Advanced degradation of brominated epoxy resin and simultaneous transformation of glass fiber from waste printed circuit boards by improved supercritical water oxidation processes

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A B S T R A C T

This work investigated various supercritical water oxidation (SCWO) systems, i.e. SCWO1 (only water), SCWO2 (water + H2O2) and SCWO3 (water + H2O2/NaOH), for waste printed circuit boards (PCBs) detoxification and recycling. Response surface methodology (RSM) was applied to optimize the operating conditions of the optimal SCWO3 systems. The optimal reaction conditions for debromination were found to be the NaOH of 0.21 g, the H2O2 volume of 9.04 mL, the time of 39.7 min, maximum debromination efficiency of 95.14%. Variance analysis indicated that the factors influencing debromination efficiency was in the sequence of NaOH > H2O2 > time. Mechanism studies indicated that the dissociated ions from NaOH in supercritical water promoted the debromination of brominated epoxy resins (BERs) through an elimination reaction and nucleophilic substitution. HO2/C5, produced by H2O2 could induce the oxidation of phenol ring to open (intermediates of BERs), which were thoroughly degraded to form hydrocarbons, CO2, H2O and NaBr. In addition, the alkali-silica reaction between OH/C0 and SiO2 induced the phase transformation of glass fibers, which were simultaneously converted into anorthite and albite. Waste PCBs in H2O2/NaOH improved SCWO system were fully degraded into useful products and simultaneously transformed into functional materials. These findings are helpful for efficient recycling of waste PCBs.

1. Introduction

Supercritical water oxidation (SCWO) has recently grown as a green process for treating toxic organic compounds (Qian et al., 2016; C. Wang et al., 2011; S. Wang et al., 2011). Supercritical water is relatively non-polar because of diminished hydrogen bonding allowing organic species, oxygen, and water to form a single homogeneous phase, which results in rapid oxidation due to the elimination of mass transport limitations at the interface. The unique properties of supercritical water, such as its miscibility with oxygen in all proportions, negligible surface tension, high diffusivity, low viscosity, and low solubility of inorganic salts, make it an ideal for treatment of toxic compounds and most toxic organic compounds are rapidly oxidized in supercritical water (Bröll et al., 1999; Savage, 1999).

Waste printed circuit boards (PCBs), including organic polymers, glass fibers, and various metals, are difficult to dispose of due to its complicated composition (Fogarasi et al., 2015; Hadi et al., 2015; Zhang et al., 2012). Besides, there are large amounts of bromine flame retardants and heavy metals in waste PCBs. If such kinds of electronic wastes are disposed in improper ways such as discard or landfill in a random way, the heavy metals and organic pollutants may infiltrate into groundwater and soil. Through such natural processes of migration, conversion, food chain cycle and biological concentration, it will consequently do harm to ecological environment and further pose risk to human health and life safety (Duan et al., 2011; Huang et al., 2009). At present, active researches related to recycle of waste PCBs have been focused on pyrometallurgy and hydrometallurgy (Akcil et al., 2015; Quan et al., 2010; Wang and Xu, 2014; Yang et al., 2011). However, these methods generally involve a number of drawbacks from an environmental point of view, e.g. low treatment efficiency, high treatment cost, secondary pollution and poisonous gases (Huang et al., 2009; Li et al., 2012). Hence, considering alternatives for recycling these materials in an environmental benign process is attracting the attention of many researchers in different fields.

