Recovery of copper and lead from waste printed circuit boards by supercritical water oxidation combined with electrokinetic process

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ABSTRACT

An effective and benign process for copper and lead recovery from waste printed circuit boards (PCBs) was developed. In the process, the PCBs was pre-treated in supercritical water, then subjected to electrokinetic (EK) process. Experimental results showed that supercritical water oxidation (SCWO) process was strong enough to decompose the organic compounds of PCBs, and XRD spectra indicated that copper and lead were oxidized into CuO, Cu₂O and β-PbO₂ in the process. The optimum SCWO treatment conditions were 60 min, 713 K, 30 MPa, and EK treatment time, constant current density were 11 h, 20 mA cm⁻², respectively. The recovery percentages of copper and lead under optimum SCWO + EK treatment conditions were around 84.2% and 89.4%, respectively. In the optimized EK treatment, 74% of Cu was recovered as a deposit on the cathode with a purity of 97.6%, while Pb was recovered as concentrated solutions in either anode (23.1%) or cathode (66.3%) compartments but little was deposited on the electrodes. It is believed that the process is effective and practical for Cu and Pb recovery from waste electric and electronic equipments.

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1. Introduction

Printed circuit boards (PCBs) are widely used in many electrical and electronic equipments such as household appliances, computers, etc. It is estimated that as many as 500 million personal computers (PCs) have become obsolete and enter the municipal solid waste stream between 2000 and 2007 [1]. Waste PCBs are particularly difficult to dispose because of the heterogeneous mix of polymer materials, multiple kinds of metals, and glass fiber. Currently, waste PCBs are either incinerated, which can lead to the formation of toxic atmospheric pollution through the release of dioxins and furans [2], or sent to landfill, which can lead to toxic matter such as heavy metal Pb (around 2% in PCBs) leaching into the groundwater. Previous study [3], using the toxicity characteristic leaching procedure (TCLP) of the US Environmental Protection Agency (USEPA), has shown that Pb concentrations in the extracts of a vast majority of the PCBs are higher than the limit levels. On the other hand, the quantity of valuable metals, especially Cu (around 20% in PCBs), turns the wastes into an interesting raw material from the economic point of view. Therefore, it is of great importance to develop effective and environmental benign processes for treatment of these types of wastes so as to recover the valuable matters and simultaneously remove the toxic substances.

In recent years, supercritical water oxidation (SCWO) technique has been widely applied to the process of decomposition of stable toxic organic wastes [4,5]. At supercritical conditions ($T > 647.3$ K, $P > 22.1$ MPa), water has a high solubility for both organics and oxygen, and organic compounds, oxygen, and water form a single and homogeneous phase, which allows oxidation to proceed rapidly by an elimination of the potential interface mass transport limitations [6,7]. Recently, this technique has been successfully applied to the degradation of waste polymer materials [8,9]. Polymers could be degraded and recovered as monomers or low molecular weight organic compounds in a very short residence time in supercritical water without causing air pollution [9]. Recently, it has been reported that polymers in waste PCBs could be degraded into CO₂ and H₂O in the SCWO process, and the formation of brominated polycyclic aromatic hydrocarbons (PAHs) was eliminated at the same time [10]. Thus far, many studies on the application of SCWO have focused on the removal or recovery of organic substances for wastes treatment, only a little information is available on the behavior of the metallic elements in the process. Lately, Fang et al. [11] reported the behavior of some heavy metals during oxidation of industrial wastes in supercritical water. It also has been reported [10] that copper (Cu) in waste PCBs can be oxidized to oxides during SCWO treatment. However, little is known about the behavior of Pb, one of the most significant heavy metals in waste PCBs, during SCWO process.

For many years, electrokinetic processes (EK) have been widely investigated and applied in soil and groundwater remediation

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[12–13]. The method uses direct current as the “cleaning agent”, combining the electrokinetic movement of ions in the matrix. Recently, some researchers [14–21] reported the use of such techniques for metal recovery or removal from solid wastes, and more lately, Guillaume et al. [22] reported an effective EK process which combines electroleaching and electrodeposition in a single-cell to recover zinc from some zinc-rich solid wastes, without transportation of solids or fluids from one chamber to another by pumps or other mechanical processes, and the principle of which has been well described. This achievement induced us to test the process for the treatment of SCWO-treated PCBs particles, and evaluate the feasibility of the application of such process to recover or remove metallic elements from waste PCBs that contain large numbers of Cu and Pb.

