6$, treatment time 1 h, temperature 60 °C, (c) temperature = 20–80 °C, $V_{\text{NaCl}}/m_{\text{CuSO}_4} = 6$, $[\text{Cu}]/[\text{Cu}^{2+}] = 1.05$, treatment time 1 h, (d) treatment time = 5–60 min, $V_{\text{NaCl}}/m_{\text{CuSO}_4} = 6$, $[\text{Cu}]/[\text{Cu}^{2+}] = 1.05$, temperature 60 °C.

Fig. 3c illustrates the effect of operation temperature on cuprous chloride synthesis (experiment condition: $V_{\text{NaCl}}/m_{\text{CuSO}_4} = 6$, $[\text{Cu}]/[\text{Cu}^{2+}] = 1.05$, treatment time 1 h). The results indicated that the conversion percentage of cuprous chloride increased with the temperature increasing from 20 °C to 60 °C. The conversion percentage of cuprous chloride at 60 °C and 80 °C had no obvious difference. 60 °C was the optimal temperature as the solution volatilized seriously at 80 °C.

The results of cuprous chloride conversion versus time are presented in Fig. 3d (experiment condition: $V_{\text{NaCl}}/m_{\text{CuSO}_4} = 6$, $[\text{Cu}]/[\text{Cu}^{2+}] = 1.05$, operation temperature 60 °C). It can be found from Fig. 3d that copper reacted very fast. 64% cuprous chloride was produced 5 min after the reaction started, which implied that at least 64% of the metallic copper had dissolved during the first 5 min. The conversion percentage of cuprous chloride had no significant increase when the reaction time was extended more than 30 min. Accordingly, 30 min was the optima time from both economic and efficiency point of view. As a recovery method for copper from waste PCBs, the process proposed in this study has a much faster reaction rate compared with other recovery methods. For example, Zhu et al. obtained $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ by leaching copper using electro-oxidation method, 3.5 h was needed in the presence of electro oxidation [31]. Kim et al. reported a process leaching copper using electro-generated chlorine at the anode in HCl solution. In the separate reactor, 71% of copper was leached at a current density of 714 A/m², 323 K temperature in 240 min [32]. The standard redox potential of Eq. (3) was 0.039 V [33]. The redox potential of reaction Eq. (3) in the leaching system was calculated to be 0.224 V. Therefore, copper could be dissolved rapidly in the NaCl–CuSO₄ system.

It can be summarized from the experiment results that the optimum conditions of cuprous chloride synthesis from MPs of waste PCBs were: $V_{\text{NaCl}}/m_{\text{CuSO}_4} = 6$, $[\text{Cu}]/[\text{Cu}^{2+}] = 1.05$, treatment time 30 min, operation temperature 60 °C, respectively.

3.3. Characterization of prepared cuprous chloride

The cuprous chloride prepared by this method is a white crystalline powder that remains practically unchanged for an indefinite period if kept dry. Cuprous chloride content and other characteristics (contents of cupric chloride, acid non-soluble substance, iron and sulfate) of the obtained product were measured according to Chinese chemical industry standard, cuprous chloride for industrial use (HG/T 2960-2000). The result is shown in Table 2. The product quality meets the prescribed standards of premium grades.

The XRD pattern of the obtained product is shown in Fig. 4, which displays only three obvious diffraction peaks that can be indexed to the (1 1 1), (2 2 0) and (3 1 1) crystal planes of cubic phase CuCl. The lattice constant calculated from its XRD data is 5.414 Å, which is also consistent with that of cubic phase CuCl reported in the JCPDS card No. 6-344. Fig. 5 shows the SEM image of the synthesized cuprous chloride. As can be seen, the obtained product consists of numerous tetrahedron crystallites with the side length of about 1–10 μm.

During the reaction of aniline coupling, the CuCl tetrahedra have the highest catalytic activity among four different crystallites (tetrahedra, face centered-etched tetrahedra, tripod dendrites, and

Table 2
Quality of the synthesized cuprous chloride.

Item	Obtained product	Chemical industry standard		
		First-class	Second-class	Third-class
Cuprous chloride (calculated as CuCl)	≥ 98.7	98.0	97.0	96.5
Cu ²⁺ (calculated as CuCl ₂)	≤ 0.68	0.8	1.0	2.0
Acid non-soluble substance	≤ 0.02	0.08	0.1	0.3
Fe	≤ 0.005	0.005	0.005	0.01
Sulfate (calculated as SO ₄)	≤ 0.05	0.05	0.1	0.3

Fig. 4. XRD pattern of the obtained CuCl product.

tetrapods). It is believed that the increasing catalytic activity is correlated with the increasing ratio of (1 1 1) to (1 1 0) crystal planes in aniline coupling [26]. XRD pattern of the CuCl also shows a high (1 1 1) diffraction peak, which implies that the obtained cuprous chloride have a high activity in the catalysis of organic reactions.

