Co-treatment of waste printed circuit boards and polyvinyl chloride by subcritical water oxidation: Removal of brominated flame retardants and recovery of Cu and Pb

Fu-Rong Xiu^{a,c,*}, Yingying Qi^a, Fu-Shen Zhang^b

^a Department of Environment and Equipment Engineering, Fujian University of Technology, Fuzhou 350108, People's Republic of China

^b Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, People's Republic of China

^c Key Laboratory of Solid Waste Treatment and Recycle (SWUST), Ministry of Education, Mianyang 621010, People's Republic of China

HIGHLIGHTS

- We report an effective process for co-treatment of waste PCBs and PVC.
- Brominated flame retardants can be decomposed efficiently in co-treatment.
- Dechlorination of PVC was complete and safe.
- Cu and Pb in waste printed circuit boards can be recovered efficiently.
- Sn and Cr can be immobilized efficiently in the residue after co-treatment.

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ABSTRACT

In this work, an effective process for removal of brominated flame retardants (BFRs) and recovery of Cu and Pb from waste printed circuit boards (PCBs) was developed. In the process, waste PCBs and polyvinyl chloride (PVC) were co-treated by subcritical water oxidation (SBWO). PVC was used as a hydrochloric acid source and waste PCBs was used as a neutralizing reagent for the produced HCl. The dechlorination of PVC, removal of BFRs, and recovery of Cu and Pb could be achieved simultaneously by the one-step SBWO reaction. Experimental results showed that the dechlorination of PVC was complete when SBWO temperature exceeded 250 °C. SBWO co-treatment was high efficient for the leaching of Cu and Pb from waste PCBs, and XRD spectra indicated that Sn was immobilized as SnO₂ in the residue after co-treatment. The optimum SBWO co-treatment conditions were temperature of 350 °C, time of 60 min, solid-liquid ratio of 1:9 g/ml, and PVC-to-PCBs ratio of 1:1, respectively. In the optimized co-treatment, 98.9% of Cu and 80% of Pb were recovered, while the leaching efficiencies of Sn and Cr were 15.3% and 3.9%, respectively. Meanwhile, approximately 100% of the bromine was changed into HBr and enriched in water after co-treatment.

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1. Introduction

Waste electric and electronic equipment (WEEE) has been taken into consideration not only by the government but also by the public due to its content of valuable materials and hazardous matters [1]. As the primary elements in most WEEE, printed circuit boards (PCBs) are widely used as the platform upon which microelectronic components such as semiconductor chips and capacitors are mounted. Waste PCBs contain approximately 70% nonmetals and

30% metals [2]. The nonmetal portions of waste PCBs consist of resins and brominated flame retardants (BFRs) [3]. Improper disposition of waste PCBs may cause serious pollution due to the formation of brominated dioxin-like compounds from BFRs [4]. The typical metals in waste PCBs consist of Cu, Pb, Sn, Cr, Cd, Zn, Ni, and Mn [5]. Previous study [6], using the toxicity characteristic leaching procedure (TCLP) of the US Environmental Protection Agency (USEPA), indicated that Pb (around 2% in PCBs) concentrations in the extracts of a vast majority of the PCBs were higher than the limit levels. On the other hand, the quantity of valuable metal such as Cu (around 20% in PCBs) turns the wastes into an interesting raw material from the economic point of view.

Currently, pyrometallurgical process [7,8] and hydrometallurgical process [9–11] are the two traditional approaches for the

* Corresponding author at: Department of Environment and Equipment Engineering, Fujian University of Technology, Fuzhou 350108, People's Republic of China. Tel.: +86 591 22863268.

E-mail address: xiu_chem@hotmail.com (F.-R. Xiu).

recovery of metals from waste PCBs. In addition, many researchers have used various mechanical methods as pre-treatment to separate metals from waste PCBs [2,5]. Other recycling techniques for metals in waste PCBs such as bioleaching [12,13] and vacuum metallurgy technology [14] also have been developed. However, the foregoing processes not only can not remove efficiently toxic organic matters such as BFRs in waste PCBs, but also have a considerable loss of valuable metal due to the insufficient liberation [15,16]. Among various recovery technologies, hydrometallurgical processes with relatively low capital costs and suitability for small scale applications are promising options for the treatment of waste PCBs, and the leaching of metals is the most important procedure in a hydrometallurgical process [11]. However, the metals and polymers in waste PCBs are intermingled very much and also have other materials embedded inside, which is the main obstacle for the leaching of metals from waste PCBs.

