Possibility of BFRs Extraction from E-waste

Cong-Cong ZHANG\textsuperscript{a} and Fu-Shen ZHANG\textsuperscript{b}

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

\textsuperscript{a}email: zhang_rcees@163.com, \textsuperscript{b}email: fszhang@rcees.ac.cn (corresponding author)

Keywords: E-waste; Brominated flame retardants; Extraction; Solvothermal process

Abstract. E-waste contains high amount of brominated flame retardants (BFRs) which are toxic, bioaccumulative and recalcitrant. In the present study, an effective and environmental-friendly process using solvothermal treatment to extract tetrabromobisphenol A (TBBPA), a typical BFR from waste computer housing plastic was developed. After the solvothermal process, TBBPA were transferred into a special solvent phase and the bromine content in plastic after solvothermal treatment was greatly reduced, which confirmed the feasibility of solvothermal procedure for TBBPA extraction. This work provides a clean and applicable process for extraction of BFRs from plastic in e-waste.

Introduction

Brominated flame retardants (BFRs), mainly polybrominated diphenyl ether (PBDE) and tetrabromobisphenol A (TBBPA) \cite{1, 2}, are organic compounds containing bromine and added to polymeric materials to increase the fire resistance in diverse applications such as electrical and electronic (E&E) equipment. It is estimated that electronic waste (e-waste) contains approximately 18\% plastics, mainly styrenic polymers such as acrylonitrile-butadiene-styrene (ABS), high impact polystyrene (HIPS) and polystyrene (PS) \cite{3}. These plastics are one of major consumptions of BFRs. With the rapid growth of e-waste during the last two decades \cite{4}, there is increasing concern about the effects of BFRs on the environment and human health \cite{5} especially due to the lipophilic and bioaccumulative nature of BFRs \cite{6}. Development of extraction method of BFRs from e-waste is urgently desired, which also meets the requirement of European Union’s Directive on Waste E&E Equipment \cite{7, 8}.

Conventional extraction of BFRs from polymeric materials is usually performed by Soxhlet extraction, which requires long extraction time and high solvent consumption \cite{3}. Various advanced solvent extraction techniques \cite{9, 10}, including ultrasonic-assisted extraction \cite{11}, pressurized liquid extraction \cite{12}, microwave-assisted extraction \cite{13} and supercritical fluid extraction \cite{14} have been developed in recent years with shorter extraction time, lower solvent consumption as compared to conventional Soxhlet extraction \cite{3}. Nevertheless, these advanced solvent extraction techniques means high energy cost and equipment requirement, which have become challenges faced by them to recycle BFRs from polymeric materials \cite{15}.

An alternative approach may be explored to use solvothermal process \cite{11}, which is usually conducted at lower temperature and pressure in comparison with supercritical fluid extraction. Recently, we have revealed that solvothermal process was a powerful method to remove organic pollutants from soil matrix \cite{17}. As a consequence, we applied this technique to the extraction of BFRs from plastic in e-waste. To our knowledge, there is no report regarding application of solvothermal procedure for the extraction of BFRs from plastic in e-waste.
The primary objective of this study was to evaluate the possibility of solvothermal procedure for the extraction of BFRs from plastic in e-waste.

Experimental section

Materials. Waste computer housing plastic, identified as ABS resin flame retarded with TBBPA, was obtained from an e-waste recycling company in Xiamen, China. The plastic 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., and anhydrous sodium sulfate (Na₂SO₄) was analytical reagent from domestic manufacturers.

Experimental procedures. Solvothermal experiments were carried out in a series of reactors consisted of 100 mL Teflon interiors and stainless exteriors. In a typical run, 15 mL isopropanol and 1.0 g weighed plastic pellets were introduced into a reactor and the reactor was sealed. Subsequently, the reactor was heated 90 ℃ and held for 2 h in an oven. After the treatment, the reactor was cooled quickly by an electric fan to room temperature. Then the solid and liquid mixture was removed from the reactors and filtrated through a filter paper for separation. The solvent phase was subjected to gas chromatography-mass (GC/MS) analysis of TBBPA. The solid phase was allowed to air-dry overnight followed by oxygen bomb combustion and ion chromatography (IC) analysis.