In this study, we attempted to develop a highly efficient and benign process for copper and lead recovery from waste PCBs. The integrated process combined SCWO and EK techniques in the treatment of PCBs. The SCWO process was used as a pre-treatment to degrade the polymers and oxidize copper and lead in waste PCBs. The EK process relied upon application of an electric field to the SCWO-treated PCBs, and metal ions or ionic complexes are formed and migrate to the cathode or anode, and form enriched solutions or reduce to form a deposit on the cathode.

2. Materials and methods

2.1. SCWO experiments

Waste PCBs used in this work were supplied by HUAXING Environment Protection Company of Beijing. After the components (relays, capacitors, etc.) were disassembled, the PCBs were sent to comminute in a cutting mill until the fractions reached particle size smaller than 0.1 mm. All chemicals were purchased from Chemical Reagent Company of Beijing in analytical grade.

In the SCWO treatment experiments, 10 g of the sample and 50 ml of distilled water were employed, while hydrogen peroxide (H_2O_2 , 30 wt.%) was used as oxygen source. Experiments were conducted in a 200-ml high-pressure reactor made of 316 alloy. Referring to a previous report [10], 713 K and 30 MPa was selected for SCWO treatment, since most of the polymer in PCBs could be decomposed to CO_2 and H_2O at foregoing conditions. Six SCWO treatments were performed with treatment time of 15, 30, 60, 90, 120 and 150 min, respectively. Metal content in the raw PCBs and in the SCWO treatment residues were measured by ICP-OES after aqua regia digestion [23]. Cu and Pb concentrations in the solutions after SCWO treatments were also measured by ICP-OES and the pH of the solutions were measured by Radiometer Analytical pH electrode. Organic matter weight of the initial PCBs and the SCWO-treated PCBs were determined by loss of ignition at 550 °C for 1 h.

2.2. EK experiments

Fig. 1 shows a schematic drawing of the EK setup. After each SCWO treatment, the suspension obtained was filtrated using a vacuum filter and 2 g of the residue was transferred into compartment II of EK cell after dryness, while 20 ml of HCl (1 M) solutions were added. The SCWO-treated PCBs was kept in the suspension by constant stirring (1600 rpm) with magnetic stirrer (SH-3 from JBD, Beijing, China). The anolyte and catholyte were separated by two porous glass frits with 1 mm thickness and pore size below 50 μm . Platinum-coated electrodes from LEICI (Shanghai, China) were used as working electrodes. The electrodes were plates with an active area of 2 cm^2 , and the power supply was a TPR-6405D (LONGWEI, H.K). Either anolyte or catholyte initially consisted of 20 ml 1 M HCl without adjusting all along the

Fig. 1. Schematic drawing of the EK setup.

experiment. The constant current density was 10, 20, 30 mA/cm^2 , respectively.

After each EK experiment, electrodes were dipped in 5 M HNO_3 overnight. Volumes of the cleaning acids and the electrolytes were measured followed by analysis of the metal concentrations by ICP-OES.

The structure of the PCB solid residue after SCWO treatment and deposits on the cathodes after EK process were characterized by X-ray diffraction spectroscopy (XRD) at 50 kV and 100 mA using Cu $\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Chemical composition of the deposits obtained on the cathodes was determined by X-ray fluorescence (XRF).

3. Results and discussion

3.1. Effect of SCWO treatment on Cu, Pb species and organic compounds

For understanding the species of Cu and Pb after SCWO process, crystal properties of the solid residue from 1 h SCWO-treated PCBs was studied by X-ray diffraction spectroscopy. Fig. 2 shows clearly that CuO, Cu_2O are the main species in the solid residue, in agreement with a previous report that CuO, Cu_2O and $\text{Cu}(\text{OH})_2$ are the main products in PCBs residue in the presence of NaOH after SCWO treatment [10]. It can be seen in Fig. 2 that PbO_2 is the preponderant specie of Pb in the solid residue. The peaks at 2θ of 25.3, 32.2 and 49.2 indicate the forming of $\beta\text{-PbO}_2$. This could be attributed to the complete oxidation of Pb, whereas copper may not be oxidized completely in the SCWO process [10]. Cu(0) and Pb(0) species could not be observed in the XRD pattern indicating the entire oxidation of Cu(0) and Pb(0).

Fig. 2. X-ray diffraction patterns of the solid residue from 1 h SCWO-treated PCBs.

Fig. 3. Effect of SCWO treatment time on organic compounds decomposition.