SCWO has ever been used as an environmentally friendly method for treating hazardous organic polymers in electronic waste, which are broken down into small molecules (Wang et al., 2015; Xiu et al., 2013, 2015). Actually, most recent studies in this field have focused on this method of degradation (Xing and...
Zhang, 2013; Yin et al., 2011). Compared with the traditional pyrometallurgy and hydrometallurgy, the SCWO method of treating waste PCBs has many advantages, including no production of volatile organic compounds, no emission of poisonous and hazardous gas, high metal recovery rate and cleaner production process. Table 1 summarizes the previous research about using SCWO techniques to dispose waste PCBs. From Table 1, it can be seen that high-molecular polymers in the waste PCBs could effectively degrade into low molecular organic compounds in SCWO system, and valuable metals could be also recovered simultaneously. Despite its advantages, the SCWO method of treating waste PCBs presents certain problems. For instance, brominated epoxy resins (BERs) are degraded into phenols and HBr in supercritical water. Discharge of phenols should be limited as they are harmful compounds that pollute the air and water (Ding et al., 1995). Thus, it is urgent to develop an environmentally friendly SCWO system that can convert the polymers and glass fibers directly or indirectly originating from oil products to usable chemical products or materials. This new SCWO system not only improves the recycling rate of waste PCBs, but also helps to eliminate ecological risks that result from landfill, incineration or pyrolysis.

The aim of the present study was to develop an improved SCWO system for waste PCB disposal. The improved SCWO system (H2O2 or H2O2/NaOH as additive) could successfully convert waste PCBs into chemical products and functional materials with high added value. Meanwhile, harmful impact caused by waste PCBs to the environment could be completely eliminated. The effects of various SCWO systems on the debromination of BERs were evaluated. The degradation and transformation mechanisms of waste PCB components in various SCWO systems were also discussed in detail.

2. Experiment

2.1. Materials

Waste PCBs were supplied by XIAMEN OASIS Sources Co., Ltd. The composition of the waste PCBs is given in Table 2. All other chemicals were analytical grade and were purchased from Chemical Reagent Company of Beijing.

2.2. Treatment process

Waste PCBs were shredded and crushed by a universal pulverizer before SCWO treatment. The powder was passed through an 80-mesh filter and dried in an oven at 100 °C for 1 h. SCWO experiments were conducted in a 100 mL high-pressure reactor made of 316 alloys. Three SCWO systems, i.e. SCWO1 (only water), SCWO2 (water + H2O2) and SCWO3 (water + H2O2/NaOH), were investigated for the treatment of waste PCBs. The reaction conditions for each experiment are described in Table 3. The schematic diagram and physical map of supercritical hydrothermal reactor are described in Figs. S1 and S2, respectively.

SCWO experiment process: 2.5 g waste PCBs powder, 40 mL water and a certain proportion of additive (H2O2 or H2O2/NaOH) were introduced into the supercritical hydrothermal reactor. Hydrogen peroxide (H2O2, 30 wt%) that don’t decompose at the room temperature released oxygen dissolved into supercritical water (H2O2 = H2O + 1/2O2). The reactor was heated to a selected temperature. The pressure inside the reactor was monitored by a pressure gauge attached to the reactor. Once the reactor had reached the selected temperature, it was held at this temperature for selected residence time. After the SCWO reaction, the reactor was cooled naturally to the room temperature. The SCWO residue and the supernatant were separated by vacuum filtration. The SCWO residue was washed by deionized water.

2.3. Analysis methods

Oxygen combustion bomb-ion chromatography (IC, Dionex ICS2000, USA) was used to determine the bromine content of the solid residue. Debromination efficiency was calculated from the bromine content before and after SCWO. The organic products after SCWO treatment were analyzed with gas chromatography mass spectrometry (GC/MS, Agilent 7890A/5975C, USA).

The crystalline phases of the waste PCBs and the solid samples were characterized using X-ray diffraction (XRD, Bruker D8 X-ray powder diffractometer) at 50 kV and 100 mA using Cu Kα radiation (k = 1.5418 Å). The morphological properties and element content of the SCWO residue were examined using scanning electron microscopy and energy disperse X-ray analysis (SEM-EDX, Hitachi S-3000 N, Japan).