3.4. Recovery of Pd and Ag

In the leaching process, Cu^{2+} played the role of oxidant and accepted one electron according to the following half-reaction [34]:

$$E_{\text{Cu}} = E^0 + \frac{RT}{ZF} \ln \left(\frac{a_{\text{Cu}^{2+}} \cdot a_{\text{Cl}^-}^2}{a_{\text{CuCl}_2^-}} \right) \quad (6)$$

where $a_{\text{Cu}^{2+}}$, a_{Cl^-} , $a_{\text{CuCl}_2^-}$ are the ion activities of Cu^{2+} , Cl^- , CuCl_2^- , respectively.

Ag and Pd were leached by forming a stable chloride complex as follows [33]:

And the redox potentials of Eqs. (7) and (8) can be calculated as:

$$E_{\text{Ag}} = E^0 + \frac{RT}{ZF} \ln \left(\frac{a_{\text{AgCl}_2^-}}{a_{\text{Cl}^-}^2} \right) \quad (9)$$

Fig. 5. SEM image of the obtained CuCl product.

Table 3

Calculated redox potentials of reaction Eqs. (5), (7) and (8).

	E_{Cu}	E_{Ag}	E_{Pd}
Leaching solution	$0.516 + 0.06612 \lg(a_{\text{Cu}^{2+}})$	0.1485	0.4243

$$E_{\text{Pd}} = E^0 + \frac{RT}{ZF} \ln \left(\frac{a_{\text{PdCl}_4^{2-}}^{1/2}}{a_{\text{Cl}^-}^2} \right) \quad (10)$$

where $a_{\text{AgCl}_2^-}$, $a_{\text{PdCl}_4^{2-}}$ are the ion activities of AgCl_2^- , PdCl_4^{2-} , respectively.

It can be seen from Eqs. (6), (9) and (10) that the dissolution percentages of Ag and Pd depend on concentrations of ligand (Cl^-) and oxidant (Cu^{2+}). As there was a saturated solution of NaCl in the reaction solution, it could be deduced that the key factor in determining the dissolution percentages of Ag and Pd was $[\text{Cu}]/[\text{Cu}^{2+}]$. Table 3 presents the calculated redox potentials of Eqs. (5), (7) and (8) in the leaching solution (experiment condition: $V_{\text{NaCl}}/m_{\text{CuSO}_4} = 6$, temperature: 60°C). To obtain a high recovery percentages of Ag and Pd, over dosage of Cu^{2+} was needed to meet the condition of $E_{\text{Cu}} > E_{\text{Ag}}$ and $E_{\text{Cu}} > E_{\text{Pd}}$, i.e., $0.516 + 0.06612 \lg(a_{\text{Cu}^{2+}}) > 0.4243$. Hypothesize that $a_{\text{Cu}^{2+}} = [\text{Cu}^{2+}]$, it is calculated that $[\text{Cu}]/[\text{Cu}^{2+}] < 0.934$ in the leaching solution under this experiment condition. Under this

Fig. 6. Effect of $[\text{Cu}]/[\text{Cu}^{2+}]$ ratio on the dissolution of Pd and Ag during CuCl synthesis ($[\text{Cu}]/[\text{Cu}^{2+}] = 0.85\text{--}1.15$, $V_{\text{NaCl}}/m_{\text{CuSO}_4} = 6$, treatment time 30 min, temperature 60°C).

Fig. 7. Distribution of Cu, Ag and Pd under the optimum conditions ($V_{\text{NaCl}}/m_{\text{CuSO}_4} = 6$, $[\text{Cu}]/[\text{Cu}^{2+}] = 0.95$, treatment time 30 min, temperature 60°C).

condition, Ag and Pd were dissolved according to the following reaction:

