



Full Length Article

Chlorine-Char composite synthesized by co-pyrolysis of biomass wastes and polyvinyl chloride for elemental mercury removal



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HIGHLIGHTS

- Effects of pyrolysis temperature, mixing ratio and heating mode were investigated.
- Hg⁰ removal by Cl-Char was much higher than that by raw char (2.5–5 times).
- The mechanism of Hg⁰ adsorption was studied by XPS and TPD analysis.
- A novel method was proposed to synthesize Cl-Char composite for Hg⁰ removal.
- Biomass/PVC wastes are adaptive materials for synthesizing Hg⁰ removal sorbents.

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ABSTRACT

A novel method using the co-pyrolysis of polyvinyl chloride (PVC) and biomass wastes (wood and paper) was adopted to synthesize chlorine on the surface of the char, and the synthesized Cl-Char composite was tested for removal of elemental mercury as a sorbent. The mercury removal efficiency of Cl-Char was much higher than that of raw char (2.5–5 times) and reached nearly 90% at 140 °C. Brunauer-Emmett-Teller (BET) measurements, X-ray photoelectron spectroscopy (XPS) and ion chromatography (IC) were used to characterize the sorbents derived from wastes. The introduction of PVC could increase the yield of sorbents, but it decreased the specific surface area of the sorbents because melted PVC adhered to the paper (or wood) molecules and blocked the development of the porous structure. The IC and XPS analysis results indicated that a synergistic effect occurred during the co-pyrolysis process and Cl released from PVC was partly fixed into the pyrolyzed chars to form C-Cl functional groups. This was the primary effective component for the mercury capture via chemical adsorption in contrast to simple physical adsorption on the chlorine-free char. The data also suggested that the existing forms of mercury on the used sorbent were HgCl_x via a temperature-programmed decomposition (TPD) experiment because the chemisorbed mercury species could be completely released from 200 to 400 °C. The elemental mercury removal efficiency increased as a function of temperature from 20 °C to 140 °C and then decreased at 170 °C. The presence of O₂ enhanced Hg⁰ removal whereas SO₂ inhibited Hg⁰ removal; NO had little influence on Hg⁰ removal.

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1. Introduction

Mercury, a heavy metal, is a concern because of its toxicity, volatility, persistence, bioaccumulation and worldwide migration into the environment [1,2]. All species of mercury are harmful to human beings and can be easily absorbed by human beings and

damage our nervous system [3,4]. The average content of mercury in Chinese coal is 0.22 mg/kg and 0.09–0.126 mg/kg in the United States [5]. Coal combustion is the largest anthropogenic source of mercury emission because of the large quantity of coal that is consumed worldwide. In 2011, the Emission Standard of Air Pollutants for Thermal Power Plants (GB13223-2011) stated that the emission concentration of mercury and its compounds in the stack flue gas should not exceed 0.03 mg/m³.

During combustion, mercury is released in three forms: oxidized forms (Hg²⁺), particle-bound (Hg^p) and elemental mercury (Hg⁰) [6,7]. Hg²⁺ and Hg^p can be removed efficiently by wet flue

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gas desulfurization systems and de-dusting devices such as electro-static precipitators and/or fabric filters [8–10]. However, Hg^0 is very hard to remove in the post-combustion control units due to its high volatility and nearly insolubility in water [11–13]. Therefore, Hg^0 Capture is essential to controlling the mercury emission [14]. Injecting activated carbon (AC) has been conventionally known as a commercialized technology for mercury removal from coal combustion flue gas [15]. Yet, the cost of modified-AC is relatively high for full-scale applications—this limits the popularization of the injection technology particularly in developing countries. Thus, the development of a low-cost, environmentally friendly and high-efficiency sorbent is a research hotspot.

There are three major approaches to resolve the Hg^0 removal issues of high operation cost. One approach is to develop regenerable sorbents for circular use. Such sorbents include silver incorporated composites [16], magnetic particles [17], etc. The second approach is to reduce the consumption rate of mercury sorbents by strengthening their capacity for Hg^0 adsorption. The adsorption capacity could be improved by loading sulfur or halogen on activated carbons [18–20]. The third approach is to use cheap substitute for activated carbon. The latest research by Shen et al. [20–22] showed that bio-chars pyrolyzed from municipal solid waste (MSW) were promising substrates for subsequently producing chemical impregnated mercury sorbents as an alternative to replace AC. However, the chemical impregnation process would weaken its price competitiveness and environmental friendliness.

