



Full Length Article

Enhancing the adsorption of elemental mercury using hydrogen peroxide modified bamboo carbons

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ABSTRACT

Bamboo carbon (BC) is a renewable and low-cost material used as sorbent in the industry. Hydrogen peroxide (H₂O₂) has been used to modify BCs to enhance its mercury adsorption ability. However, the mechanism of enhancement needs to be further investigated because the H₂O₂ modification technique is environment-friendly. The Brunauer–Emmett–Teller (BET) method, ultimate analysis (UA), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were used to reveal the physicochemical characteristics of the modified BCs. Our results indicated that the action of H₂O₂ on BC increased the number of C–O and OH oxygen functional groups on the surface of BC, thus significantly enhancing the efficiency of mercury adsorption. At the same time, H₂O₂ modification increased the BET surface area of BCs. Increasing both the number of oxygen functional groups and BET surface area of BCs helped improve the adsorption of elemental mercury (Hg⁰). The presence of oxidized mercury (Hg²⁺) both in the flue gas and on the surface of BCs after the adsorption process indicated that chemisorption occurred on the surfaces of the H₂O₂ modified BCs. Simulating a pseudo-second-order reaction model also demonstrated that the chemisorption of Hg⁰ occurred on the surfaces of H₂O₂-modified BCs. When compared with commercial activated carbon (AC), H₂O₂-modified BC was demonstrated to be a promising sorbent for mercury removal from flue gas.

1. Introduction

Mercury can harm the central nervous system and can also cause stomach ulcers, diarrhea, mental illness, difficult breathing, pulmonary edema, and even death. More than 70% of the primary energy in China is generated by combusting coal, and coal-fired power plants are thought to be important sources of mercury emission. This topic has been the focus of worldwide research in recent years [1,2]. There are three types of mercury in the flue gas generated during coal combustion: elemental (Hg⁰), oxidized (Hg²⁺), and particulate mercury (Hg^p). Hg⁰ is considered an important type of mercury in flue gas, which is difficult to be captured due to its very high volatility and insolubility [3–5]. Among the mercury removal technologies, the adsorption method using activated carbon (AC) injections is commercially used in coal-fired flue gas in the USA and China [6,7]. However, a large amount of AC should be injected into the flue gas due to the low concentration of mercury, which results in high running cost for this procedure. Using biochar is considered a prospective alternative to AC because of its accessibility and affordability. According to recent studies, biochars from cotton, municipal solid waste, etc., can exhibit a wide range of surface physical and chemical properties, thus demonstrating different

mercury adsorption capacities [8,9]. Modifying AC using various methods has been reported to enhance its adsorption abilities. For example, Abbas et al. [45] reported that carbon supported ionic liquids could be highly efficient at capturing mercury. Qiu et al. [46] concluded that sulfurized AC represented a good type of adsorbent for mercury removal.

Bamboo, which is a fast growing biomass in China, has been used to manufacture many versatile raw products. Moreover, bamboo waste has been investigated as a potential material for char production [10], which could be used for waste water treatment, dehumidification, air purification, etc. [11]. Bamboo carbon (BC) can be produced using two carbonization methods: pyrolysis and hydrothermal treatment. Biochar produced by hydrothermal carbonization has been proven to efficiently remove pollutants from waste water [12,13]. Bamboo pyrolysis is a simple procedure, and the BC thus obtained could be used to remove indoors gas pollutants such as benzene, toluene, ammonia, and some volatile organic carbons (VOCs) [14]. Therefore it would be very interesting to use BC to adsorb mercury in flue gas, due to the economic potential of the method.

Nitric acid (HNO₃) or hydrogen peroxide (H₂O₂) have been used to oxidize carbon materials to enhance their adsorption abilities. Previous

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studies reported the use of H₂O₂ modified char to adsorb mercury [15], while HNO₃ treatment was reported to enhance the acidity, surface area, and pore sizes of BC, consequently promoting the catalytic cracking activity in the reaction systems [16–19,24]. However, the mechanism, kinetic modeling, and utility evaluation of H₂O₂ modification need to be further investigated because H₂O₂ has mild oxidation susceptibility and modifying carbon using H₂O₂ is an environment-friendly technique compared to using HNO₃. The mercury adsorption properties of H₂O₂ modified BC were investigated and the mercury adsorption mechanism was discussed in detail in this paper.

