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

Kang Liu, Zhiyuan Zhang, Fu-Shen Zhang *

Department of Solid Waste Treatment and Recycling, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China
University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

This work investigated various supercritical water oxidation (SCWO) systems, i.e. SCWO1 (only water), SCWO2 (water + H_2O_2) and SCWO3 (water + H_2O_2/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 H_2O_2 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 > H_2O_2 > 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. HO_2, produced by H_2O_2 could induce the oxidation of phenol ring to open (intermediates of BERs), which were thoroughly degraded to form hydrocarbons, CO_2, H_2O and NaBr. In addition, the alkali-silica reaction between OH^- and SiO_2 induced the phase transformation of glass fibers, which were simultaneously converted into anorthite and albite. Waste PCBs in H_2O_2/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

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* Corresponding author.
E-mail address: fszhang@rcees.ac.cn (F.-S. Zhang).

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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 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 (H_2O_2 or H_2O_2/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.

Table 2
Composition of the waste PCBs sample (wt%).

Component Elemental	Organics CH_nO_mBr	Glass fiber CaO and SiO_2	Metals	
			Cu	Al
Content (%)	43.12	45.22	7.80	3.86

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 + H_2O_2) and SCWO3 (water + H_2O_2/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 (H_2O_2 or H_2O_2/NaOH) were introduced into the supercritical hydrothermal reactor. Hydrogen peroxide (H_2O_2, 30 wt%) that don't decompose at the room temperature released oxygen dissolved into supercritical water ($H_2O_2 = H_2O + 1/2O_2$). 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

Table 1
Summary of waste PCBs treatment using SCWO method.

Sample	Additive	T (°C)	Time (min)	Organic products	Metal products	Non metallic products	Reference
Waste memory modules	None	350–550	120–360	Phenol, HBr	Cu, Au	SiO_2	Li and Xu (2015)
Waste PCBs	None	200–400	30–120	Phenol, HBr	Cu	SiO_2	Xing and Zhang (2013)
Waste PCBs	None	280–400	0–90	Not detected	Cu, Au	SiO_2	Matsumoto and Oshima (2014)
Waste PCBs	NaOH	320–520	10	Phenol, NaBr	Cu_2O, $Cu(OH)_2$, CuO	Not detected	Chien et al. (2000)
Waste PCBs	NaCl/HAc/NaOH	240–400	0–60	Phenol, HBr/NaBr	Not detected	Not detected	Yin et al. (2011)
Waste PCBs	Polyvinyl chloride	150–400	0–180	Not detected	SnO_2, $CuCl_2$	Not detected	Xiu et al. (2014)
Computer housing plastic	NaOH/KOH/$Ca(OH)_2$	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	Sb_2O_3	None	Onwudili and Williams (2009)