In recent years, sub- and supercritical water (sub/SCW) is used as an environment-friendly method to decompose hazardous matters due to its extraordinary properties, such as low viscosities, high mass transport coefficient, high diffusivity and high solubility for organics [17,18]. In sub/SCW conditions, water can act not only as a solvent but also as a reactant, catalyst or product due to the different properties in different temperature and pressure [19]. Onwudili and Williams [20,21] found that pure flame-retarded plastics could be degraded effectively in sub/SCW and bromine-free oil could be obtained by adding alkaline additives. Yin and Xing [22,23] also reported that toxic organic matters such as BFRs in waste PCBs could be degraded efficiently in sub/SCW under reducing atmosphere, and the formation of toxic brominated organic compounds was eliminated at the same time. However, little is known about the debromination behavior of BFRs during the subcritical water oxidation (SBWO) process in the presence of oxygen.

In our latest study [24], a two-step process for metals recovery from waste PCBs by supercritical water pre-treatment combined with acid leaching was developed. In the proposed process, waste PCBs were pre-treated by supercritical water, then the separated solid phase product with concentrated metals was subjected to an acid leaching process for metals recovery. In this work, we attempted to develop a highly efficient one-step process for the treatment of waste PCBs by SBWO reaction, in which the removal of BFRs and the recovery of Cu and Pb from PCBs could be achieved simultaneously. In the process, another waste, polyvinyl chloride (PVC), was introduced into the SBWO reaction system of waste PCBs in consideration of the ubiquity of PVC plastics in WEEE. Currently, PVC wastes are mainly incinerated for thermal recovery. However, the incineration of PVC can lead to the formation of chlorinated toxic organics such as dioxins [25,26]. Hence, it is important for PVC waste to be treated in a safe process. In the co-treatment of waste PCBs and PVC, the lixiviant (HCl) in situ generated by PVC decomposition is expected to extract Cu and Pb from waste PCBs. In other words, by co-treating the two wastes in SBWO, waste PCBs is used as both a secondary source for metals and a neutralizer for HCl from waste PVC, and PVC waste is used as an acid source for the leaching of metals in PCBs. Meanwhile, the BFRs contained in waste PCBs can be removed safely during the co-treatment. Hence, the dechlorination of PVC, the debromination of BFRs, and the leaching of metals would occur in the same reaction system, which is quite different from the process in our previous report [24]. During the co-treatment system, the characteristics and influence factors of dechlorination, debromination, and metals leaching are needed to be clarified. The objectives of the present work are (1) to evaluate the dechlorination behavior of PVC in the SBWO process, (2) to examine the removal efficiency of BFRs from waste PCBs in the co-treatment process, and (3) to investigate the effects of mixing ratio of waste PVC to PCBs,

co-treatment temperature, time, and solid–liquid ratio on the leaching activity of different metals contained in waste PCBs. Cu, Pb, Sn, and Cr were selected as target elements, among which Cu is the richest metallic element in waste PCBs, while Pb, Sn, and Cr are of environmental and public health concern.

2. Materials and methods

2.1. Materials

Waste PCBs used in this work were mainly collected and disassembled from discarded telephones, PCs, and other electrical equipments. After the components (relays, capacitors, etc.) were disassembled, the PCBs were sent to be comminuted in a cutting mill until the particle size <1 mm. The composition of the waste PCBs sample is given in Table 1. The CHNSO content of the PCBs samples was measured by an Elemental Analyzer (vario EL, Elementar Analysensysteme GmbH). A commercially available poly(vinyl chloride) (PVC) (DAXIANG Chemical Company of Beijing, degree of polymerization ≈ 1100) was used in this study. The diameter of the PVC powder was around 500 μm . Other chemicals used in this study were purchased from Chemical Reagent Company of Beijing in analytical grade and all of them were used as received.

2.2. SBWO co-treatment of waste PCBs and PVC

The SBWO co-treatment experiments were carried out in a 200-ml high-pressure reactor made of 316 alloy (WYF-2 from HUAAN, China). The mixture of waste PCBs, PVC and different amounts of distilled water were introduced into the reactor, while 40 ml of hydrogen peroxide (H_2O_2 , 30 wt.%) was used as oxygen source [19]. H_2O_2 was decomposed and the released O_2 was dissolved in subcritical water ($\text{H}_2\text{O}_2 = \text{H}_2\text{O} + 1/2\text{O}_2$). The amount of waste PCBs used in every experiment was 5 g. The adding volume of water was controlled at 10, 20, 30, 40, 50, and 60 ml, respectively. The reaction temperature was varied from 150 to 400 $^\circ\text{C}$, and the residence time was controlled at 30, 60, 90, 120, 150, and 180 min, respectively. The reactor was heated to selected temperatures, and kept at these temperatures for selected residence time. The increase of temperature was at the rate of 10 $^\circ\text{C}$ per minute. The mixing ratios of PVC to PCBs were controlled at 0:1, 0.25:1, 0.5:1, 1:1 and 1.5:1 (w/w), respectively. The pressure inside was monitored by a pressure gauge attached to the reactor. The pressure in the reactor was changed during the reaction process and whose value depended upon the reaction conditions and the filling rate of the reactor. When the reactor was heated to selected temperature, the pressure at this point was defined as the initial pressure. After that, the reaction was held at this temperature for selected residence time. The pressure inside was defined as the final pressure when the residence time reached the selected value. The reaction conditions of each experiment were described in Table 2.