Effect of SCWO treatment on organic compounds decomposition is shown in Fig. 3. Organic compounds decomposition is expressed as

$$\text{organic compounds decomposition (\%)} = \frac{M_1 - M_2}{M_1} \times 100 \quad (1)$$

where M_1 is the organic matter weight of the initial PCBs and M_2 the organic matter weight of the SCWO-treated PCBs. Organic compounds decomposition of waste PCBs increased with the increase of SCWO treatment time, and the organic compounds decomposition at 713 K, 30 MPa and 1 h SCWO treatment was 97.8%. The supercritical water exhibited a unique characteristic of a slightly polar organic solvent. Therefore, organics and oxygen became completely miscible in supercritical water [10]. The results showed that organic compounds in the waste PCBs were oxidized very effectively in supercritical water.

Therefore, it is believed that 1 h SCWO treatment is sufficient for the pre-treatment.

3.2. Mass balance of Cu and Pb in the SCWO process

Table 1 presents the mass balance of Cu and Pb in the six treatments. The definition of metal recovery yield in residue after SCWO process is expressed as

$$\text{metal recovery yield in residue (\%)} = \frac{\text{metal content in PCBs residue after SCWO}}{\text{initial metal content in PCBs}} \times 100 \quad (2)$$

It can be seen that Cu recovery yield in the residue after SCWO increased with the treatment time during the first 60 min but decreased thereafter, and reached a steady level after 90 min. This could be attributed to the variation of the pH in the system in different SCWO treatment time. It can be seen in Fig. 4 that the effect of SCWO treatment time on the pH of the system. One inter-

Fig. 4. Effect of SCWO treatment time on pH values.

esting result from Fig. 4 and Table 1 is that the variation trend of the system pH consistent with that of Cu recovery yield in residue. The highest Cu recovery yield in the residue and the highest solution pH were all obtained at 1 h SCWO treatment, and moreover, the least loss of Cu (3.65 mg) in the filtrate was also at this point. All of the foregoing results could be attributed to the higher pH of the system, leading to the less dissolution of the solid phase such as the metal oxides. One possible reason for the variation of the system pH was the degradation of the polymer in PCBs during the SCWO process. At the first stage (about 15 min of SCWO treatment), the polymer (mainly epoxy resin) in the PCB wastes decomposed to lower molecular organic compounds rapidly and produce many organic acids and CO_2 [24]. Thus the produced organic acids and CO_2 could lead to the low pH of the system and the increase of the dissolution of the metal oxides. In addition, Br species in waste PCBs exist as $\text{H}^+ + \text{Br}^-$ in water after the SCWO process [10]. After the first stage, pH increased when Br^- was oxidized to Br_2 along with the increase of time and the organic acids decreased due to the complete oxidation of the organic acids to CO_2 and H_2O . The maximal recovery yield of Cu in the residue (about 99.8%) was obtained at 60 min, while the pH value of the system was the highest (6.5) at this point. Subsequently, more CO_2 that was produced from the complete oxidation of the organic acids dissolved in the system, leading to the decline of the pH and the dissolution of the solid phase. But the pH reached a steady level after 90 min, which could be attributed to the dissolution equilibrium of CO_2 in the system.

It can also be seen from Table 1 that the recovery of Pb approached 100% after 15 min SCWO treatment, thus it can be concluded that the effect of SCWO treatment time on the recovery of Pb in this process is negligible. Accordingly, from both economic and efficiency point of view, 60 min SCWO-treated PCBs was used in the following EK experiments.

3.3. Migration of Cu and Pb in the EK process

Figs. 5 and 6 illustrate the recovery of Cu and Pb in the anodic or cathodic compartments at different EK treatment times. The metal recovery yield was expressed as

$$\text{metal recovery yield (\%)} = \frac{M}{\text{initial metal content in PCBs}} \times 100 \quad (3)$$

where M is the content of metal (Cu or Pb) in anode compartment, cathode compartment, or deposited on cathode.

The recovery of Cu in the anodic compartment was negligible, mainly attributing to the diffusion throughout the glass frit. Most of Cu was recovered in cathodic compartment or deposited on cathode. The recovery of Pb in anodic or cathodic compartment was increased along with the increase of EK time.

Table 1
Mass balance of Cu and Pb in different SCWO treatments.

	SCWO time (min)					
	15	30	60	90	120	150
Cu1 (%)	94.0	95.1	99.8	97.4	96.5	96.5
Cu2 (mg)	120.1	97.55	3.65	52.52	71.4	71.3
Pb1 (%)	98.9	100	102	99.6	101	103
Pb2 (mg)	0.2	0.1	n.d.	n.d.	0.05	n.d.