2.4. Statistical analyses

The response surface methodology (RSM) was used to analyze the interaction of several independent factors by the

| Sample | Additive | T (°C) | Time (min) | Organic products | Metal products | Non metal products | Reference |
|--------|----------|--------|------------|------------------|---------------|-------------------|-----------|
| Waste memory modules | None | 350–550 | 120–360 | Phenol, HBr | Cu, Au | SiO2 | Li and Xu (2015) |
| Waste PCBs | None | 200–400 | 30–120 | Phenol, HBr | Cu | SiO2 | Xing and Zhang (2013) |
| Waste PCBs | NaOH | 320–520 | 10 | Phenol, NaBr | CuO2, Cu(OH)2 | Not detected | Matsumoto and Oshima (2014) |
| Waste PCBs | NaOH/HAc/NaOH | 240–400 | 0–60 | Phenol, HBr/NaBr | Not detected | Not detected | Chien et al. (2000) |
| Waste PCBs | Polyvinyl chloride | 150–400 | 0–180 | Not detected | SnO2, CuCl2 | Not detected | Xiu et al. (2014) |
| Computer housing plastic | NaOH/KOH | 300–420 | 30–120 | Phenol, NaBr | None | None | Wang and Zhang (2012) |
| Brominated flame-retarded plastics | NaOH/KOH/Ca(OH)2 | 450 | 0–30 | Phenol, NaBr | Sb2O3 | None | Onwudili and Williams (2009) |
Design-Expert software (version 8.0.5, Stat-Ease, Inc., Minneapolis, MN). Experiments were conducted in a standard RSM design called Box-Behnken Design (BBD) for the optimization of debromination efficiency. The NaOH amount, H$_2$O$_2$ volume and time were selected as factors on the response debromination efficiency with the coded values at three levels ($-1$, $0$ and $+1$). Firstly, single factor experiments were conducted to define the range of operation conditions for respective factors. The results of single factor experiments are shown in Fig. S3. Fig. S3 showed the maximum value of factor A, B and C were 0.15, 12 and 30, respectively. Therefore, central values were designed into A = 0.15, B = 12 and C = 30. Before processing the experiment data, it was necessary to code different experiment factors into code values ($-1$, $0$ and $+1$) which could be inputted into the Design-Expert software in advance. The ranges and the levels of variables are given in Table 4.

3. Results and discussion

3.1. Debromination efficiencies of SCWO systems

The debromination efficiencies of the SCWO systems are shown in Fig. 1. The results in Fig. 1 show that SCWO1 systems were able to debrominate BERs in the waste PCBs. Only a small amount of bromine was detected in the SCWO1 residues, suggesting that oxidation of supercritical water is effective to promote the decomposition of BERs. However, debromination efficiency decreased significantly upon addition of H$_2$O$_2$ in the SCWO2 systems, suggesting that H$_2$O$_2$ inhibits the release of bromine from BERs. In the SCWO3 systems, debromination efficiency increased obviously with increasing temperature, and the debromination efficiency of the SCWO3 systems were superior. In the SCWO3 systems, the bromine from the BERs was first released as HBr and then neutralize by NaOH to form NaBr, which can reduce the equipment corrosion during the treatment process (Chien et al., 2000). The pH value of SCWO reaction solution is shown in Fig. S4. Therefore, bromine content in SCWO3 residues can be easily reduced after SCWO3 treatment. These results demonstrate that the addition of NaOH is important in facilitating debromination and high temperature is beneficial for the BERs debromination.

3.2. GC–MS analysis of oil products

The oil-phase products that were produced under the condition of 425 °C in Table 3 were identified by GC–MS. Fig. 2 shows that the oil-phase products of the SCWO1 systems were mainly phenols. This result was consistent with previous studies (Li and Xu, 2015; Xing and Zhang, 2013; Yin et al., 2011). Moreover, the sole addition of NaOH could increase the debromination efficiency in the SCWO systems, but the degradation products of BERs are still phenol and HBr (Table 1). In contrast, the oil-phase products after treatment by SCWO2 systems and SCWO3 systems were mainly long-chain hydrocarbons. These results indicate that the addition of H$_2$O$_2$ results in oxidative ring opening of phenols resulting in the formation of hydrocarbons. It is also possible that the addition of NaOH could reduce the production of oil-phase products. The SCWO3 system was therefore deemed the most efficient system for the removal of bromine and the deep degradation of BERs from waste PCBs.