Table 1
Composition of the waste PCBs sample.

Element	Content (% w/w)
Cu	25.00 $\pm$ 0.05
Pb	1.90 $\pm$ 0.03
Sn	5.90 $\pm$ 0.06
Cr	0.04 $\pm$ 0.02
C	23.62 $\pm$ 0.07
H	2.73 $\pm$ 0.03
N	1.21 $\pm$ 0.04
S	0.02 $\pm$ 0.01
O	16.84 $\pm$ 0.06

Table 2Conditions of co-treatment experiments (P_i : initial pressure; P_f : final pressure).

Experiment	Temperature (°C)	Time (min)	PVC-to-PCBs ratio	P_i (MPa)	P_f (MPa)
1	150	60	1:1	1	2
2	200	60	1:1	4	5
3	250	60	1:1	10	12
4	300	60	1:1	15	17
5	350	60	1:1	18	20
6	400	60	1:1	23	25
7	350	30	1:1	18	19
8	350	90	1:1	18	21
9	350	120	1:1	18	22
10	350	150	1:1	18	22
11	350	180	1:1	18	22
12	350	60	0:1	12	14
13	350	60	0.25:1	13	15
14	350	60	0.5:1	16	17
16	350	60	1.5:1	19	21

Three phases (solid, aqueous, and gaseous) were produced after reaction. After each SBWO co-treatment, the gaseous phase was passed through a NaHCO_3 solution to capture inorganic bromine. Solid phase and aqueous phase were separated using a vacuum filter (VF204A from LEADER, China). The obtained solid residue was dried in an oven (DHG-9055A from HASCU, China) at 105 °C overnight for subsequent characterization. The bromine content in the solid sample was measured by an oxygen combustion bomb-ion chromatography (IC, DionexICS2000, USA). Because the high content of metals contained in PCBs and the reactions between metals and Br during the oxygen combustion process may result in the formation of insoluble Br-contained products and influence the determination of Br, the sulfuric acid- H_2O_2 leaching system was used to remove the metals prior to the analysis of Br. The digestion-measurement process is as follows: 50 ml H_2O_2 solution (30 wt.%) was added in 50 ml sulfuric acid solution ($\text{H}_2\text{SO}_4\text{:H}_2\text{O} = 1\text{:}3$), and then 5 g PCBs sample was introduced into the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$ leaching solution. After the reaction of 24 h, the solution was filtrated and the filtrate was diluted to 250 ml. The Br may exist in filtrate (mainly inorganic bromine) and solid residue (mainly organic bromine). Then 0.2 ml of 0.2 mol/l KI solution was added into 0.5 ml of the diluted filtrate. After that, the obtained solution was diluted to 100 ml and bromine content (C1) was measured by ion chromatography. The obtained solid residue was dried at 105 °C for 3 h in an oven, then 0.5 g of the dried residue was introduced into the oxygen combustion bomb and 1 ml ethanol was added as combustion improver at the same time. Before combustion reaction, 40 ml of 0.5 mol/l NaOH solution was added to absorb the produced bromine. Then 0.2 mol/l KI was added into the combusted solution and the bromine content (C2) was determined by ion chromatography after dilution. The bromine content in the solid sample was the summation of C1 and C2. The standard deviations on these values of bromine contents are $\leq \pm 0.08$. Debromination ratio was calculated according to the content of bromine before and after the co-treatment.

Metals contents in raw PCBs sample were measured by ICP-OES (OPTIMA 2000, PerkinElmer) after digestion [9]. Metals concentrations in the solutions after SBWO co-treatments were also measured by ICP-OES and the pHs of the solutions were measured by a Radiometer Analytical pH electrode (PHS-3D, LEIC). The metal leaching efficiency is defined as follows:

$$\text{Metal leaching efficiency (\%)} = W_1 \times 100 / W_2 \quad (1)$$

where W_1 is the metal mass leached and W_2 the initial metal mass in waste PCBs sample.

