Journal of Hazardous Materials 221–222 (2012) 193–198

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Removal of brominated flame retardant from electrical and electronic waste plastic by solvothermal technique

Cong-Cong Zhang, Fu-Shen Zhang*

Research Center For Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, China

ARTICLE INFO

Article history:
Received 29 January 2012
Received in revised form 21 March 2012
Accepted 12 April 2012
Available online 20 April 2012

Keywords:
WEEE
Brominated flame retardant
Solvothermal process
Debromination

ABSTRACT

Brominated flame retardants (BFRs) in electrical and electronic (E&E) waste plastic are toxic, bioaccumulative and recalcitrant. In the present study, tetrabromobisphenol A (TBBPA) contained in this type of plastic was tentatively subjected to solvothermal treatment so as to obtain bromine-free plastic. Methanol, ethanol and isopropanol were examined as solvents for solvothermal treatment and it was found that methanol was the optimal solvent for TBBPA removal. The optimum temperature, time and liquid to solid ratio for solvothermal treatment to remove TBBPA were 90 °C, 2 h and 15:1, respectively. After the treatment with various alcohol solvents, it was found that TBBPA was finally transferred into the solvents and bromine in the extract was debrominated catalyzed by metallic copper. Bisphenol A and cuprous bromide were the main products after debromination. The morphology and FTIR properties of the plastic were generally unchanged after the solvothermal treatment indicating that the structure of the plastic maintained after the process. This work provides a clean and applicable process for BFRs-containing plastic disposal.

1. Introduction

With the market expansion of electrical and electronic (E&E) equipment during the last two decades, around 20–50 million tons of waste electrical and electronic equipment (WEEE) are generated worldwide every year [1]. Generally, WEEE contains 18% styrenic polymers such as acrylonitrile–butadiene–styrene (ABS), high impact polystyrene (HIPS) and polystyrene (PS) [2]. In view of the growing interest in the sustainable use of resources, recycle use of E&E waste plastic is becoming more and more important, especially since European commission published the directive on WEEE, which has set high recycling targets for E&E waste plastic [3,4]. Moreover, it should be noted that high concentration of brominated flame retardants (BFRs), mainly polybrominated diphenyl ether (PBDE) and tetrabromobisphenol A (TBBPA) [5,6], were added to plastic matrices during the manufacture of E&E equipment to increase the fire resistance of the product. Owing to the lipophilic and bioaccumulative nature of these BFRs [7], the recovery of E&E waste plastic has further become a challenging task for decades.

Various technologies, including landfills [8], incineration [9], pyrolysis [10] and mechanical recycling [11] have been developed for disposal of E&E waste plastic. However, among these techniques, contamination by harmful bromine-containing compounds is inevitable [8–11]. Elimination of BFRs before recycling E&E waste plastic and following destruction of BFRs is imperative to reduce such negative environmental effects.

A promising way of removing BFRs from E&E plastic is supercritical carbon dioxide (Sc-CO_2) extraction, in which harmless plastic as well as high-priced BFRs were recycled [12]. Further studies [13] indicated that the removal efficiency of BFRs by solvent extraction was better than that of Sc-CO_2 modified with solvents. Recently, we have revealed that solvothermal process was a powerful method to remove organic pollutants from soil matrix [14]. As a consequence, we applied this technique to the removal of BFRs from E&E waste plastic. As for dehalogenation of aromatic halides, a few methods using metals (Fe, Ni, Zn, etc.) were developed thus far [15–20]. Among these studies, it was discovered that metallic calcium in ethanol was highly effective at ambient temperature [15,16]. Moreover, copper has been extensively studied due to possible Ullmann reactions (i.e. coupling of aryl halides with copper) [17–20]. Meanwhile, zinc dust/sodium hydroxide/ammonium formate system is highly effective for the debromination of TBBPA to bisphenol A [21]. Therefore, we also combined these methods to conduct the debromination of BFRs. To our knowledge, there is no report regarding application of solvothermal procedure for the removal and debromination of BFRs from E&E waste plastic.

The primary objective of this study was to evaluate the effectiveness of solvothermal procedure for the removal of BFRs from E&E waste plastic. Effects of various conditions on BFRs removal efficiency were evaluated, and a suitable procedure for debromination of BFRs in organic solvent was also established.

---

* Corresponding author. Tel.: +86 10 62849515; fax: +86 10 62849515.
E-mail address: fszhang@rcees.ac.cn (F.-S. Zhang).

0304-3894/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2012.04.033

2. Experimental

2.1. Materials

Waste computer housing plastic was supplied by HuaXing Environment Protection Co. Ltd. The plastic, which was ABS resin with TBBPA as additive flame retardant, was cut into small pieces and ground to 14–20 mesh by a grinder under cooling with liquid nitrogen. HPLC grade acetone, methanol, ethanol and isopropanol were purchased from J&K Chemical Ltd., USA. Standard stock solution of bromine ion (1000 mg/L) was purchased from the National Research Center for Certified Reference Materials of China and TBBPA (≥97% purity) was supplied by ACROS Ltd., USA. Anhydrous sodium sulfate (Na_2SO_4) and copper powder (200 mesh) were analytical reagents from domestic manufacturers.

2.2. Experimental procedures

A series of reactors consisted of 100 mL Teflon interiors and stainless exteriors were employed for the solvothermal experiments. In a typical run, a certain amount of organic solvent and weighed plastic were introduced into a reactor and the reactor was sealed. The reactor was then placed into an oven, raised to the desired temperature and held for a specified time. On the termination of the reaction, the mixture was separated by centrifugation (10,000 *g*, 10 min, TG16-WS, China). The solid phase was allowed to air-dry overnight, followed by oxygen bomb combustion and ion chromatography (IC) analysis to determine the bromine content in the solid phase. The solvent phase was first evaporated on the vacuum rotary evaporator for solvent substitution with acetone and then dehydrated by anhydrous sodium sulfate. After concentrated, the solvent phase was transferred to Kuderna–Danish (K–D) concentrator and evaporated to 1 mL under a stream of nitrogen flow for gas chromatography–mass (GC/MS) analysis of TBBPA.