Table 3
SCWO experimental conditions.

| System No. | Temperature (°C) | NaOH (g) | H$_2$O$_2$ (mL) | Pressure (MPa) |
|------------|-----------------|----------|----------------|---------------|
| SCWO1 1    | 375             | 0        | 0              | 23            |
| 2          | 400             | 0        | 0              | 28            |
| 3          | 425             | 0        | 0              | 36            |
| SCWO2 1    | 375             | 0        | 20             | 23            |
| 2          | 400             | 0        | 20             | 28            |
| 3          | 425             | 0        | 20             | 36            |
| SCWO3 1    | 375             | 0.25     | 20             | 23            |
| 2          | 400             | 0.25     | 20             | 28            |
| 3          | 425             | 0.25     | 20             | 36            |

Table 4
Factors and levels of RSM.

| Independent variables | Levels  |
|-----------------------|---------|
| A: NaOH (g)           | -0.05   |
|                       | 0.15    |
|                       | 0.25    |
| B: H$_2$O$_2$ (mL)    | 4       |
|                       | 12      |
|                       | 20      |
| C: Time (min)         | 0       |
|                       | 30      |
|                       | 60      |

Fig. 1. Debromination efficiencies of various SCWO systems.

Fig. 2. GC–MS analysis of oil products.
3.3. Optimization of SCWO3 system parameters

To obtain the highest debromination efficiency of SCWO3 system, optimum design was developed by applying BBD under RSM. Factors and responses values of BBD are shown in Table 5. The results showed that the debromination efficiency of SCWO3 system varied obviously at different reaction condition. The optimum conditions for the SCWO3 system were determined by means of BBD under RSM. The analysis results were outputted by Design-Expert software 8.0. The response was fitted using the empirical second-order polynomial model. The analyses of variance (ANOVA) are shown in Table 6. As can be seen, the model F-value of 13.86 implies the model is significant. There is only a 0.11% chance that a “Model F-value” this large could occur due to noise. Values of “prob > F” less than 0.0500 indicate model terms are significant. The interaction between each factor is no significant. In this case, A, B, A2, B2, C2 are significant model terms. Furthermore, the results show that the order of factors influenced debromination efficiency is: NaOH > H2O2 > time.

The three-dimensional (3D) response surface plots of debromination efficiency under the interaction of different factors were given for better understanding of three variables, which are shown in Fig. 3. As seen in Fig. 3, the debromination efficiency had a growing trend as the NaOH amount rose. This can be explained that increasing amount of NaOH can enhance the efficiency of debromination. Besides, the debromination efficiency rose at first and gone down later with the rose of H2O2 volume. In addition, the debromination efficiency increased with the increase of time. This showed that the extended reaction time was conducive for bromine removal.

The regression analysis was implemented using all the independent variables and their interactions. The coefficients for the modified mode were calculated by Design-Expert software 8.0. The empirical relationship between the debromination efficiency (YD) and the three variables can be written as follows:

\[
Y_D = 94.25 + 2.06A + 1.13B + 0.72C + 0.11AB + 0.47AC - 0.28BC - 1.64A^2 - 3.85B^2 - 1.56C^2
\]

By investigating the starting points in the response surface changes, the best solution was found to be the NaOH of 0.21 g, the H2O2 volume of 9.04 mL, the time of 39.7 min, maximum

### Table 5

Factors and the experimental responses.