2. Materials and methods

2.1. Sample preparation

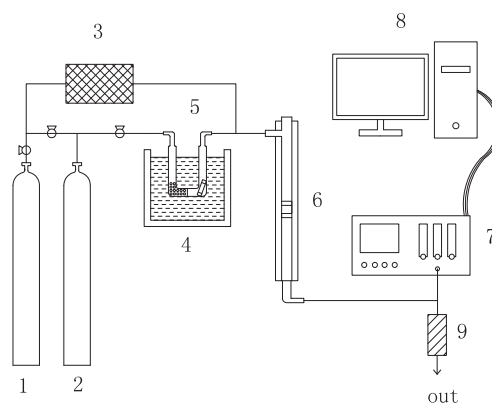
After being pulverized and sieved, bamboo (0.20–0.45 mm) was added to deionized water (the volume of water was twice the volume of bamboo), stirred at 80 °C for 3 h, and subsequently dried at 110 °C for 12 h. Carbon dioxide (CO₂) was selected as reductant during pyrolysis because it could produce more micropores. Approximately 2 g of bamboo was pyrolyzed at 900 °C under CO₂ flow (600 mL/min) for 30 min in a tube furnace. Before and after the pyrolysis process, bamboo was heated and cooled in a nitrogen environment for 5 min. After cooling, the pyrolyzed BCs were dipped into H₂O₂ solutions of different concentrations. The most common concentration of H₂O₂ used in industry is approximately 30 wt%, therefore, three concentrations (0, 15, and 30 wt% H₂O₂ solutions) were selected for our experiments, and the volume of the H₂O₂ solution was approximately twice the volume of bamboo during each experiment. Ultrasonic assistance was introduced to enhance the process. The modified BC samples were then dried in an oven at 90 °C for 4 h and cooled down to room temperature. These carbons will be referred to as BC, BC1, and BC2, representing the raw, 15 wt% H₂O₂ modified, and 30 wt% H₂O₂ modified BCs, respectively.

2.2. Sample characterization

The surface area, pore volume, and pore size distribution of the samples were determined using N₂ sorption at 77 K using a NOVA 2000 automated gas sorption system (Quantachrome Instruments, USA). The total surface area of the samples was evaluated using the Brunauer–Emmett–Teller (BET) method. The pore size distributions of the samples were calculated using the Barrett–Joiner–Halenda (BJH) method using data from the N₂ adsorption isotherm. An EuroEA3000 element analyzer (LEEMAN EuroVector) was used to determine the elemental chemical compositions of the samples. X-ray photoelectron spectroscopy (XPS, Shimadzu Corporation, Japan) utilizing Al-K α radiation ($h\nu = 1486.6$ eV) was used to determine the concentrations and valence states of the elements on the surfaces of the materials, utilizing the binding energies calibrated using the C1s signal at 284.6 eV. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet Magna-560 infrared spectrometer (U.S. Bio-rad Laboratories) over a 4000–400 cm⁻¹ range.

2.3. Mercury adsorption experiments

As shown in Fig. 1, several Hg⁰ removal experiments were carried out. The Hg⁰ in flue gas originated in a mercury permeation tube (VICI Metronics, US) and moved through a U-shaped quartz tube using N₂ (~200 mL/min) as carrier gas. The U-shaped quartz tube was immersed in a water bath. The concentration of mercury in the flue gas was maintained constant by adjusting the temperature of the water bath (30–50 °C). Other gases, such as O₂, SO₂, H₂O, and N₂ (which acted as carrier gas) were introduced in the flue gas afterward. The flow rate of the mixed gases was adjusted to 800 mL/min using 5 vol% O₂, and 37.0 ± 1 µg/m³Hg⁰ passed through a pre-heater (120 °C). The temperature inside the quartz fixed reactor was maintained at 120 °C using



1. Gas cylinder(O₂); 2. Gas cylinder(N₂); 3. Mixed preheater;
4. Water bath; 5. U-shaped tube; 6. Fixed-bed reactor;
7. Mercury analyzer; 8. Computer; 9. Tail gas treatment device

Fig. 1. Schematic arrangement of mercury adsorption experimental apparatus. 1. Gas cylinder (O₂); 2. Gas cylinder (N₂); 3. Mixed preheater; 4. Water bath; 5. U-shaped tube; 6. Fixed-bed reactor; 7. Mercury analyzer; 8. Computer; 9. Tail gas treatment device.

a temperature-indicating controller. Heating tapes were twined around the inlet and outlet tubes of the reactor to decrease the amount of Hg⁰ condensing. A weight (W) of 100 mg of sorbent was selected for all experiments. The concentrations of mercury were determined using an H11-QM201H online cold vapor atomic mercury analyzer (Jiangsu Qing'an Ins. Co. China). All experimental data were obtained by averaging three values to eliminate errors. The errors for the mercury analyzer were within 6%.

The removal efficiency (η) of the BCs samples for Hg⁰ was calculated using Eq. (1). The accumulative adsorption amount of the sorbents (q expressed in µg/g) was determined using Eq. (2):

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

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

where C_{in} and C_{out} represent the inlet and outlet Hg⁰ concentrations (µg/Nm³) in the fixed-bed reactor, F represents the gas flow rate (Nm³/min), and W is the mass of sorbent (g). To investigate the escape of mercury species in the outlet flue gas, a gas washing bottle containing either a 10% stannous chloride (SnCl₂) or 10% potassium chloride (KCl) solutions was set in front of the mercury analyzer. The total concentration of mercury was measured as the flue gas passed through the 10% SnCl₂ solution to reduce the Hg²⁺ in the gas to Hg⁰. The concentration of Hg²⁺ was determined from the difference between the total concentration of mercury and the concentration of Hg⁰.

3. Results and discussion

3.1. Characterization of the BC samples

The N₂ adsorption/desorption isotherms for the BC samples are shown in Fig. 2. The adsorption volume increased quickly and then remained almost unchanged until P/P₀ reached 1.0. According to the pores classification of the International Union of Pure and Applied Chemistry (IUPAC), these types of isotherms belong to the “I” type, indicating the presence of a lot of micropores inside the samples. The graph depicted monolayer adsorption which was common for the adsorption of N₂ on charcoal as well [47]. According to the literature,

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