



# Development of waste-derived sorbents from biomass and brominated flame retarded plastic for elemental mercury removal from coal-fired flue gas



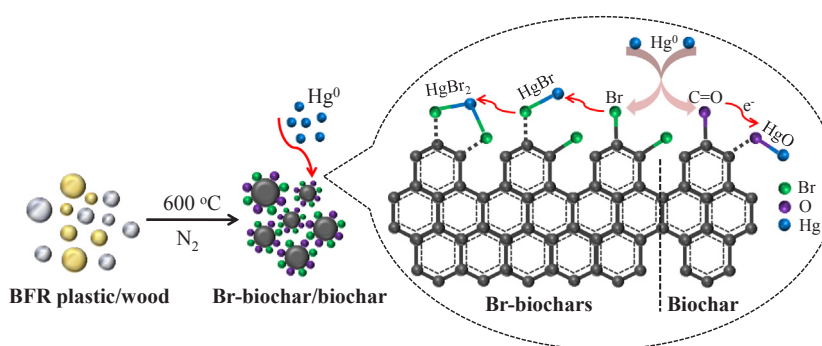
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## HIGHLIGHTS

- A novel method was proposed to prepare cost-effective sorbents for mercury removal.
- Biomass and BFR plastic in municipal solid waste were chosen as raw materials.
- Br-biochars exhibited far better  $\text{Hg}^0$  removal performance compared to virgin biochars.
- The  $\text{Hg}^0$  adsorption capacity of Br-sorbents was close to those of commercial activated carbons.
- The  $\text{Hg}^0$  removal mechanism was revealed by experimental data and kinetic model.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Keywords:

Mercury  
Biochar  
Municipal solid waste  
Pyrolysis  
Bromine  
Flue gas

## ABSTRACT

A novel method using one-step pyrolysis of waste biomass and brominated flame retarded (BFR) plastic was proposed to prepare brominated biochars (Br-biochars) for elemental mercury ( $\text{Hg}^0$ ) removal from coal-fired flue gas. This method could simultaneously realize the disposal of municipal solid waste and the preparation of mercury sorbents. The sample characterization showed that an interaction effect between BFR plastic and biomass occurred during the co-pyrolysis process. The addition of BFR plastic would deteriorate the pore structure of sorbents because the melted plastic residues were aggregated on their surface. But Br emitted from BFR plastic was fixed into the co-pyrolyzed chars in the form of  $\text{Br}^-$  and C–Br group. Br-biochars exhibited far better  $\text{Hg}^0$  removal performance compared to virgin biochar. The optimum pyrolysis temperature and plastic/biomass mass ratio were 600 °C and 1:1, respectively. The effects of gas hourly space velocity, adsorption temperature and individual flue gas on  $\text{Hg}^0$  removal performance were also explored. The  $\text{Hg}^0$  adsorption capacity of Br-sorbents was close to those of commercial activated carbons. Both the experimental data and kinetic model showed that the  $\text{Hg}^0$  adsorption over Br-biochars was mainly controlled by chemisorption, where C–Br bonds were the active sites for oxidizing  $\text{Hg}^0$  into  $\text{HgBr}_2$ . This was confirmed using mercury temperature programmed desorption experiments.

## 1. Introduction

It has long been recognized that exposure to mercury can cause diseases such as neurological, immune, behavioral, and sensory

dysfunctions [1,2]. Medical literature and data from US officials specified that children's idiopathic autism is also induced by mercury pollution [3,4]. These issues can be traced back to the victims of contaminated fish (Minamata disease in Japan) or grain (Iraq, Guatemala,

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and Russia). Coal combustion is considered as one of the largest anthropogenic sources of mercury discharge due to the increasing world energy demands [5–7]. In March 2005, the US Environmental Protection Agency (EPA) announced the Mercury and Air Toxics Standards (MATS) to reduce mercury emissions from coal-fired power plants [8,9]. Moreover, 128 countries signed the Minamata Convention on Mercury, which took effect on 16 August 2017 [10].