| Runs | A (NaOH/g) | B (H2O2/mL) | C (Time/min) | Y_D (%) |
|------|------------|-------------|-------------|--------|
| 1    | 0.05       | 4           | 30          | 85.17  |
| 2    | 0.05       | 12          | 0           | 87.95  |
| 3    | 0.05       | 20          | 30          | 88.80  |
| 4    | 0.05       | 12          | 60          | 89.48  |
| 5    | 0.15       | 20          | 60          | 89.11  |
| 6    | 0.15       | 4           | 60          | 89.0   |
| 7    | 0.15       | 20          | 0           | 89.26  |
| 8    | 0.15       | 4           | 0           | 88.0   |
| 9    | 0.25       | 12          | 0           | 91.69  |
| 10   | 0.25       | 20          | 30          | 92.58  |
| 11   | 0.25       | 4           | 30          | 88.51  |
| 12   | 0.25       | 12          | 60          | 95.09  |
| 13   | 0.15       | 12          | 30          | 94.18  |
| 14   | 0.15       | 12          | 30          | 94.52  |
| 15   | 0.15       | 12          | 30          | 93.97  |
| 16   | 0.15       | 12          | 30          | 94.40  |
| 17   | 0.15       | 12          | 30          | 94.19  |

### Table 6

Results of variance analysis.

| Source            | Sum of squares | df | Mean square | F-value | Prob > F |
|-------------------|----------------|----|-------------|---------|----------|
| Model             | 141.09         | 9  | 15.68       | 13.87   | 0.0011   |
| A-NaOH            | 33.96          | 1  | 33.96       | 30.04   | 0.0009   |
| B-H2O2            | 10.29          | 1  | 10.30       | 9.10    | 0.0195   |
| C-Time            | 4.17           | 1  | 4.17        | 3.69    | 0.0962   |
| AB                | 0.0450         | 1  | 0.050       | 0.044   | 0.8401   |
| AC                | 0.88           | 1  | 0.88        | 0.79    | 0.4069   |
| BC                | 0.32           | 1  | 0.32        | 0.29    | 0.6086   |
| A2                | 11.34          | 1  | 11.34       | 10.03   | 0.0158   |
| B2                | 62.33          | 1  | 62.33       | 55.14   | 0.0001   |
| C2                | 10.25          | 1  | 10.25       | 9.07    | 0.0196   |
| Lack of fit       | 7.73           | 3  | 2.58        | 55.93   |          |
| Residual          | 7.91           | 7  | 1.13        |         |          |
| Pure Error        | 0.18           | 4  | 0.046       |         |          |
| Cor Total         | 149.0          | 16 |             |         |          |
debromination efficiency of 95.14%. According to the above results, 0.21 g, 9.0 mL, 40 min were chosen as the optimal system parameters for debromination. The verification test was performed as the optimal parameters. The results indicate that the efficiency of debromination was 94.61%, which was similar to the predictions. Therefore, the optimal stoichiometric ratio of the SCWO method of treating BERs was NaOH 0.19 g/g, H2O2 8.35 mL/g and the solid-liquid ratio of 26.95 g/L (m_{waste PCBs} = 2.5 g; m_{BERs} = 1.078 g for each test).

3.4. BERs degradation mechanism

Based on the identified GC–MS products, the probable decomposition pathways of BERs in SCWO3 systems were investigated (Fig. 4). Generally, the degradation of BERs in supercritical water follows a free radical mechanism, where polymers are broken down into small molecules through chain initiation, growth, transmission and termination. When the reaction system provides energy greater than the dissociation energy of chemical bonds in the epoxy resins, those bonds break forming free radicals. These free radicals trigger a chain reaction breaking more bonds, forming new substances and free radicals, which eventually react to form a stable substance, thus terminating the reaction (Hunter and Savage, 2004; Luda et al., 2002).

Under supercritical conditions, high temperatures break down the hydrogen-bonding network between water molecules, which weakens the dielectric shielding effect of the water molecules (Savage, 1999). The solvent water then undergoes homolytic cleavage to form very active HO \cdot (H2O + H + \cdotHO), which can attack the weak CH2-O—benzene ring on the BERs, breaking down the polymers into small molecules. The weak bonds in the small molecules induce further free radical reactions ultimately resulting in bromophenols (1 2 3) (Li and Xu, 2015).