1: metal recovery yield in residue after SCWO; 2: metal content in filtrate after SCWO; n.d.: non-detectable.

Fig. 5. Effect of EK time on the recovery of Cu in anode and cathode compartments (current density: 20 mA/cm²).

Fig. 6. Effect of EK time on the recovery of Pb in anode and cathode compartments (current density: 20 mA/cm²).

Cu and Pb can form complexes with Cl⁻ and the complexes can be positive, negative or uncharged (MeCl⁺, MeCl₂(aq), MeCl₃⁻ and MeCl₄²⁻), especially Pb form stable complexes with Cl⁻ [25].

Since most Cu moved as cations, free Cu ion and CuCl⁺ dominated in the solution. Pb moved towards both cathode and anode compartments during the EK process, indicating both positively (Pb²⁺ and PbCl⁺) and negatively (PbCl₃⁻ and PbCl₄²⁻) charged Pb species existed in the solution. The formation of dissolved heavy metal complexes could increase the solubility and the mobility of the metal in the EK process [26].

In the EK process, lead oxides (PbO₂) dissolved in compartment II and produced high valence lead ions such as Pb⁴⁺, which was unstable in HCl system and could be reduced to low valence lead ions such as Pb²⁺ by Cl⁻ or Cu⁺ because the standard reduction potential (*E*⁰) of PbO₂/Pb²⁺, 1.455 V, is larger than that of Cl₂/Cl⁻, 1.36 V, and Cu²⁺/Cu⁺, 0.153 V, then the Pb²⁺ formed chlorocomplexes of lead such as PbCl₃⁻ or PbCl₄²⁻ and moved towards anode. Another possible route for the forming of PbCl₃⁻ or PbCl₄²⁻ is that high valence lead ions moved to cathode in the electric field and were reduced to low valence lead ions near the cathode, then chlorocomplexes of lead formed and migrated to anode in the electric field. All these resulted in the decrease of the content of lead species in the liquid of compartment II, which could break the fol-

lowing chemical reaction equilibriums:

Accordingly, the reactions (4) and (5) move towards right, and more lead dissolved, forming more ions or chloride complexes that move towards cathode or anode. One interesting result from Fig. 6 is that the recovery of Pb in the anode compartment after 7 h treatment decreased to a certain degree, which could be attributed to the oxidation of Cl⁻ near the anode and the conversion of some Pb from negative complexes to positive complexes or free ions. The smell of chlorine gas was noticed near the anode after 5 h EK treatment.

3.4. Effect of current density on total recovery yield of Cu and Pb in EK process

The effect of current density on total recovery yield of Cu and Pb in EK process is shown in Table 2. Total metal recovery yield was calculated as follows:

$$\text{total metal recovery yield (\%)} = \frac{\text{summation}}{\text{initial metal content in PCBs}} \times 100 \quad (6)$$

where summation is the total amount of metal found in the electrolytes (except compartment II) and electrodes after each experiment.

Current efficiency was determined as the ratio of the weight of copper *W*₁ deposited on the cathode with electrical quantity *Q*, to the theoretical weight of deposited metal *W*₂ calculated by using Faraday's law:

$$W_2 = \frac{M_{\text{Cu}} Q}{Z_{\text{Cu}} F} \quad (7)$$

where *F* is the Faraday's constant, *M*_{Cu} the molar weight of copper (63.54 g mol⁻¹), and *Z*_{Cu} is the valence of copper, i.e. 2. *Q* (electric quantity) is the product of the applied current *I* and the period of time, *t*. Eq. (8) gives the current efficiency (CE):

$$\text{CE (\%)} = \frac{W_1}{W_2} \times 100 \quad (8)$$

The total recovery yield of Cu and Pb at 11 h EK treatment increased with the increase of applied current density, and the higher current density applied, the higher initial potential gradient was observed (Table 2). Although the highest total recovery yield of Cu and Pb were all obtained when 30 mA/cm² current density was applied, it is too high energy consumption and not economic due to the too low current efficiency, 51%. The reason for the low CE is that the increase of potential gradient could result in much more side reactions such as the reduction of H⁺ on the cathode. The 20 mA/cm² current density was applied in the optimized EK treatment because the relatively high total recovery yield of Cu, Pb and current efficiency could be obtained at the same time.

Variation of potential gradient during EK process (current density = 20 mA/cm²) was shown in Fig. 7. During the first 80 min, the potential gradient increased rapidly which could be attributed

Table 2
Effect of current density on total recovery yield of Cu and Pb in EK process.