The structure of the solid residue obtained after SBWO co-treatment was characterized by X-ray diffraction spectroscopy (XRD,

Bruker D8 X-ray powder diffractometer) at 50 kV and 100 mA using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

2.3. PVC dechlorination in SBWO process

The PVC dechlorination experiments also were carried out in the 200-ml high-pressure reactor which was the same as the one used in SBWO co-treatment. 5 g PVC and 50 ml distilled water were introduced into the reactor, and then 40 ml H_2O_2 was added. The operation details are the same as the SBWO co-treatment experiments. After each reaction, the gaseous phase was passed through a NaHCO_3 solution with the purpose of capturing inorganic chlorine, and the liquid-solid mixture was filtered by a vacuum filter. Ion chromatography was applied for the analysis of the chlorine content in the solution.

The content of chlorine in raw PVC and in SBWO-treated PVC residue was also analyzed by the oxygen combustion bomb-ion chromatography. The detail of the determination of Cl in the samples is the same as the Br. The standard deviations on the values of Cl contents are $\leq \pm 0.06$. The content of chlorine in raw PVC is $56.2 \pm 0.06 \text{ wt.}\%$. Dechlorination ratio was calculated according to the Cl content before and after the SBWO treatment.

3. Results and discussion

3.1. Dechlorination behavior of PVC in SBWO process

To investigate the dechlorination behavior of PVC in SBWO process, the percentages of the PVC dechlorination were examined under different conditions, including reaction temperature and residence time. The effect of reaction temperature on the PVC dechlorination is shown in Fig. 1a. The reaction temperature was varied from 150 to 400 °C. No noticeable dechlorination of PVC was observed below 200 °C. The dechlorination increased significantly above 200 °C, and reached 93% at 250 °C. It was reported that in this temperature region the dechlorination of PVC occurred by thermal degradation [26]. Takeshita et al. [25] also reported that the PVC dechlorination was controlled by thermal degradation in water with saturated pressure. Similar behavior of PVC was observed in the presence of oxygen in our SBWO process. The dechlorination reached approximately 100% after treatment for the temperature ≥ 300 °C. To investigate the distribution of Cl decomposed from PVC in products after SBWO process, the Cl contents in gaseous product and aqueous phase product were analyzed. It was found that the Cl decomposed from PVC during SBWO process was completely transferred to aqueous phase, indicating that nearly all of the Cl in PVC could be dissolved as HCl in water in the temperatures varied from 300 to 400 °C.

Fig. 1b shows the effect of residence time on the dechlorination of PVC at 350 °C. The PVC dechlorination at 30 min was 96%, and then reached a stable level at around 100% for all residence time studied. The results indicated that the dechlorination did not depend upon the residence time after 30 min. Therefore, we infer that 30 min is sufficient for all of the Cl in PVC to be dissolved as HCl in water in SBWO process at 350 °C.

3.2. Debromination behavior of waste PCBs in SBWO co-treatment

The effect of temperature on the debromination of waste PCBs in SBWO co-treatment is shown in Fig. 2a. No debromination could be found when the temperature was < 200 °C, which could be attributed to that the energy provided by the system was not enough to break chemical bond of BFRs. The debromination efficiency increased quickly with the increase of temperature. The debromination efficiency reached approximately 100% at 350 °C. The results

Fig. 1. Effects of (a) temperature and (b) time on PVC dechlorination.

showed that temperature was an important influence factor on debromination efficiency. The temperature region in which the HBr was released from BFRs was between 200 and 300 °C. It has been reported that in traditional thermal degradation process, BFRs was decomposed from 297 °C to 400 °C [27]. Hence, compared with the traditional thermal degradation process, the degradation temperature region of BFRs can be obviously reduced under the SBWO reaction conditions.

Fig. 2b shows the effect of residence time on the debromination of waste PCBs in SBWO co-treatment. BFRs in waste PCBs could be decomposed rapidly in the first 30 min (98.5%). HBr and aromatics were released with the decomposition of BFRs. In subcritical region, dissolving capacity of organic molecules and oxygen in water is enhanced significantly due to the low dielectric constant of water, which causes water to behave more like an organic solvent and allows reaction to proceed rapidly by an elimination of the potential interface mass transport limitations [28]. Therefore, the aromatics produced from BFRs could be oxidized to CO₂ and H₂O quickly in the SBWO co-treatment. When the residence time was >30 min, the debromination increased slightly with the increase of time. Considering the debromination efficiency and energy consume, it is recommended that 30–90 min is the optimum residence time range.