Due to these disadvantages mentioned above, it is critical to find a way to synthesize halogen/carbon composite sorbents featuring high mercury capture performance without unwelcome chemical impregnation process. Obviously, we could reduce the sorbent price if the sources of carbon and halogen could be obtained cheaply and with an affordable synthesis routine. It is well known that plastics and biomass are the typical components of MSW [23], and polyvinyl chloride (PVC) is the major source of chlorine in MSW. The chlorine content of PVC can reach over 50 wt%. A large amount of hydrochloric (HCl) is generated during PVC incineration, and this causes serious problems, e.g. equipment corrosion and dioxin generation [24–26]. Previous research [25–27] on co-pyrolysis of biomass and PVC was motivated by the reduction of HCl emission because hemicelluloses served as strong HCl absorbents. Chlorine plays a critical role in the removal of Hg^0 [28–30], in which chemisorption is more important than physisorption [31]. Thus, the feasibility of using the method—co-pyrolysis of waste PVC and biomass wastes to synthesize Cl-Char to remove Hg^0 —needs to be investigated. If feasible, economic conversion of the hazardous chlorine into useful active component on sorbents can succeed in synthesizing high performance mercury sorbent as well as partly solving the chlorine issues related to PVC.

Herein, waste-derived sorbents for removing Hg^0 were synthesized by pyrolyzing two biomass wastes (wood and paper) with waste PVC at different temperatures, mixing ratios, and heating modes. The mercury capture performance was investigated by determining removal efficiency. The Brunauer-Emmett-Teller (BET) technique, X-ray photoelectron spectroscopy (XPS) and ion chromatography (IC) were used to characterize the sorbents. The effects of SO_2 , NO and O_2 on mercury capture were also determined.

2. Materials and methods

2.1. Sample preparation

Three wastes, PVC, paper and wood, were selected as raw materials for preparing sorbents. The wastes were dried for 8 h at 45 °C

and then pulverized in a liquid nitrogen cold crusher and sieved to the desired particle size range (150–200 μm). Four binary blends were prepared at a mass ratio mixing paper/PVC (10:0, 3:1, 9:1) and wood/PVC (3:1). A blend of 1.6 g was loaded in a cylindrical quartz basket (55 mm in diameter and 50 mm in height) suspended inside the reaction tube in a vertical tube furnace. 1 L/min N_2 was used to purge air from the reaction tube before pyrolysis. The paper/PVC blends were pyrolyzed in 1 L/min N_2 for 10 min at constant temperature of 600 °C, 700 °C and 800 °C, respectively. The wood/PVC blend was pyrolyzed at 700 °C in three heating modes: isothermal heating under 1 L/min N_2 , non-isothermal heating under 1 L/min N_2 from 25 °C to 700 °C at a heating rate of 25 °C/min and kept at 700 °C for 10 min, and isothermal smoldering. After pyrolysis, the quartz basket was lifted to the cold upper end of the reaction tube and cooled to ambient temperature to prevent further pyrolysis. The samples were weighed before and after pyrolysis.

2.2. Sample characterization

The ultimate analysis and proximate analysis were performed by the Chinese National Standards GB476-91 and GB/T 212-2008, respectively. The specific surface area (S_{BET}) and pore volume were measured by N_2 adsorption at 77 K using a Micromeritics ASAP 2020. X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD-600 W) was used to verify the elemental states on the surface of sorbents. The binding energy was corrected by the C 1 s peak at 285 eV. The chlorine content of sorbents was analyzed by IC (IC-2010) following digestion with nitric acid (HNO_3 , Guaranteed Reagent) and hydrogen peroxide (H_2O_2 , Guaranteed Reagent). The 0.035 g sample was mixed with 2 ml HNO_3 and 2 ml H_2O_2 , and heated in a muffle furnace at 180 °C for 10 h. The solution was then diluted to an appropriate concentration and analyzed by IC-2010.

2.3. Hg^0 adsorption experiment

A schematic representation of the experimental apparatus has been shown in our previous study [32]. It consisted of several parts: a gas supply system, an elemental mercury generator, a quartz tube reactor (500 mm in length and 20 mm in internal diameter), a temperature-controlled fixed-bed, and an online mercury analyzer. A nitrogen gas flow of 2 L/min passed through an elemental mercury permeation tube housed within a U-tube that was placed in a temperature-controlled water bath. The sorbent (0.1 g) was placed into the fixed-bed reactor and was heated to 140 °C; N_2 containing Hg^0 vapor then flowed into the reactor. During adsorption, the Hg^0 Concentration at the outlet of the reactor was continuously monitored by the online mercury analyzer (VM3000, made by Mercury Instruments in Germany) based on cold vapor absorption spectrometry. The capacity for Hg^0 removal was measured by the removal efficiency (η), which was calculated by the following formula:

$$\eta = (C_{\text{inlet}} - C_{\text{outlet}}) / C_{\text{inlet}} \times 100\% \quad (1)$$

C_{inlet} and C_{outlet} denoted the Hg^0 Concentration ($\mu\text{g}/\text{m}^3$) at the inlet and outlet of the reactor, respectively.

2.4. Temperature-programmed desorption (TPD) of used sorbent

After the Hg^0 adsorption test, the TPD experiment was carried out in the same fixed-bed for the Hg^0 adsorption test. The released Hg^0 was monitored by VM3000. In the TPD experiment, about 1 g sorbent was packed in the quartz tube reactor and 1 L/min N_2 flowed through the reactor. The sorbent was heated from ambient temperature to 600 °C at a heating rate of 10 °C/min. Mercury

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