



# Elemental mercury removal using biochar pyrolyzed from municipal solid waste



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## ABSTRACT

The paper investigated the Hg<sup>0</sup> capture using a low-cost biochar pyrolyzed from municipal solid waste. The results indicated that C6WN5 (represents the biochar prepared by both microwave and 5 wt.% NH<sub>4</sub>Cl loading) was a cost-effective Hg<sup>0</sup>-capture sorbent when compared with other sorbents. Proximate and ultimate analyses, Brunauer–Emmett–Teller (BET) analysis, and inductively coupled plasma mass spectrometry (ICP-MS) were used to characterize the sorbents (C400 and C600), and X-ray photoelectron spectroscopy (XPS) was applied to investigating elemental states of C6WN5. The results indicated that the biochar pyrolyzed at 600 °C showed better performance for Hg<sup>0</sup> removal than that pyrolyzed at 400 °C. Both microwave activation and NH<sub>4</sub>Cl modification enhanced the Hg<sup>0</sup>-removal capacity of the sorbents, whereas chemisorption of Hg<sup>0</sup> was the main reaction. It was proven by XPS analysis that most of the combined Cl in the C–Cl groups on the surface of C6WN5 was converted into ionic Cl in the Hg<sup>0</sup>-adsorption process, which illustrated that the main mechanism of Hg<sup>0</sup> removal was the oxidation of Hg<sup>0</sup> to HgCl<sub>2</sub> by the C–Cl groups. C=O groups and possibly O<sub>2</sub> served as electron acceptors facilitating electron transfer for Hg<sup>0</sup> oxidation during this process.

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## 1. Introduction

Due to the increase in the population and rapid urbanization, the treatment and disposal of municipal solid waste is a public concern. The main treatment methods of municipal solid waste comprise landfill use, waste incineration and biodegradation. Landfills are still considered as good options for municipal solid waste treatment because they are economic [1]. However, it takes a long time to stabilize municipal solid waste for landfills, and a large quantity of leachate is generated during this process, which pollutes the underground water [2]. Waste incineration is another popular method to treat municipal solid waste and it can facilitate a volume reduction greater than 90% [3]. However, the process of waste incineration emits toxic chemicals [4,5]. Biodegradation is a clean choice for municipal solid-waste treatment [6]. Nevertheless, it requires that the municipal solid waste has a sufficiently high biodegradable (BOD/COD) ratio. Furthermore, the release of odor from the waste decomposition is nuisance to the population surrounding the facilities [7]. As a new technology, the pyrolysis of municipal solid waste has gradually received more attention because of the predominance of environments and the various products obtained. Previous research has found that the pyrolysis of municipal waste is an efficient

method to control the emission of PCDD, PCDF, and PCB [8]. After pyrolysis, gas, oil and char by-products can be obtained and used as renewable energy.

The emission of mercury from coal combustion has received significant attention in recent years. The mercury from combusted flue gas consists of three forms: oxidized mercury (Hg<sup>2+</sup>), particle-bound mercury (Hg<sup>p</sup>) and elemental mercury (Hg<sup>0</sup>). Hg<sup>2+</sup> and Hg<sup>p</sup> can be easily removed by flue gas desulfurization (FGD) systems and de-dusting devices, respectively [9,10]. However, Hg<sup>0</sup> is able to pass through the post-combustion control units. Hg<sup>0</sup> has receiving increasing attention due to its volatility, high toxicity, bioaccumulation and neurological health impact [11]. Various technologies have been applied to control the Hg<sup>0</sup> emission from coal combustion [12]. Activated carbon modified with sulfur and halogens performs well in the adsorption of Hg<sup>0</sup> in flue gas [13–15]. However, the high price of activated carbon makes this technology economically unfavorable.