After each experiment, gas phase product was introduced into NaHCO₃ solution to capturing HBr. However, the results indicated that no inorganic bromine was detected in the gas phase product in all experiments. Because HBr has a high solubility in water, it could be completely transferred into water during the cooling process after reaction.

3.3. Effect of the mixing ratio of PVC to PCBs on the leaching of different metals in SBWO co-treatment

To investigate the effect of the mixing ratio of PVC to PCBs on the leaching of metals in co-treatment, different PVC-to-PCBs ratios (0:1, 0.25:1, 0.5:1, 1:1, and 1.5:1) were used in experiments at 350 °C and 60 min. The results are shown in Fig. 3. The leaching of all metals studied was negligible when no PVC was introduced into the reaction system. In the experiment with the PVC-to-PCBs ratio of 0.25:1, 14.9% of the Cu, 5.7% of the Pb, 3.6% of the Sn, and 0.2% of the Cr were converted from insoluble species to soluble species. With further increasing the PVC-to-PCBs ratio, there was little change in the concentration of Sn and Cr in the aqueous phase, while the leachability of Cu and Pb tended to increase remarkably. The leaching of Cu and Pb in aqueous phase rose from 14.9% and 5.7% (PVC/PCBs = 0.25) to 98.9% and 80% (PVC/PCBs = 1), respectively. Afterwards, the leaching of Cu and Pb changed slightly with further increasing the PVC-to-PCBs ratio. Also, it can be found in Fig. 3 that the leaching of Sn and Cr began to increase slowly when the PVC-to-PCBs ratio was >0.5. The experiment results indicated that during the co-treatment process, the leaching of Cu and Pb was prior to Sn and Cr in the presence of HCl, which was derived from the decomposition of PVC, when the PVC-to-PCBs ratio was controlled at 1:1 (Fig. 3).

The leaching efficiency of Cr was very low (approximately 0%) at low mixing ratios of PVC to PCBs (PVC:PCBs < 1:1). In the co-treatment process, PVC was decomposed to produce HCl at a shorter time according to the dechlorination experiment. Cr³⁺ could be formed by the reactions between Cr⁰ and HCl.

Fig. 2. Effects of (a) temperature and (b) time on debromination efficiency of waste PCBs.

Fig. 3. Effect of the mixing ratio of PVC to PCBs on the leaching of different metals in co-treatment (reaction temperature = 350 °C, reaction time = 60 min, solid-liquid ratio = 1:9).

In the SBWO co-treatment process, soluble chromate could be formed by the oxidation of Cr^{3+} due to the high temperature, high pressure and oxidizing atmosphere [29]. The interaction between chromate and Pb species could result in the formation of insoluble PbCrO_4 [29]. Because of the higher mole ratio of Pb/Cr (12/1) in our study, we infer that the Cr can be thoroughly converted from soluble chromate to insoluble PbCrO_4 at 350 °C and 60 min. With increasing the mixing ratio of PVC to PCBs ($\text{PVC:PCBs} \geq 1:1$), the leaching of Cr tended to increase slightly. The variation tendency of Sn leaching was very similar with that of Cr. Fig. 4a and b shows X-ray diffraction spectra measured for the residues of waste PCBs and PVC co-treated at 200 °C and 400 °C, respectively. A considerable part of Sn was oxidized to SnO_2 quickly even at 200 °C in the SBWO co-treatment according to XRD analysis. There are no significant reactions between SnO_2 and HCl, resulting in a low leaching efficiency of Sn at low mixing ratios of PVC to PCBs ($\text{PVC:PCBs} \leq 0.5:1$). The leaching of Sn and Cr increased slightly when the mixing ratio of PVC to PCBs was $\geq 1:1$, which could be attributed to the excess HCl and the noticeable decline of pH in the co-treatment system. To study the effect of the mixing ratio of PVC to PCBs on pH, the system pH after co-treatment at different mixing ratios was measured. The results are given in Fig. 5. The system pH decreased from 6.5 to 1.0 with the increase of the mixing ratio of PVC to PCBs from 0:1 to 1.5:1.

In the co-treatment process, H_2O_2 was decomposed and the released O_2 was dissolved in subcritical water. Oxygen can react with metal copper to form cupric oxide, which can further react with hydrochloric acid to form copper chloride. It can be found in Fig. 5 that the system pH was higher than 4.3 when the PVC-to-PCBs ratio $\leq 0.5:1$. Because copper (II) may precipitate as hydroxy chloride even at pHs as low as 2–3, a notable proportion of the Cu cannot be leached in the co-treatment system (Fig. 3). However, with further increasing the PVC-to-PCBs ratio, the leaching of Cu was enhanced remarkably. The leaching of Cu reached 98.9% when the PVC-to-PCBs ratio was increased to 1:1 (Fig. 3). This could be attributed to the rapid falling of the system pH (Fig. 5). The pH declined to 1.8 at the PVC-to-PCBs ratio of 1:1. An evaporation–concentration–cooling–crystallization process was conducted for the metals recovery from the leaching solution. The product from crystallization of leaching solution was examined by XRD technique. The XRD pattern of the product is showed in Fig. 6, which is a pure $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ pattern according to the analysis result.