Any Na+ which dissociates from NaOH in SCWO3 system is positively-charged and can react with Br in bromophenols leading to the formation of NaBr, while OH\cdot mainly undergoes nucleophilic substitution with Br-containing organic substances thereby eliminating Br (Lin and Wang, 1999). OH\cdot also accelerates the ring opening of benzene rings and further debromination (Chien et al., 2000; Sun et al., 2007). Therefore, both Na+ and OH\cdot ions, through different paths, accelerate debromination and promote the removal of Br from the benzene rings (4). Thus, the presence of

Fig. 4. Degradation mechanism of BERs in SCWO3 system.
NaOH in the SCWO3 system accelerates the removal of Br, leading to the highest debromination efficiency.

Hydroxyl in phenol is an electron-withdrawing group, where the electrons from the benzene ring are donated through the inductive effect to the hydroxyl group, facilitating its removal. Thus, transitional product phenol may form benzene oxygen free radical under SCWO conditions (Gopalan and Savage, 1994). In the ring-opening reaction of phenol, the highly oxidative free radical HO₂ (H₂O₂ → H₂O + O₂, H + O₂ → HO₂) is added to the benzene oxygen free radicals, leading to the transfer of π electrons and the destabilization and breakdown of benzene rings. There are two main paths for this reaction. (I) HO₂ reacts with the free radical of cyclohexadiene, which is a resonance structure of the benzene oxygen free radical. The steps of this reaction are the rupture of the O=O bond, removal of the HO₂ radical, migration of free radicals, and opening of the benzene ring (Dong et al., 2015; Guan et al., 2011; Li et al., 2005). (II) The oxidation of the phenol group results in p-benzoquinone, which contains an unsaturated C=C bond that can undergo an additive reaction. HO₂⁻ (H₂O₂ → 2HO⁻) can easily abstract protons from most organic reactants (RH + HO⁻ → R⁻ + H₂O) and can also undergo an additive reaction with the unsaturated C=C bond in p-benzoquinone. The migration of free radicals leads to the breakdown of the molecule and subsequent ring opening. After endo rearrangement (2), the resulting ketones can undergo further free radical fragmentation forming organic acids, which are further oxidized to form CO₂ and H₂O (Dong et al., 2015; Guan et al., 2011; Li et al., 2005).

In general, the degradation of BERs in the SCWO3 system results from the oxidation reaction between HO₂ and H₂O (G). The resulting acyl-group free radicals undergo further fragmentation reactions, decarboxylation and aldehyde removal, resulting in ketone and organic acids, which are ultimately oxidized to CO₂ and H₂O (G). The degradation process is divided into three major steps: (1) free radical attacks the BERs polymers to form monomers; (2) The intermediates, including bromophenol, are debrominated by HO₂⁻ and NaOH, and the free radicals released by HO₂ attack the oxidized ring opened products to form small-molecule organic acids and ketone; (3) The ketone and organic acids are finally oxidized to form CO₂ and H₂O. As confirmed by analysis of the degraded products, steps (1) and (2) are very quick, but step (3) is very slow.

3.5. Glass fiber transformation

3.5.1. XRD, SEM and EDX analysis of solid products

Fig. 5 shows that the peak Cu intensity in the SCWO1, SCWO2 systems was weakened and that CuO was detected, indicating some Cu was oxidized during the SCWO treatment. In contrast, XRD of the SCWO3 system showed the generation of CaCO₃ from calcium and copper hydrate from copper (Chien et al., 2000). Additionally, SiO₂ was not completely converted in the SCWO1 and SCWO2 systems. However, SiO₂ in SCWO3 systems can combine with base metals such as Ca, Na, and Al to generate the albite (NaAlSi₃O₈, NaCaAl(SiAl)O₅) and anorthite [(CaAl₂Si₂O₈), (Ca, Na)(Si,Al)₂O₅ and (Ca,Na)(Al,Si)₂O₈] in the presence of NaOH. These XRD results reveal that the addition of NaOH can induce the transformation of glass fiber in SCWO3 system.

