



Comparative study of element mercury removal by three bio-chars from various solid wastes



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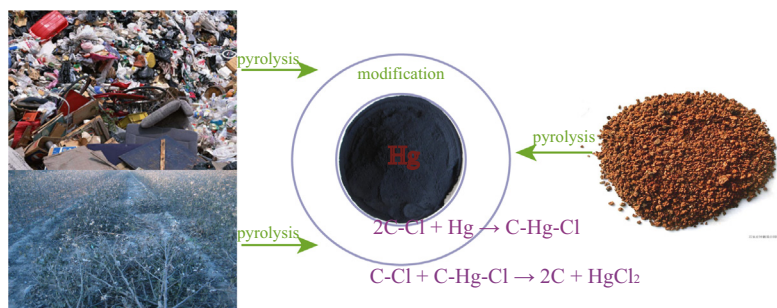
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HIGHLIGHTS

- Combined physical and chemical modification was used to modify the bio-chars.
- Hg⁰ removal by chemical modification was 2–3 times of that by physical modification.
- The mechanism of chemisorptions of Hg⁰ by bio-chars was investigated.
- C6WN5 showed to be a cost-effective Hg⁰ capture sorbent.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 16 September 2014

Received in revised form 23 December 2014

Accepted 25 December 2014

Available online 5 January 2015

Keywords:

Element mercury

Bio-chars

Solid wastes pyrolysis

Mechanism of mercury removal

Cost-effective

ABSTRACT

Three kinds of bio-chars derived from various solid wastes, such as municipal solid wastes, agricultural wastes and medicinal residues, were modified by physical and/or chemical modification. The Hg⁰ adsorption capacities of the modification bio-chars in flue gas were comparatively studied. Physical modification increased the surface areas of the bio-chars, which was favorable in the physisorption of Hg⁰. Chemical modification resulted in the chemisorption of Hg⁰. Both physisorption and chemisorptions played a role in Hg⁰ capture, whereas chemisorption was more important. The X-ray photoelectron spectroscopy (XPS) analysis results suggested that chemisorption of Hg⁰ was due to the C–Cl groups generating on the surfaces of bio-chars during NH₄Cl impregnation, which could transform Hg⁰ into HgCl₂ or other Hg–Cl complexes. The bio-chars modified by combined physical and chemical modification all had an excellent performance for Hg⁰ removal, especially for C6WN5 exhibiting higher Hg⁰ adsorption than modified activated carbons or modified activated carbon fibers. It indicated that the sequence for Hg⁰ removal capacity decreased as: C6WN5 (from agricultural wastes, 11,400 μg/g) > MW6N5 (from medicinal residues, 840 μg/g) > W6WN5 (from municipal solid wastes, 160 μg/g).

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1. Introduction

Elemental mercury (Hg⁰) emission from coal-fired power plant is a distinct environment problem for atmosphere [1]. Injecting activated carbon (AC) has been conventionally used to capture

Hg⁰ emissions from coal combustion system [2]. However, the cost of the AC injection is high for the commercial operation. As a result, low-cost and effective alternative of AC is imperative in the Hg⁰ removal.

Pyrolysis was considered as an efficient process to minimize the solid wastes such as municipal solid waste and biomass. This study focused on the studies of using the bio-chars from the pyrolysis of solid wastes to removal Hg⁰ in flue gas. The bio-chars from the pyrolysis of solid wastes always contained ash including Mg, Ca,

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Fe, Mn, Cl and etc. The existence of chlorine was harmful to the combustion system whereas beneficial to Hg⁰ capture [3–5]. In addition, the metals, like Mg, Ca, Fe and Mn in ash, may be favorable in Hg⁰ adsorption [6,7].

The bio-char was considered as a prospective alternative to AC because of its accessibility and affordability [8–10]. However, the low mercury adsorption impeded the practicability of bio-chars in mercury capture. Therefore, there were two methods to improve Hg⁰ removal: optimization of pore structure and oxygen-containing functional groups [8,11,12]; loading of active elements, like S and halogen on the surface of bio-char [13–15].

In this paper, three kinds of solids i.e. municipal solid wastes (high ash content), agricultural wastes (high chlorine content) and medicinal residues (high volatile content) were pyrolyzed to generate bio-chars for Hg⁰ adsorption. In order to develop the pore structure of chars, microwave was further used to modify the pyrolyzed bio-chars. Many studies had proved that the chlorine was an effective and low-cost modification element for Hg⁰ adsorption [3,4]. In our previous studies, a series of chlorides (NH₄Cl, HCl and ZnCl₂) were added to chemically modify bio-chars and the results indicated that the NH₄Cl was an optimal modification method due to its high efficiency and low price. The purpose of this paper is to comparatively study the feasibility of using the modified bio-chars from three wastes to remove Hg⁰ in flue gas.