Coal combustion flue gas contains three kinds of mercury species: oxidized mercury ( $\text{Hg}^{2+}$ ), particulate-bound mercury ( $\text{Hg}^{\text{p}}$ ) and elemental mercury ( $\text{Hg}^0$ ) [11,12].  $\text{Hg}^{2+}$  is soluble in water and can be trapped in the wet flue gas desulfurization device (WFGD).  $\text{Hg}^{\text{p}}$  attached to fly ash can be captured by electro-static precipitators (ESP) and/or fabric filters (FF). However,  $\text{Hg}^0$  is difficult to be removed because of its high volatility and nearly insolubility in water [13–16]. Two approaches have been developed to remove  $\text{Hg}^0$ : i) catalytic oxidization of  $\text{Hg}^0$  into  $\text{Hg}^{2+}$  [17–20], and ii) the transformation of  $\text{Hg}^0$  into  $\text{Hg}^{\text{p}}$  [21–27]. Among them, activated carbon (AC) injection is one of the most promising technologies and has been commercially available in the U.S. One drawback of this approach is that a high C/Hg ratio is required to achieve high  $\text{Hg}^0$  removal efficiency, which hinders its popularization in developing countries. Biochar (BC), a low-cost carbonaceous material with similar properties as AC, has been demonstrated as a promising alternative to AC [28–31]. However, virgin BC shows poor performance for  $\text{Hg}^0$  removal. Chemically impregnating BC with S and halogens (Cl/Br/I) can effectively solve this problem [12,32–34], but the impregnation procedure is generally complex and consumes expensive chemical reagents. This would hinder the development and commercialization of AC injection technology in developing countries. Hence, it is attractive to activate the BC and improve the  $\text{Hg}^0$  removal performance during the sample preparation process but without an extra activation process.

Biomass and plastic are the main components of municipal solid waste (MSW). Brominated flame retarded (BFR) is added to electrical and electronic equipment with the aim of avoiding fires. However, the presence of BFR plastics is the major obstacle for MSW treatment because polybrominated dibenzo-p-dioxins and furans (PBDD/Fs) may be generated during its incineration [35]. Pyrolysis, as an environmentally friendly method for recycling waste plastics, is superior to incineration or landfill [36]. For example, Jiang et al. [37] conducted the pyrolysis of BFR plastic/biomass mixtures to produce liquid chemical feedstock without the generation of PBDD/Fs. The experimental results indicated that more than 90 wt% of bromine was enriched in pyrolyzed oil and char, which could be easily recovered by further treatments. It is well known [31,38,39] that appropriate valence state of bromine is beneficial for  $\text{Hg}^0$  adsorption and the fixed bromine into pyrolysis-char may provide active sites for  $\text{Hg}^0$  removal. If so, environmentally harmful Br can be utilized to activate BC and improve the  $\text{Hg}^0$  removal performance. The pyrolyzed oil/gas can also be used as fuel or chemical feedstock. Therefore, it is essential to explore the feasibility of using copyrolysis of waste biomass and BFR plastic to prepare sorbents for efficient removal of mercury.

Based on the above analysis, a novel method using one-step pyrolysis of BFR plastic/biomass mixtures was proposed to prepare brominated biochars (Br-BCs) for  $\text{Hg}^0$  removal from coal-fired flue gas. This method could combine solid waste disposal and mercury sorbent preparation in one process. The effects of pyrolysis temperature (500 °C, 600 °C and 700 °C), biomass/BFR plastic mass ratio (10:0, 4:1, 2:1, 1:1 and 1:2), individual flue gas components ( $\text{SO}_2$ , NO,  $\text{O}_2$  and HCl), gas hourly space velocity (GHSV) and adsorption temperature (25 °C, 80 °C, 140 °C, 180 °C and 220 °C) on  $\text{Hg}^0$  removal performance were explored. Furthermore, the mechanism involved in  $\text{Hg}^0$  capture over virgin and brominated BCs was explained.