Fig. 4. X-ray diffraction patterns of the solid residue from SBWO co-treated (PCBs + PVC) at PVC-to-PCBs ratio of 1:1.

Fig. 5. Effect of the mixing ratio of PVC to PCBs on the system pH (reaction temperature = 350 °C, reaction time = 60 min, solid-liquid ratio = 1:9).

In the co-treatment process with the mixing ratio of 0.25:1, Pb could not only be converted to insoluble PbCl_2 by the reaction with HCl decomposed from PVC, but also be oxidized and further react with CrO_4^{2-} to form insoluble PbCrO_4 . The CrO_4^{2-} was derived from the oxidation of Cr in the SBWO process [29]. With further increasing the mixing ratio of PVC to PCBs, the influence of mixing ratio on the leaching of Pb was similar to that of Cu. When the mixing ratio of PVC to PCBs was increased to 1:1, approximately 80% of the Pb was leached due to the excess HCl, which could form stable complexes with Pb [30].

3.4. Effect of temperature on the leaching of different metals in SBWO co-treatment

Fig. 7 shows the effect of co-treatment temperature on the leaching of different metals at temperatures ranging from 150 °C to 400 °C for 60 min. The leaching of all metals studied was negligible when co-treatment temperature was below 200 °C. This could be attributed to the inefficient dechlorination of PVC below 200 °C according to the dechlorination experiments. With

Fig. 6. X-ray diffraction patterns of the product obtained after the leaching solution was crystallized.

increasing reaction temperature, the leaching of Cu, Pb, Sn and Cr increased significantly. The leaching of Cu, Pb, Sn and Cr at 250 °C increased to 38%, 60%, 25%, and 35%, respectively.

At 250 °C, the dechlorination of PVC reached 93% (Fig. 1a). However, only 38% of the Cu was leached at 250 °C. The possible reason is that a considerable portion of Cu cannot be oxidized at low temperature and may still exist as metallic Cu or be converted to its alloy phases with Sn according to the XRD analysis (Fig. 4a). Cu was completely oxidized with further increasing reaction temperature, leading to the significant increase of Cu leaching (>98%) when the temperature was higher than 350 °C. Similarly, the leaching of Pb increased with further increasing temperature after 250 °C. Pb can form stable complexes with Cl^- in the presence of excess HCl. Therefore, with the remarkable increase of PVC dechlorination after 250 °C and the further enrichment of HCl in the reaction system, the Pb leaching increased. Approximately 80% of the Pb was leached at 350 °C.

In contrast to Cu and Pb, the leaching efficiencies of Sn and Cr decreased with increasing the reaction temperature after 250 °C. Particularly, the leaching of Cr decreased markedly and declined to a very low level (<4%) after 350 °C. This may be attributed to that Cr was completely oxidized to chromate with increasing the reaction temperature, and the formed chromate reacted with Pb (approximately 80% of the Pb was in the aqueous phase at 350 °C, Fig. 7) to produce insoluble PbCrO_4 , resulting in the very low leaching of Cr. The low leaching efficiency of Sn at 250 °C

Fig. 7. Effect of co-treatment temperature on the leaching of different metals (PVC:PCBs = 1:1, reaction time = 60 min, solid-liquid ratio = 1:9).

(25%) can be attributed to the oxidation of Sn from Sn^0 to SnO_2 (Fig. 4a), which is more difficult to be leached in HCl compared to Sn^0 . When the reaction temperature was >250 °C, the Sn leaching further decreased with increasing reaction temperature, which could be due to the complete transformation of Sn from Sn^0 to SnO_2 (Fig. 4b).