Analytical procedures. The type of plastic was identified by in situ Fourier transform infrared (FTIR) spectrometer (BrukerTensor27). TBBPA in solvent phase was analyzed by an Agilent 7890A gas chromatograph equipped with an Agilent 5975C mass spectrometry detector and a HP-5 capillary column (USA). Five TBBPA calibration solutions were prepared for the quantification and the corresponding bromine contents were calculated according to the chemical formula of TBBPA. The oxygen bomb combustion-IC was applied for the analysis of bromine content in raw plastic and solid phase after solvothermal treatment [18, 19]. IC analysis was performed using an ion chromatograph (ICS-2000, Dionex, USA) with an IonPac AS18 (4 × 250 mm) analytical column and IonPac AG18 (4 × 50 mm) guard column, coupled to an ASRS-300 4 mm suppressor.

Results and discussion

FTIR properties of the raw plastic. As shown in FTIR spectra of raw plastic (Fig. 1), the broad band in the region 2800～3000 cm⁻¹ are assigned to vibrations of saturated C-H or CH₂; the band at 3000～3100 cm⁻¹ correspond to aryl-H stretching. The strong peak at 1604 cm⁻¹ is attributed to vibration of styryl (C=C aromatic), and the peaks at 964 cm⁻¹ and 2239 cm⁻¹ are respectively assigned to the vibration of butadienyl and nitrile group [20]. This result confirms that the sample is typical ABS resin.
Fig. 1. FTIR spectra of the raw plastic

**GC/MS chromatogram of the extracts.** The GC/MS chromatograms of solvent phase illustrates that TBBPA is the major component of extracts in all cases (Fig. 1) and a small quantity of impurities was observed due to the dissolution of polymeric materials, which was in accordance with a previous report indicating that flame retardants in the extract were not absolutely pure as discussed for Sc-CO₂ extraction [20].

Fig. 2. GC/MS chromatograms of extracts by solvothermal treatment. Conditions: solvent isopropanol; liquid to solid ratio 15:1; (a) temperature 150 °C; time 10 h; (b) temperature 150 °C; time 30 min; (c) temperature 50 °C; time 10 h.

**Effect of temperature on Br extraction.** According to Fig. 3, bromine in solvent increased with temperature below 90 °C and then basically kept constant in a certain range at higher temperature (90 °C ~ 170 °C). By contrast, the residue amount of bromine in the solid phase decreased rapidly
with a drastic drop at lower temperature (50 °C ~ 90 °C) and then remained almost the same below 170 °C. In this case, 90 °C is considered as optimal temperature with the lowest remaining of bromine in plastic after solvothermal treatment.

Fig. 3. Effect of temperature on Br extraction. Conditions: solvent isopropanol; time 10 h; liquid to solid ratio 15:1.

**Analysis of the debromination products.** Oxygen bomb combustion–IC analysis (Fig. 4a) of raw plastic indicated that the bromine content accounted for 7.45% of the total plastic (wt.%). After solvothermal treatment at 90 °C for 2 h (Fig. 4b), the residue amount of bromine in the plastic was reduced to 1.87% (wt.%), indicating that 25.1% of TBBPA was remained in the plastic. Further treatment under the same condition (Fig. 4c) showed that no bromine was detected in the plastic. This result further confirmed the feasibility of solvothermal procedure for TBBPA extraction from plastic in e-waste.
Summary

This study demonstrated that solvothermal process was a practical and efficient technique for extraction of BFRs from plastic in e-waste. For plastic from e-waste containing flame retarded TBBPA, a complete extraction of TBBPA with low solvent toxicity and consumption, and short extraction time was achieved. The optimum temperature for TBBPA extraction was 90 °C. Accordingly, the bromine content in plastic was greatly reduced after the solvothermal process. The extracted TBBPA was transferred into a special solvent phase after the solvothermal process, which could be easily recovered by vacuum rotary evaporation.

Acknowledgements

The authors are grateful for financial supports from China Post-doctoral Science Foundation (2013M530750) and the National Natural Science Foundation of China (21077120, 51278485).

References