There solvents, i.e. methanol, ethanol and isopropanol were examined to compare their solvothermal removal efficiency for TBBPA. The temperature varied from 50 °C to 170 °C at constant time and liquid to solid ratio, the treating time varied from 0.5 h to 15 h at constant temperature and liquid to solid ratio, and the liquid to solid ratio varied from 5:1 to 20:1 (mL/g) at constant temperature and time were performed to optimize the parameters of solvothermal process to remove TBBPA.

Since it is hard to separate copper and plastic if they were combined and this is unfavorable for recycle use of copper and plastic, only the solvent extract and copper powder were combined for possible debromination of TBBPA. In this section, methanol extract (15 mL) and copper powder (0.50 g) were introduced to the 100 mL Teflon interior placed inside the stainless exterior. The reactor was sealed, placed into the oven, and the temperature was increased to 150 °C and maintained for 10 h. After cooling to room temperature, the mixture was separated by centrifugation (10,000 *g*, 10 min, TG16-WS, China). The spent copper powder was allowed to air-dry and subjected to X-ray diffraction (XRD) analysis. The liquid product was subjected to GC/MS and high performance liquid chromatography (HPLC) analysis after solvent substitution and sodium sulfate dehydration. This mixture of methanol extract (15 mL) and copper powder (0.50 g) was also stirred at room temperature for 24 h and compared with the above results.

2.3. Analytical procedures

The oxygen bomb combustion-IC was applied for the analysis of bromine content in raw plastic and solid phase after solvothermal treatment [22,23]. In a typical run, 10 mL Milli-Q water (Millipore, USA) was transferred to the bomb with moistening of its inner surface. Accurately weighed solid sample (0.2–0.5 g) was placed into a stainless steel capsule. The bomb was assembled and purged with oxygen for 1 min. The bomb was then immersed in a water bath at room temperature, ignited by an electric discharge and kept in the water bath for 30 min. After the pressure of the bomb was reduced, the sample capsule and the interior of the bomb were rinsed with Milli-Q water and collected in a 100 mL volumetric flask. The sample solution was filtered through a 0.45 μm membrane filter before IC analysis. IC analysis was performed using an ion chromatograph (ICS-2000, Dionex, USA) with an IonPac AS18 (4 mm × 250 mm) analytical column and IonPac AG18 (4 mm × 50 mm) guard column, coupled to an ASRS-300 4 mm suppressor. Hydroxide eluent gradients were generated online using EGC II KOH cartridge. A continuously regenerated anion trap column (CR-ATC) was installed at the EGC eluent outlet. The optimized hydroxide eluent gradient was: 0–7 min: 12 mM isocratic; 7–8 min: gradient from 12 to 40 mM; 8–15 min: 40 mM isocratic; 15–20 min: 12 mM isocratic.

As for the identification of bromine in the spent copper powder, spent copper powder (0.50 g) was stirred in 10 mL of 0.1 M HNO_3 for 24 h. On the termination of the reaction, the mixture was separated by centrifugation (10,000 *g*, 10 min, TG16-WS, China). The obtained solution was used in Mohr's titration [15] after adjusting pH to 6.5–10.5 with 1 M $NaHCO_3$.

TBBPA in solvent phase was analyzed by an Agilent 7890A gas chromatograph equipped with an Agilent 5975 C mass spectrometry detector and a HP-5 capillary column (USA). High purity He was used as carrier gas with a flow rate of 1 mL/min. The column temperature of chromatographic analysis was programmed as follows: the initial oven temperature was set at 50 °C and ramped to 150 °C at 20 °C/min, then to 180 °C at 10 °C/min, finally to 280 °C at 3 °C/min hold for 2 min. HPLC analysis was accomplished by Agilent 1200 (USA) with a C_{18} reversed-phase column (150 mm × 4.6 mm, 5 μm particles, Agilent, USA), a diode array detector and an auto sampler controlling under a Chemstation data acquisition system. The measurement was performed in a methanol/water = 85:15 (v/v) as mobile phase with a flow rate of 1 mL/min and a detection wavelength of 230 nm. The type of plastic was identified by in situ Fourier transform infrared (FTIR) spectrometer (BrukerTensor27). XRD analysis was carried out using Philips PW 1700 X-ray diffractometer.

Procedure blanks were run to determine background levels. Blank levels for the solvothermal procedure were typically ≤3% of the concentrations of TBBPA in the samples. The presented concentrations were corrected accordingly. Bromine ion was not detected in blank test for oxygen bomb combustion. Each experiment was carried out in triplicate for parallel test, and average values with standard errors were reported.

3. Results and discussion

3.1. Characterization of the solvothermal products

The chromatogram of solvent phase by solvothermal treatment reveals TBBPA was the major component of extract in all cases (Fig. 1), followed by corresponding hexadecanoic esters and octadecanoic esters. As shown in Fig. 1(a)–(c), ethyl ester, methyl ester and isopropyl ester of hexadecanoic acid and octadecanoic acid were formed respectively with ethanol, methanol and isopropanol as solvents, which means a small amount of alcohol solvents participated the reaction. These products were not observed under milder conditions such as lower temperature and less time (Fig. 1(d) and (e)). Five TBBPA calibration solutions were prepared for the quantification and the corresponding bromine contents were calculated according to the chemical formula of TBBPA.

Oxygen bomb combustion-IC analysis of raw plastic indicated that the bromine content accounted for 7.45% of the total plastic