3.5. Effect of residence time on the leaching of different metals in SBWO co-treatment

The effect of co-treatment time on the leaching of different metals at 350 °C is shown in Fig. 8. During the first 30 min of reaction, 84.7% of the Cu, 77.4% of the Pb, 25.5% of the Sn, and 33.6% of the Cr were converted from insoluble to soluble species in co-treatment process. When the residence time was increased to 60 min, the leaching of Sn and Cr tended to decrease significantly. The leaching efficiencies of Sn and Cr declined to 15.3% and 3.9%, respectively. With further increasing residence time (>60 min), there was little change in the Sn and Cr leaching. Little Cr could be detected in the aqueous phase after 60-min reaction, indicating the complete immobilization of Cr in solid residue. It can be found in Fig. 8 that during the first 60 min of co-treatment, Sn and Cr experienced a stage from partial leaching to re-immobilization. During the first 30 min of co-treatment process, part of the Sn and Cr might still remain in the metallic form, resulting in their part leaching at this reaction stage. With further increasing residence time, Sn and Cr were converted into their insoluble species, leading to the decrease of leaching efficiencies. The high mole ratio of Pb/Cr led to a very low concentration of soluble Cr for the 60-min residence time. The complete oxidation of Sn from Sn^0 to SnO_2 resulted in the decrease of Sn leaching after 60 min residence time.

There was little change in the Pb leaching during all of the residence times studied. Fig. 1b indicated that 30 min was sufficient for all of the Cl in PVC to be dissolved as HCl in water in SBWO process. The excess HCl in system could form stable complexes with Pb and led to a higher leaching of Pb at the first 30 min of reaction.

Interestingly, during the whole reaction process, Cu experienced the process of leaching enhancement-leaching reducing (re-immobilization). The 60 min residence time was the turning point. However, the re-immobilization tendency of Cu was slight. Only a very small part of the Cu was re-immobilized. It has been reported that Cu^{2+} species can be used as an oxidation catalyst in SBWO process of organics [31]. It was observed that the Cu^{2+} was reduced to Cu^+ during the catalytic reaction in the SBWO process, and the Cu^+ was re-oxidized by the oxidant (O_2) in the subcritical water [31]. In our experiment (350 °C, PVC:PCBs = 1:1),

Fig. 8. Effect of co-treatment time on the leaching of different metals (PVC:PCBs = 1:1, reaction temperature = 350 °C, solid-liquid ratio = 1:9).

Cu was completely oxidized and leached in HCl to form copper chloride. Part of the Cu^{2+} species (copper chloride) could act as a catalyst and be reduced to Cu^+ species along with the oxidation of organics in the system. The re-oxidation of Cu^+ species to Cu^{2+} species such as CuO in the presence of the oxygen in system could result in the re-immobilization of partial Cu. On the other hand, the formed Cu^{2+} species could be precipitated from system due to its low solubility in subcritical water and might enter the mineral crystal lattice of the residual solid particles of waste PCBs, which also lowered the Cu leaching activity.

3.6. Effect of solid–liquid ratio on the leaching of different metals in SBWO co-treatment

To investigate the effect of pulp ratio on the leaching of metals, different water volumes were used in the experiments, and the results are shown in Fig. 9. In every experiment, PCBs and PVC were fixed at 5 g, respectively, and hydrogen peroxide was fixed at 40 ml. The volume of water was controlled at 10, 20, 30, 40, 50, and 60 ml, respectively. Therefore, the solid–liquid ratio was 1:5, 1:6, 1:7, 1:8, 1:9, and 1:10 g/ml, respectively. From Fig. 9, it can be found that solid–liquid ratio plays an important role in the leaching efficiency of metals, especially for Cu and Pb. From Fig. 9, it can be found that the leaching efficiencies of Cu and Pb increased with the increase of the volume of water.

The volume of water in the reactor is directly related to the reaction pressure. The system pressure increased with increasing the water volume. With the increase of system pressure, the nature of the subcritical water changed significantly: the density and viscosity of the subcritical water decreased rapidly while the diffusivity and mass transport coefficient increased. As a result, BFRs and PVC could be quickly decomposed into low molecular weight organic compounds and oxidized in the subcritical water, and the dehalogenation efficiency increased. With the removal of organic matters contained in PCBs, the metals embedded were exposed to the lixiviant in the reaction system, which markedly enlarged the contact area and enhanced the leaching of metals. On the other hand, a higher pressure environment also may be favorable for improving the mass transfer efficiency of the leaching reaction of metals during the SBWO co-treatment process. Hence, a higher leaching efficiency of metals could be obtained in a higher volume of water. However, if further increasing the water volume, the HCl decomposed from PVC could be diluted and the increase of metals leaching was negligible (Fig. 9, solid–liquid ratio = 1:10 g/ml). Therefore, the solid–liquid ratio was controlled at 1:9 g/ml in this study.

Fig. 9. Effect of solid–liquid ratio on the leaching of different metals (PVC:PCBs = 1:1, reaction temperature = 350 °C, reaction time = 60 min).