2. Materials and methods

2.1. Bio-chars preparation

Three wastes, Chinese traditional medicinal residues (MR), cotton straw (CS) and municipal solid waste (MW), were naturally dried at air and then dried for 2 h at 90 °C in an oven. The wastes were crushed and sieved in a 4 Chinese mesh (<5.0 mm). 200 g of each waste was pyrolyzed for 1 h at a temperature-controlled tube furnace (at 600 °C) under the protection of N₂ (100 mL/min). The furnace was then cooled to room temperature under a N₂ atmosphere. Three bio-chars derived from MR, CS and MW were noted as M6, C6 and W6, respectively.

2.0 g of above chars were put in a quartz bottle reactor (50 cm³) under a constant flow of N₂ (40 mL/min). The reactor was putted within a microwave stove (950 W). Deionized water (2.0 mL/h) was injected into the reactor which was controlled by a peristaltic pump to generate steam. The chars were activated for 4 h by microwave and steam. The three activated products were denoted as M6 W, C6 W and W6 W, respectively.

The above six bio-chars (M6, C6, W6, M6 W, C6 W and W6 W) were then mixed with 1 wt.% NH₄Cl solution to get a 5 wt.% loading (weight ratio of NH₄Cl to bio-chars). The mixtures were stirred for 12 h and then dried at a water bath for 4 at 80 °C. The mixtures were further dried at oven for 12 h at 90 °C. The chemical modified products from M6, C6, W6, M6 W, C6 W and W6 W were denoted as M6N5, C6N5, W6N5, M6WN5, C6WN5 and W6WN5, respectively.

2.2. Bio-char characterization

The proximate analysis of three dried wastes was measured with the method of Chinese National Standards (GB/T 212-2008). The ultimate analysis of three dried wastes was determined by Elemental Vario El CUBE (German). The specific surface area (S_{BET}), micro-pore volume and total pore volume of various bio-chars were determined by N₂ adsorption at –196 °C on a NOVA 2000 automated gas adsorption system (Quantachrome Instruments, USA). The S_{BET} was evaluated by the Brunauer–Emmett–Teller

(BET) method and pore volume was determined by Barrett–Joyner–Halenda (BJH) method. The surface elements binding was analyzed by X-ray photoelectron spectroscopy (XPS) using X-ray photoelectron spectrometer Axis Ultra DLD (Kratos Analytical Ltd., Britain) with Mg X-ray source. The binding energies were calibrated by the C1s peak at 284.6 eV.

2.3. Mercury adsorption testing

Fig. S1 presented the experimental setup used to evaluate the performance of various bio-chars for Hg⁰ capture. The simulated flue gas, comprising of N₂ and O₂ (6 vol.%), went through the mixer maintained at 120 °C. A flow N₂ (200 mL/min) passed through an Hg⁰ permeation tube placed in a U-type glass tube, which was placed in a temperature-controlled water bath to maintain the Hg⁰ concentration at 29.0 ± 1 µg/m³. The total inlet gas flow into a reactor kept 850 mL/min. The quartz fixed reactor was heated by electricity controlled at 120 °C. 0.1 g bio-chars were placed in the reaction zone of the reactor. The space velocity is 260,000 h⁻¹. The inlet and outlet gas line were kept warm to avoid Hg⁰ condensation. The element mercury concentration at the inlet and outlet of the reactor was measured continuously by using the H11-QM201H online cold vapor atomic mercury analyzer (Jiangsu Qinanin instrument Co. China).

The activity of the sorbent was measured by Hg⁰ removal efficiency (η) calculated by Eq. (1).

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

where η is the Hg⁰ removal efficiency, C_{in} and C_{out} (µg/Nm³) are the Hg⁰ concentrations at the inlet and outlet of the fixed-bed reactor, respectively.

The accumulative adsorption amount of the sorbent was measured by Hg⁰ removal efficiency (η) calculated by Eq. (2).

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

where F is the gas flow rate (Nm³/min), W is the mass of sorbent (g) and t is the adsorption time. Since the experimental error is inevitable, the Hg⁰-removal efficiency is the average of two parallel experimental data and the relative error of all parallel experimental data is less than 8%.

3. Results and discussion

3.1. Proximate and ultimate analysis

The proximate and ultimate analysis of three raw materials was listed in Table 1. The moisture content of three raw materials was similar and low after drying. The fixed carbon (FC) content of MR, CS and MW was close with 25.7%, 28.5% and 35.1%, respectively. However, the volatile and ash contents for the three materials were fairly different. The CS had the highest volatile content (63.0%) and the lowest ash content (8.3%) among three wastes. The low ash content was beneficial to the development of pore structure during pyrolysis [16]. On the contrary, MR and MW showed relative high ash content with 32.9% and 45.8%, respectively. The ash might block the pore during pyrolysis process and prevent the pores formation.

According to ultimate analysis, the H and N content showed a low content among three wastes. The C content occupied principal part in the ultimate analysis for the three wastes, especially for MW with 59.0%. The O content of MW was low at 28.7% while those of MR and CS were relative high at 41.4% and 49.8%, respectively. The presence of O possibly in the bio-chars contributed to

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