## 2. Materials and methods

### 2.1. Sample preparation

Two kinds of raw materials were used in this work: a discarded BFR plastic computer shell and waste wood, which were collected from a local salvage station. After natural drying, these two materials were crushed in liquid nitrogen and sieved to a particle size of 100–200  $\mu\text{m}$ . The ultimate and proximate analyses are shown in Table S1. It can be seen that the Br content of the BFR plastic is 9.37 wt%. Five binary blends were prepared at certain wood/plastic ratios (10:0, 4:1, 2:1, 1:1 and 1:2). The pyrolysis of wood/plastic mixtures were conducted in a temperature-controlled system, comprised by a horizontal furnace, a water-cooling device and a quartz reactor. When the system was heated to the desired temperatures (500, 600 and 700 °C), the mixtures were put into the reactor and remained for 30 min with a  $\text{N}_2$  flow (200 ml/min). After pyrolysis, the system was cooled down to ambient temperature under  $\text{N}_2$  atmosphere. Then the BCs were obtained and used for further  $\text{Hg}^0$  adsorption experiment.

The abbreviation TXWYPZ was applied to label the obtained BCs. The X represents pyrolysis temperature (500 °C, 600 °C and 700 °C). Y/Z represents the wood/plastic mixing ratios (10:0, 4:1, 2:1, 1:1 and 1:2). For example, an abbreviation of T6W2P1 represents the Br-BC pyrolyzed at 600 °C, and the wood/plastic ratio was 2:1.

### 2.2. Sample characterization

The proximate analysis and ultimate analysis of raw materials were carried out according to Chinese National Standards GB/T212—2008 and GB476-91, respectively. The specific surface area and pore structure parameters were determined by  $\text{N}_2$  isothermal adsorption at 77 K on a Micromeritics ASAP 2020 system (USA). The range of relative pressure  $P/P^0$  was 0.05–0.35. The surface morphology of BCs was observed by an environmental scanning electron microscope (SEM, Quanta 200, Poland). Before measurement, samples were first degassed at 110 °C for 12 h to eliminate several atmospheric gases, and then coated with C to increase its conductivity. Energy dispersive X-ray (EDX) analysis was also used to estimate the elemental composition on the sample surface. Crystal structures of various samples were identified by X-ray diffraction (XRD; Empyrean, Poland) with a Cu-K $\alpha$  radiation source (60 kV /55 mA). Functional groups on the surface of BCs were qualitatively characterized by Fourier transform infrared spectrometer (FT-IR, VERTEX 70, Germany) and the scanned spectral range was 4000–400  $\text{cm}^{-1}$ . X-ray photoelectron spectroscopy (XPS, VG Multilab 2000, Germany) with Mg X-ray source were applied to measure the valence of the elements (C, Br, and Hg) on the surface of BCs. All binding energies were calibrated by C 1s peak at 284.6 eV.

### 2.3. Elemental mercury adsorption testing

$\text{Hg}^0$  adsorption performances of sorbents were assessed in a down-flow fixed bed. A schematic diagram of experimental apparatus is shown in Figure S1, which is comprised of several units: a simulated flue gas supply system, a mercury vapor generator, a vertical electric heating furnace, a quartz tube, an online  $\text{Hg}^0$  analyzer and an exhaust gas treatment unit. A  $\text{N}_2$  flow passed through the mercury permeation tube within a U-type glass tube housed in a constant-temperature water bath. The  $\text{Hg}^0$  concentration and total gas flow was respectively maintained at 90  $\mu\text{g}/\text{m}^3$  and 1 L/min with  $\text{N}_2$  serving as the balanced gas. The sorbents (0.05 g), occupying a volume of approximately 0.286  $\text{cm}^3$ , were placed into a quartz reactor (inner diameter of 9 mm) which was heated by the electric furnace to 140 °C. The corresponding GHSV was 209 790  $\text{h}^{-1}$  and the interaction reaction time was approximately 0.017 s. The  $\text{Hg}^0$  concentration at the reactor outlet was continuously monitored using a VM3000 (Mercury Instruments, Germany). The instantaneous  $\text{Hg}^0$  removal efficiency ( $\eta$ ), average  $\text{Hg}^0$  removal efficiency

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