The microstructure and element content of the solid products at various stages (raw waste PCBs and SCWO residue) were investigated by SEM-EDX analysis. Fig. 5a shows after mechanical crushing, raw waste PCBs is cylindrical glass fiber with variable lengths, where metal components and organic compounds disperse. Fig. 5b shows that after treatment in SCWO1 system, glass fibers were in a state of erosion but still kept their original shapes, which indicated that the SCWO1 system’s erosion on glass fibers was limited. Fig. 5c shows that after the treatment of SCWO2 system, the shape of glass fibers have changed significantly. Fig. 5d shows that glass fibers from raw waste PCBs change into uniform solid powder after SCWO3 system treatment. It indicates that the transformation degree of glass fiber in SCWO3 system is more thorough than that in SCWO1 system and SCWO2 system.

Table S1 shows the information about solid residue before and after SCWO treatment, including EDX analysis (pink trims are detection range). SCWO residue productivity and chemical oxygen demand (COD). In order to estimate the decomposition efficiency of BERs, we use the variation of element C to calculate the COD disposed by BERs in different SCWO systems. However, when SCWO disposes waste PCBs, not only oxygen is consumed but also atom O in solvent water is involved in the reaction. Meanwhile, parts of C product phases are CnH2n+2, which are not fully CO₂ and H₂O. Therefore, the presented figure of COD is estimated value. As seen from Fig. 6, due to the great molecular weight of BERs (C₃₀H₃₂O₆Br₂: 1200 g/mol), the COD of SCWO degrading the BERs are much larger. The COD of SCWO3 disposing the BERs are 54.17 g/L.

3.5.2. Transformation mechanisms of glass fiber

In the proposed SCWO3 system, glass fiber can be transformed by reacting with NaOH through the alkali-silica reaction (ASR). The possible transformation mechanism of the SiO₂ from glass fiber in SCWO3 system is as follows (García-Díaz et al., 2006):

$$2\text{SiO}_2 + \text{OH}^- \rightarrow \text{SiO}_3^{2-} + \text{SiO}_2^2^- \quad (1)$$

$$\text{SiO}_3^{2-} + \text{H}^+ \rightarrow \text{SiO}_2^- + \text{H}_2\text{O} \quad (2)$$

$$\text{SiO}_3^{2-} + \text{Na}^+ + \text{Ca}^{2+} + \text{Al}^{3+} \rightarrow \text{Na}-\text{Ca}-\text{Al}-\text{Si}-\text{O} \quad (3)$$

where Na–Ca–Al–Si–O compounds represent albite and anorthite.

“Silanol” sites are negatively charged in the SCWO3 system due to attack of the hydroxide ions on the siloxane bonds in SiO₂ (Eq. (1)). These silanol sites are neutralized following the equilibrium reaction in Eq. (2). In contact with NaOH, the major Si species present is SiO₃⁻. The negatively charged silanol sites are counter-balanced by Na⁺, Ca²⁺ and Al³⁺ cations. Afterwards, precipitation of the silica ions by the cations (Na⁺, Ca²⁺ and Al³⁺) will form albite and anorthite (Eq. (3)) (Gao et al., 2013).

Elliott et al. (1983) reported chemical reagents that can produce OH⁻ in SCWO systems, will act as a catalyst and induce a water gas shift (WGS) reaction. In the SCWO3 system, the WGS reaction drives the chemical equilibrium in the forward direction. The Gibbs free energy of the WGS reaction is $-41.5 \text{kJ/mol}$, indicating that the reaction is exothermic. Therefore, the WGS reaction in SCWO3
system is spontaneous (Elliott et al., 1993). NaOH induces the phase transition of the calcium species in glass fiber. The possible transformation mechanism of the CaO in glass fiber is as follows according to the following equations (Jarana et al., 2008):