As a type of inexpensive carbon material, biochar pyrolyzed from municipal solid waste was proposed to replace the activated carbon for the removal of Hg<sup>0</sup> from flue gas. The preparation and modification process of activated carbon includes three stages: carbonization, activation and modification. The pyrolysis of municipal solid waste using biochar is similar to the process of carbonization, however its temperature is lower than that for the commercial activated carbon activation (>800 °C). Activation by microwaves can improve the pore structure of the chars at low temperature (~600 °C) [16]. In this paper, microwave

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and steam activation is used to develop the pore structure of the chars from the pyrolysis of municipal solid waste. The modification precursors of S, I, Br, and Cl enhance the  $\text{Hg}^0$  adsorption in flue gas, and chloride has lower activity than the other precursors, such as S, I and Br [13,14]. However, chloride has been proven to be a stable, inexpensive and effective chemical reagent for the modification of sorbents for  $\text{Hg}^0$  adsorption in industry [17]. The aim of this study is to develop a new and cost-effective char from municipal solid waste for  $\text{Hg}^0$  removal from flue gas.

## 2. Materials and methods

### 2.1. Sample preparation

It is known that MSW may contain a lot of heavy metals in it, the use of the biochar from MSW directly may be harmful to the environment. To evaluate the possibility of the use of biochar pyrolyzed from MSW in mercury capture, the ultimate analysis of metal elements in MSW, C600 and C6N5 by ICP-MS has been demonstrated in Table S1 (in the supporting information). As shown in Table S1, there were several kinds of heavy metals existing in the MSW, including K, Mg, Cd, Cr, Cu and Pb. After pyrolysis treatment, the concentrations of all these heavy metals enhanced (almost double). The weight loss of MSW during pyrolysis was approximately 50% of the raw MSW. It indicated that most of the heavy metals remained in the biochar during pyrolysis process. After  $\text{NH}_4\text{Cl}$  modification, the heavy metals in the chars changed little. When the biochar was used as sorbent under 300 °C, these heavy metals cannot be emitted because their high volatile temperatures. In all, the biochar can be used as sorbent safely in despite of high heavy metals concentrations in it.

The raw municipal solid-waste material was obtained from a residential area. After undergoing natural drying and breaking, the municipal solid waste was placed into a fixed bed pyrolysis reactor that was temperature-controlled at a constant flow of  $\text{N}_2$  (100 mL/min). The chars were generated in the heated zone of the reactor at a specific temperature (400 or 600 °C) for 2 h and then cooled to room temperature under the oxygen-free ambient. The resultant biochars pyrolyzed at 400 and 600 °C were denoted as C400 and C600, respectively.

In our previous studies, various chloride predecessors ( $\text{NH}_4\text{Cl}$ , HCl and  $\text{ZnCl}_2$ ) were used to chemically modify chars, and the results indicated that  $\text{NH}_4\text{Cl}$  was the best modification option due to its high efficiency and low price (as shown in Fig. S1 in the supporting information). Hence,  $\text{NH}_4\text{Cl}$  was used to modify chars from municipal solid waste in this study.

#### 2.1.1. Physical activation

2.0 g of C400 and C600 were placed in a quartz bottle activation reactor (50  $\text{cm}^3$ ) at a constant flow of  $\text{N}_2$  (40 mL/min). The reactor was placed into a microwave oven. Deionized water (2.0 mL/h) was injected by a peristaltic pump into the reactor to generate steam in the process of activation. The duration of microwave activation was 4 h. After physical activation, the biochars were denoted as C4W and C6W.

#### 2.1.2. Chemical modification

The biochars C600 and C6W were impregnated with a 1 wt.%  $\text{NH}_4\text{Cl}$  solution to obtain a 5 wt.% loading (the weight ratio of  $\text{NH}_4\text{Cl}$  to biochars). The mixtures of biochar and  $\text{NH}_4\text{Cl}$  solution were stirred for 12 h and then dried in a water bath for 4 h at 80 °C. The mixtures were then dried in an oven for 12 h at 90 °C. The final products of the chemically modified sorbents (C600 and C6W) were denoted as C6N5 and C6WN5. The zeolite molecular sieve and commercial activated carbon (Guanfu, China) was modified as the same way to contrast with the biochars.