3.7. Effect of SBWO co-treatment on the crystalline phases of the solid residues

Fig. 4a and b show X-ray diffraction spectra measured for the solid residues of waste PCBs and PVC co-treated at 200 °C and 400 °C, respectively. In the XRD pattern for 200 °C (Fig. 4a), high-intensity diffraction peaks from Cu, CuSn , and SnO_2 are identified. Although noticeable SnO_2 is still observed in the spectra for the residue treated at 400 °C, the diffraction peaks from Cu and CuSn completely disappear for the residue (Fig. 4b).

It has been reported that CuO and Cu_2O were formed during supercritical water oxidation treatment of waste PCBs [19,32], but crystalline phases of these copper compounds were not found in this study when the waste PCBs and PVC were co-treated at 200 °C and 400 °C. The diffraction spectra in Fig. 4a and b clearly indicated the conversion of Cu from insoluble species into soluble species during the SBWO co-treatment process. It seemed that the oxygen produced from H_2O_2 was inclined to be used for the oxidation of Sn and organic matters contained in waste PCBs, and Cu element was converted to alloy substances with other metals such as Sn at lower temperature (200 °C). We inferred that copper was oxidized with the increase of reaction temperature, and then was leached rapidly in the presence of HCl decomposed from PVC. Hence, we cannot find the crystalline phases of copper oxides from the XRD spectra. We can conclude that the oxidation and leaching of Cu can be achieved simultaneously at higher temperature region of SBWO co-treatment.

Inversely, a considerable part of Sn element could be efficiently oxidized to SnO_2 at low temperature, even at 200 °C. High-intensity diffraction peaks from SnO_2 could still be found at 400 °C, indicating that Sn was completely immobilized in the residue after co-treatment. It is well known that metallic Sn can be leached in HCl, but it is difficult for SnO_2 to be leached in HCl due to that SnCl_4 can only exist in the strong acid system whose pH is <1.2. However, the pH was approximately 1.8 under the reaction conditions used. In addition, it is difficult for the redox reactions between SnO_2 and HCl to take place as the ΔG° values of the reactions between SnO_2 and HCl for 200 °C and 400 °C are 381 and 611 kJ/mol, respectively.

3.8. Environmental effects of SBWO co-treatment process

Waste PCBs contain high amount of BFRs and heavy metals which may bring a series of environmental and health problems. In addition, improper treatment of PVC can lead to the formation of chlorinated toxic organics such as dioxins. The debromination and dechlorination could be conducted safely in the proposed SBWO co-treatment process, with no discharge of toxic products. Simultaneously, most of the Pb, which is the most important heavy metal in waste PCBs, could be leached and recovered due to the action of the hydrochloric acid released from the PVC wastes. On the other hand, water is the only reaction medium in the proposed co-treatment process, and the toxic organic matters in waste PCBs can be decomposed effectively into CO_2 and water, which markedly reduce the environmental risk of process. Hence, the SBWO co-treatment is an environment-friendly process for the treatment of both PCBs and PVC wastes.

4. Conclusions

An effective and green SBWO process was developed for simultaneously treating waste PCBs and PVC in this study. Water was

the only reaction medium, and no hazardous reagent was needed in the process. The PVC waste could be treated safely in the proposed process. The PVC dechlorination was complete when temperature was $>300^{\circ}\text{C}$ and all of the Cl decomposed from PVC was dissolved as HCl in water, which was efficient for the leaching of Cu and Pb contained in waste PCBs owing to their conversion from insoluble metal species to water-soluble chlorides. Inversely, the Sn was immobilized in the residue after co-treatment due to that Sn was oxidized to SnO_2 quickly even at low temperature in the co-treatment process. In the co-treatment, the BFRs contained in waste PCBs could be decomposed efficiently and all of the released Br could be enriched in water as HBr, which eliminated the formation of toxic brominated organic compounds. The temperature region in which the HBr was released from BFRs was between 250 and 350°C , which was lower than that of traditional thermal degradation process. The proposed process is high-efficiency not only for the recovery of Cu and Pb from waste PCBs, but also for the removal of BFRs contained in waste PCBs. No toxic organic products are discharged during the whole treatment, markedly reducing the environmental risk of the proposed process. The SBWO co-treatment offers a promising method for the simultaneous treatment of waste PCBs and PVC. The high concentration of HCl would lead to serious acidification and corrosion of the reactor. Hence, a demanding reactor material is needed in the proposed method, which may be the economic obstacle in a real process. The further studies of this work are in progress. For example: (1) the SBWO co-treatment of PVC waste and other metal-rich wastes such as electric arc furnace dust or spent batteries, and (2) the SBWO treatment of a real and complicated WEEE system, which simultaneously contains PVC plastics, brominated resins and multiple kinds of metals.

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