Fig. 6 shows the effect of $[\text{Cu}]/[\text{Cu}^{2+}]$ ratio on distribution of Pd and Ag during CuCl synthesis. As can be seen, recovery percentages of Pd and Ag reached 95% when the values of $[\text{Cu}]/[\text{Cu}^{2+}]$ were less than 0.95 and 1, respectively. The values were slightly different from the calculated values as Cu^+ might be oxidized to Cu^{2+} in the synthesis process. Recovery percentages of Pd and Ag decreased with further increasing $[\text{Cu}]/[\text{Cu}^{2+}]$ ratios. E.g., when $[\text{Cu}]/[\text{Cu}^{2+}]$ ratio was 1.15, only 37.4% of Ag and 57.4% of Pd were detected in filtrate II. It can also be seen from Fig. 6 that Ag and Pd remaining in the residues increased with the increase of $[\text{Cu}]/[\text{Cu}^{2+}]$ ratios. However, the sum of Ag and Pd in filtrate II and the residues decreased from approximately 100% to around 67% when $[\text{Cu}]/[\text{Cu}^{2+}]$ increased from 0.85 to 1.15, indicating that more than 30% of Ag and Pd was transferred into cuprous chloride product. Accordingly, the optimal $[\text{Cu}]/[\text{Cu}^{2+}]$ ratio is ascertained to be 0.95 considering the conversion percentage of cuprous chloride and the recovering efficiencies of Pd and Ag.

3.5. Mass balance of Cu, Ag and Pd

Fig. 7 shows the distribution of Cu, Ag and Pd under the optimal conditions. 72.1% of the copper was converted to cuprous chloride. 26.3% was transferred into filtrate II, which was recovered in the next synthesis circle. Hence, approximately 98.5% of copper could be recovered. Ag and Pd extracted in filtrate II were 93.9% and 95.3%, respectively. Therefore, as a green method of synthesis cuprous chloride from waste PCBs, high percentages of Ag and Pd were simultaneously recovered.

Table 4
Raw materials consumed during the process of CuCl synthesis from waste PCBs.

Raw material	Consumption (t)	Unit price (\$USD/t)	Total price (\$USD/t)
Waste PCBs	1.00	320	320
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	1.05	2240	2352
NaCl	2.19	40	87.6
Hydrochloric acid	0.02	24	0.48
Ethanol	0.10	200	20
Sum			2780

3.6. Economic assessment

Table 4 shows the raw materials consumed during the process of CuCl synthesis from waste PCBs. As can be seen from Table 4, to disposal 1 t waste PCBs, the total raw materials cost was about \$USD 2780, and 0.61 t CuCl could be produced from 1 t waste PCBs. The current price of CuCl is around \$USD 6775/t and thus, its commercial value is supposed to be about \$USD 4130. Consequently, a profit of about \$USD 1350 can be obtained from 1 ton PCBs by the current process.

4. Conclusions

Cuprous chloride was successfully synthesized from waste PCBs in cupric sulfate and sodium chloride solution. The process was much more effective compared to other approaches though neither corrosive acid nor strong oxidant was used. High quality of cuprous chloride with a purity of 98.7% was obtained without further purification, and noble metals (Ag, Pd) were simultaneously recovered in the process. The optimum conditions were: $V_{\text{NaCl}}/m_{\text{CuSO}_4}$ ratio = 6, $[\text{Cu}]/[\text{Cu}^{2+}]$ mole ratio = 0.95, treatment time = 30 min, operation temperature = 60°C , respectively. Under these conditions, approximately 98.5% of Cu, 93.9% of Ag and 95.3% of Pd could be recovered in two synthesis circles, respectively. Economic assessment showed that it is profitable to dispose waste PCBs with the process proposed in this work.

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References

- [1] K. Huang, J. Guo, Z. Xu, Recycling of waste printed circuit boards: a review of current technologies and treatment status in China, *Journal of Hazardous Materials* 164 (2009) 399–408.
- [2] H.G. Ni, E.Y. Zeng, Law enforcement and global collaboration are the keys to containing e-waste tsunami in China, *Environmental Science and Technology* 43 (2009) 3991–3994.
- [3] O.A. Ogunseitan, J.M. Schoenung, J.D.M. Saphores, A.A. Shapiro, The electronics revolution: from E-wonderland to E-wasteland, *Science* 326 (2009) 670.
- [4] M. Wong, S. Wu, W. Deng, X. Yu, Q. Luo, A. Leung, C. Wong, W. Luksemburg, A. Wong, Export of toxic chemicals – a review of the case of uncontrolled electronic-waste recycling, *Environmental Pollution* 149 (2007) 131–140.
- [5] M. Goosey, R. Kellner, Recycling technologies for the treatment of end of life printed circuit boards (PCBs), *Circuit World* 29 (2003) 33–37.
- [6] M.K. Jha, A. Kumari, P.K. Choubey, J. Lee, V. Kumar, J. Jeong, Leaching of lead from solder material of waste printed circuit boards (PCBs), *Hydrometallurgy* 121–124 (2012) 28–34.
- [7] J. Sohaili, S.K. Muniyandi, S.S. Mohamad, A review on printed circuit boards waste recycling technologies and reuse of recovered nonmetallic materials, *International Journal of Scientific and Engineering Research* 3 (2012) 1–7.
- [8] K. Zhang, J.L. Schnoor, E.Y. Zeng, E-waste recycling—where does it go from here? *Environmental Science and Technology* 46 (2012) 10861–10867.
- [9] B.H. Robinson, E-waste: an assessment of global production and environmental impacts, *Science of the Total Environment* 408 (2009) 183–191.
- [10] 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.
- [11] J. Cui, L. Zhang, Metallurgical recovery of metals from electronic waste: a review, *Journal of Hazardous Materials* 158 (2008) 228–256.
- [12] C. Hagelüken, C.W. Corti, Recycling of gold from electronics: cost-effective use through ‘design for recycling’, *Gold Bulletin* 43 (2010) 209–220.
- [13] C. Hagelüken, A. Greinerstraß, Recycling of electronic scrap at Umicore’s integrated metals smelter and refinery, in: *European Metallurgical Conference*, 2005, pp. 307–323.
- [14] W. Lin, C. Wong, Fast etching of copper in thionyl chloride/acetonitrile solutions, *Corrosion Science* 53 (2011) 3055–3057.
- [15] H. Yang, J. Liu, J. Yang, Leaching copper from shredded particles of waste printed circuit boards, *Journal of Hazardous Materials* 187 (2011) 393–400.