\[
\begin{align*}
\text{CH}_n\text{O}_m\text{Br} + (1 - m)\text{H}_2\text{O} & \rightarrow \text{CO} + \text{HBr} + \left(n - 2m + 1\right)/2\text{H}_2 \uparrow \quad (4) \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2 \uparrow \quad (5) \\
\text{NaOH} + \text{CO} & \rightarrow \text{HCOONa} \quad (6) \\
\text{NaOH} + \text{HCOO}\text{Na} & \rightarrow \text{HCOONa} + \text{H}_2\text{O} \quad (7) \\
\text{HCOONa} + \text{NaOH} & \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2 \uparrow \quad (8) \\
\text{CaO (glass fiber)} + \text{H}_2\text{O} & \rightarrow \text{Ca(OH)}_2 \quad (9) \\
\text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 & \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaOH} \quad (10) \\
\end{align*}
\]

CO and CO₂ (the degradation products of BERs) were immobilized in the SCWO3 residue. The catalytic cycle is completed by the formation of CaCO₃. In conclusion, NaOH can change the reaction pathway and accelerate the WGS reaction, reducing the overall activation energy of the reaction (Guo et al., 2010).

3.6. Proposed SCWO3 system for the recycling of waste PCBs

Based on the obtained results and identified products, the entire proposed SCWO3 system can be integrated and proposed in Fig. 6. After treating in SCWO3 system, the bromine from the BERs was released as HBr and then neutralize by NaOH to form NaBr, which can reduce the equipment corrosion during the treatment process. The degradation products of BERs are hydrocarbons, which could be purified by a follow-up process and supplied as fuel for transportation. Meanwhile, SiO₂ from fiberglass can combine with base metals to generate the albite and anorthite. These materials have potential application on the thermal insulation and acid resistant property. Metal species (e.g. CaCO₃, copper hydrate, etc.) in SCWO residue could be recovered by a subsequent separation process (Xiu and Zhang, 2009, 2012). Hence, every part of the component in waste PCBs can be substantially recycled.

In our previous research, we once took the method of unimproved batch supercritical water to dispose waste PCBs and completed the recycling and harmless treatment of waste PCBs. Compared with traditional pyrometallurgy and hydrometallurgy, the SCWO process is greener, cleaner and more environmental friendly. Compared with the unimproved SCWO system in the terms of disposing waste PCBs and harmless treatment, the improved SCWO system has many advantages. But the improved SCWO system requires advanced crushing and screening of waste PCBs before treatment, thus the treatment cost was increased. Therefore, how to utilize the improved SCWO system to finish the batched production of completing the degradation of high-molecular organic compounds, materials transformation and metal recovery in waste PCBs and how to reduce the reaction time as well as how to lower the treating cost are going to be researched in the following studies. This study only indicates a possibility for functionalization of waste PCBs by improved SCWO system.

4. Conclusions

This study demonstrated that H₂O₂/NaOH improved SCWO3 system was the most suitable and efficient system for detoxification and resource transformation from waste PCBs. NaOH enhanced the removal efficiency of bromine through the nucleophilic substitution and elimination reaction in BERs. The optimal operational conditions for debromination were: NaOH 0.21 g, H₂O₂ 9.04 mL, reaction time 39.7 min, respectively. Maximum debromination efficiency reached 95.14%.

Waste PCBs in H₂O₂/NaOH improved SCWO system could be fully degraded into useful products and simultaneously transformed into functional materials. BERs completely degrades into harmless long-chain hydrocarbons, CO₂ and H₂O by the oxidation and ring cleavage effects of SCWO and H₂O₂. SiO₂ in the fiberglass can be successfully converted into useful materials which can be potentially used in the fields, such as heat preservation, insulation and resistance to acid corrosion. This study showed that the SCWO system improved by exogenous additives could effectively control the degradation path and degradation products for different components of the waste PCBs.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.wasman.2016.05.022.

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