CD (mA/cm ²)	PG(i) (V/cm)	PG(e) (V/cm)	Cu total recovery (%)	Pb total recovery (%)	CE (%)
10	0.24	0.37	66.3	72.7	84
20	0.35	0.53	84.2	89.4	70
30	0.42	0.89	92.1	93.5	51

EK time: 11 h; CD: current density; CE: current efficiency; PG(i): initial potential gradient; PG(e): potential gradient in the end.

Fig. 7. Variation of potential gradient in EK process (current density: 20 mA/cm²).

to the rapid decrease of H⁺ and the too low metals ions concentration in solution. After this first period, the potential gradient decreased with the increase of EK time, especially after the 300 min EK treatment, the potential gradient decreased quickly, which was consistent with the migration result of Cu ions (Fig. 5). It can be seen in Fig. 5 that the content of Cu ions increased rapidly after 5 h EK treatment, which was favorable to decrease the potential gradient. This means that the electro-leaching efficiency of metals species was higher during this period. After 8 h EK treatment, the potential gradient increased again due to the decrease of the concentrations of H⁺ and Cu ions.

3.5. Effect of time on total recovery yield of Cu and Pb in EK process

Figs. 9 and 10 illustrate the effect of time on total recovery yield of Cu and Pb in EK experiments, and the purity and crystal properties of Cu deposited on cathode are presented in Table 3 and Fig. 8, respectively. It can be seen in Fig. 5 that the recovery yield of Cu in compartment III (except the deposition) increased with the increase of EK processing time during the first 7 h and decreased thereafter. It can also be observed in Fig. 5 that little Cu deposited on the cathode in the first 3 h during the EK process, which could be attributed to the low Cu ion concentration in compartment III and the high H⁺ that could be reduced on the cathode, but Cu deposited on cathode increased quickly after 3 h, e.g., Cu deposition percentage increased about two times at 7 h compared to 5 h, which could be attributed to the highest Cu ions concentration in III compartment (Fig. 5). In such three-compartment EK system, a higher metal ion concentration in cathode compartment could allow a higher amount of deposited metal, with higher current efficiency [22].

It can be seen from Figs. 9 and 10 that about 84.2% of Cu in the waste PCBs was recovered while 74% deposited on the cathode after

Fig. 8. X-ray diffraction patterns of Cu deposited on cathode.

Fig. 9. Effect of EK time on total recovery yield of Cu.

11 h EK treatment (Fig. 5), and 89.4% of Pb was recovered while 66.3% concentrated in cathode compartment and 23.1% in anode compartment, whereas little Pb could be deposited on the cathode (Fig. 6). Although the highest total Cu recovery yield (about 84.7%) was obtained at 7 h, and that for Pb (about 90%) at 9 h in the EK process, the highest deposition yield of Cu was obtained at 11 h (Fig. 5), where Cu (crystal properties can be seen in Fig. 8.) can be directly recovered. In Fig. 8, a weak characteristic peaks of Cu₂O also can be observed, which could be attributed to the partial oxidation of Cu deposited on the cathode. Therefore, 11 h was performed in the EK process, where 89.4% of lead and 84.2% of copper were recovered, while 74% of Cu can be recovered as a precipitate on the cathode with a purity of 97.6% (Table 3).

Fig. 10. Effect of EK time on total recovery yield of Pb.

Table 3
Chemical composition of the cathode deposit analyzed by X-ray fluorescence.

	Wt.%
Cu	97.6
Pb	1.08
Sn	0.62
Fe	0.33
Zn	0.25
As	0.01
Ni	0.04
Cd	0.02
Cr	0.01

EK parameter: 20 mA/cm² constant current density, 11 h treatment.

4. Conclusions

The results of this study demonstrated that SCWO technique was efficient and benign as a pre-treatment to decompose the organic compounds of PCBs. In such a process, copper and lead were oxidized to CuO, Cu₂O and β -PbO₂, and the loss of copper and lead was negligible under optimum condition: 60 min, 713 K, 30 MPa.

In the EK process with 1 M HCl as assisting agent, most copper migrated to the cathode compartment and deposited on the cathode, while lead moved towards either anode or cathode compartment, and little was deposited on electrodes. Hence it is feasible to effectively and separately recover copper and lead in the EK process. When 11 h treatment time and 20 mA/cm² constant current density were applied in the EK process, about 84.2% of copper was recovered in the cathode compartment, among which 74% deposited on cathode with a purity of 97.6%, which can be directly reused in second industry. Meanwhile, 89.4% of lead was recovered as concentrated solutions in anode and cathode compartments.

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