- [16] 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, *Journal of the Air and Waste Management* 53 (2003) 897–902.
- [17] J. Li, H. Lu, J. Guo, Z. Xu, Y. Zhou, Recycle technology for recovering resources and products from waste printed circuit boards, *Environmental Science and Technology* 41 (2007) 1995–2000.
- [18] C. Duan, X. Wen, C. Shi, Y. Zhao, B. Wen, Y. He, Recovery of metals from waste printed circuit boards by a mechanical method using a water medium, *Journal of Hazardous Materials* 166 (2009) 478–482.
- [19] R. Liu, R. Shieh, R.Y.L. Yeh, C. Lin, The general utilization of scrapped PC board, *Waste Management* 29 (2009) 2842–2845.
- [20] R. Dawson, G. Kelsall, Recovery of platinum group metals from secondary materials: I. Palladium dissolution in iodide solutions, *Journal of Applied Electrochemistry* 37 (2007) 3–14.
- [21] R. Pyper, Extraction of gold from finely disseminated gold ores by use of acidic thiourea solution, in: *Extraction Metallurgy* 81, London, 1981.
- [22] N. Gönen, E. Körpe, M. Yıldırım, U. Selengil, Leaching and CIL processes in gold recovery from refractory ore with thiourea solutions, *Minerals Engineering* 20 (2007) 559–565.
- [23] J. Hanafi, E. Jobiliong, A. Christiani, D.C. Soenarta, J. Kurniawan, J. Irawan, Material recovery and characterization of PCB from electronic waste, *Procedia – Social and Behavioral Sciences* 57 (2012) 331–338.
- [24] 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, *Journal of Hazardous Materials* 233/234 (2012) 200–206.
- [25] Y.C. Zhang, J.Y. Tang, A green hydrothermal route to nanocrystalline CuCl , *Materials Letters* 61 (2007) 3708–3710.
- [26] T. Xie, M. Gong, Z. Niu, S. Li, X. Yan, Y. Li, Shape-controlled CuCl crystallite catalysts for aniline coupling, *Nano Research* 3 (2010) 174–179.
- [27] J. Li, H. Duan, K. Yu, L. Liu, S. Wang, Characteristic of low-temperature pyrolysis of printed circuit boards subjected to various atmosphere, *Resources, Conservation and Recycling* 54 (2010) 810–815.
- [28] 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.
- [29] J.M. Berger, R. Winand, Solubilities, densities and electrical conductivities of aqueous copper (I) and copper (II) chlorides in solutions containing other chlorides such as iron, zinc, sodium and hydrogen chlorides, *Hydrometallurgy* 12 (1984) 61–81.
- [30] J.J. Fritz, Solubility of cuprous chloride in various soluble aqueous chlorides, *Journal of Chemical and Engineering Data* 27 (1982) 188–193.
- [31] 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, *Journal of Hazardous Materials* 166 (2009) 746–750.
- [32] 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.
- [33] J. Dian, *Lange's Handbook of Chemistry*, Science Press, Beijing, 2003.
- [34] E.-Y. Kim, M.-S. Kim, J.-C. Lee, M.K. Jha, K. Yoo, J. Jeong, Effect of cuprous ions on Cu leaching in the recycling of waste PCBs, using electro-generated chlorine in hydrochloric acid solution, *Minerals Engineering* 21 (2008) 121–128.