### 2.2. Materials characterization

The proximate analysis for C400 and C600 was performed using an oven to dry them at 105 °C for 1 h. The moisture content was determined by the weight loss during this process. The oven-dried materials were then placed within a muffle furnace in a crucible covered with a lid (in inert atmosphere) at 900 °C for 7 min to determine the weight of the volatile emission. The weight of the ash was determined when the materials were combusted completely at 900 °C in air. The fixed carbon was calculated by the mass balance of C400 and C600. The ultimate analysis of C400 and C600 was performed using a Scientific Flash 2000 organic element analyzer. The C400 and C600 were analyzed by ICP-MS following acid digestion in nitric acid. Approximately 0.2 g of sample was digested with 10 mL of nitric acid ( $\text{HNO}_3$ , 70% Analytical Grade) in vessels. The vessels were sealed and transferred into a microwave at approximately 80 °C. Then, the samples were diluted to a fixed volume and analyzed using ICP-MS (Perkin Elmer ELAN DRC ICP-MS).

The specific surface area ( $S_{\text{BET}}$ ) and pore volume were determined by evaluating the physical adsorption of  $\text{N}_2$  at  $-196$  °C using a Quantachrome Instruments NOVA 2200e surface area & pore size analyzer. XPS (Kratos Analytical Ltd., Britain) with an Mg X-ray source was used to analyze the elemental states on the surface of the sorbent to determine the mechanism for  $\text{Hg}^0$  removal. The binding energy was calibrated by the C 1s peak at 284.6 eV.

### 2.3. $\text{Hg}^0$ -adsorption testing

The experimental setup used to evaluate the performance of  $\text{Hg}^0$  removal for the sorbents is shown in Fig. S2 (supporting information). It consisted of several systems: a gas-preparation system, an elemental mercury generator, a quartz tube fixed-bed reactor, a temperature-controlled heating apparatus, an online mercury analyzer and a gas flue cleaner. An  $\text{N}_2$  flow (200 mL/min) passed through an  $\text{Hg}^0$ -permeation tube housed within a glass tube. The glass tube was placed in a temperature-controlled water bath maintained at a constant temperature. The  $\text{Hg}^0$  concentration was maintained in the range of  $42.0 \pm 2$   $\mu\text{g}/\text{m}^3$ . The simulated flue gas, comprising  $\text{N}_2$  and  $\text{O}_2$  (6 vol.%), passed through a mixer maintained at 120 °C. The total inlet gas flowed into the reactor at 850 mL/min. The reactor, with an inner diameter of 10 mm and a length of 400 mm, was placed in a temperature-controlled electric furnace. The sorbents were placed within the adsorption zone of the reactor. The GHSVs from 65,000 to 520,000  $\text{h}^{-1}$  were determined by changing the weight of the sorbent. All of the gas lines were kept warm (120 °C) to avoid  $\text{Hg}^0$  condensation. The mercury concentration at the inlet and outlet of the reactor was measured continuously using an H11-QM201H online cold vapor atomic mercury analyzer (Jiangsu, China). The activity of the sorbent was measured by the  $\text{Hg}^0$ -removal efficiency ( $\eta$ ), which was calculated as follows:

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (1)$$

where  $\eta$  is the  $\text{Hg}^0$ -removal efficiency, and  $C_{in}$  and  $C_{out}$  ( $\mu\text{g}/\text{Nm}^3$ ) are the  $\text{Hg}^0$  concentrations at the inlet and outlet of the fixed-bed reactor, respectively. The  $\text{Hg}^0$ -removal efficiency is determined by the average of two parallel experimental data and the relative error of the experimental data is less than 8%.

The accumulative adsorption amount of the sorbents was measured by the  $\text{Hg}^0$ -removal efficiency ( $\eta$ ), as in Eq. (2).

$$q = \frac{F \times C_{in} \times \int_0^t \eta dt}{W} \quad (2)$$

where  $F$  is the gas flow rate ( $\text{Nm}^3/\text{min}$ ),  $W$  is the mass of the sorbent (g) and  $t$  is the adsorption time.

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