



Mercury adsorption of modified mulberry twig chars in a simulated flue gas



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HIGHLIGHTS

- ▶ Pyrolyzed mulberry twig chars were modified by steam activation and impregnation.
- ▶ Steam activation and H₂O₂-impregnation improve char's pore structure significantly.
- ▶ Cl-impregnation increase surface functional groups but deteriorates pore structure.
- ▶ Mercury adsorption of Cl-impregnated MT chars increases with increasing Cl content.
- ▶ Compare different modification process of MT chars on mercury adsorption.

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ABSTRACT

Mulberry twig chars were prepared by pyrolysis, steam activation and impregnation with H₂O₂, ZnCl₂ and NaCl. Textural characteristics and surface functional groups were performed using nitrogen adsorption and FTIR, respectively. Mercury adsorption of different modified MT chars was investigated in a quartz fixed-bed absorber. The results indicated that steam activation and H₂O₂-impregnation can improve pore structure significantly and H₂O₂-impregnation and chloride-impregnation promote surface functional groups. However, chloride-impregnation has adverse effect on pore structure. Mercury adsorption capacities of impregnated MT chars with 10% or 30% H₂O₂ are 2.02 and 1.77 times of steam activated MT char, respectively. Mercury adsorption capacity of ZnCl₂-impregnated MT char increase with increasing ZnCl₂ content and is better than that of NaCl-impregnated MT char at the same chloride content. The modified MT char (MT873-A-Z5) prepared by steam activation following impregnation with 5% ZnCl₂ exhibits a higher mercury adsorption capacity (29.55 μg g⁻¹) than any other MT chars.

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1. Introduction

Mercury emission control is a major environmental concern since mercury is considered to be one of the most toxic metals found in the environment. Mercury emissions from coal-fired power plants are one of the largest anthropogenic pollution sources (Padak et al., 2006; Yudovich and Ketris, 2005). The main forms of mercury emitted in coal combustion flue gases are elemental mercury (Hg⁰), oxidized mercury (Hg²⁺) and particulate-bound mercury (Hg^p). Most of particulate-bound mercury can be removed using air pollution control devices (APCDs). Oxidized mercury is easily captured by wet scrubbers, while gaseous elemental mercury passes through the scrubbers readily. Elemental mercury (Hg⁰) has a lifetime in the atmosphere of up to one year and can be transported over long distances because of its low melting point, high equilibrium vapor pressure, and low solubility in

water (Kolker et al., 2006; Yan et al., 2003). There are several methods that are used to control Hg⁰ emissions. Sorbent injection technology has been considered to be a promising technique for capturing mercury. The sorbent is injected into a flue gas stream and then removed in the particulate control device, either an electrostatic precipitator (ESP) or a baghouse (Pavlish et al., 2003). Generally, there are two kinds of mercury sorbents, named carbon-based and non carbon-based sorbents, in which, activated carbon (AC) is one of the most studied and applied carbon-based sorbents for capturing elemental mercury from combustion flue gas (Yang et al., 2007; Lee et al., 2006; Alptekin et al., 2008).

Biomass by-products have proved to be promising raw materials for the production of carbon-based sorbents with a high adsorption capacity, considerable mechanical strength due to their low content of sulfur, nitrogen and ash, high ash reactivity, zero net CO₂ emission, and availability at a low price (Liu et al., 2011a). Ioannidou and Zabaniotou (2007) reviewed the production of ACs from agricultural residues and pointed out that pyrolysis and activation have significant effects on properties of activated carbons.

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The adsorption capacity of ACs depends mainly on their pore structure and surface chemical state (Skodras et al, 2007). Surface oxygen functional groups have been proven to be able to enhance the adsorption capacity of ACs by chemical mechanism significantly (Li et al, 2003; Lee et al., 2009; Liu et al., 2011b). Due to non-selective adsorption of activated carbons, flue gas components (such as SO₂ and NO, etc.) will occupy active sites easily and results in decreasing adsorption efficiency significantly (Liu et al., 2008). In order to increase the utilization of AC, many efforts have been performed to increase these functional groups by modifying with compounds of chlorine (Hu et al., 2009; Zeng et al., 2004), bromine (Sasmaz et al., 2012), iodine (Lee et al., 2004), sulphur (Feng et al., 2006; Hsi et al., 2011), oxidized metals (Mei et al., 2008), acid and alkali (Li et al, 2003; Chingombe et al., 2005; Skodras et al, 2007). However, the modification process is sometimes very complex and time-consuming, which limits its industrial application widely. It is very necessary to carry out the effects of preparation of biomass-derived carbon-based sorbents on their physical–chemical structures and mercury adsorption characteristics.

In this paper, mulberry twig (MT) chars were prepared under a series of processes including pyrolysis, steam activation and impregnation with H₂O₂, ZnCl₂ and NaCl. The textual characterization and surface functional groups of MT char samples were measured by N₂ adsorption and Fourier transform infrared spectroscopy (FTIR), respectively. The mercury adsorption experiments of different MT char samples in a simulated flue gas were carried out to understand the influence of physical and chemical process on mercury adsorption.

2. Methods

2.1. Sample preparation

The proximate and ultimate analyses of as-received raw mulberry twig are shown in Table 1, in which the ash content of mulberry twig is only 2.55%, which indicates its benefit to prepare a high-performance carbon-based sorbent (Mahajan and Walker, 1979). Mulberry twig was previously air-dried, ground and sieved to obtain a particle size less than 2 mm for preparing pyrolyzed, steam activated and impregnated mulberry twig chars.

Pyrolyzed mulberry twig char (named as MT873) was prepared under a N₂ atmosphere in a quartz tube fixed-bed pyrolysis reactor surrounded by a temperature-controlled electrical furnace, in which N₂ flow rate is 5 L min⁻¹, rapid-pyrolysis residence time (τ_p) is 10 min and pyrolysis temperature (T_p) is 873 K. Steam activated mulberry twig char (named as MT873-A) was prepared from MT873 char sample under a N₂/H₂O atmosphere in the same fixed-bed reactor, in which activation temperature (T_s) is 1073 K, activation residence time (τ_s) is 30 min, and the molar ratio of N₂ to H₂O(g) equals to 1:1. Impregnated mulberry twig chars were prepared by impregnating with H₂O₂, ZnCl₂ and NaCl based on MT873-A sample, respectively. All chemicals used above were analytical grade and the preparation processes are listed as follows:

(1) H₂O₂-impregnated mulberry twig char: 10 g of each MT873-A sample was put into H₂O₂ solution with mass concentrations of 10% and 30%, respectively, in which solution to MT char ration was

10 mL/g. The weak acidic impregnation mixtures were hold at room temperature for 24 h after stirring fully, and then the samples were washed with de-ionized (DI) water to neutral condition and air-dried at 363 K for 30 h (Tan et al., 2011). The H₂O₂-impregnated MT chars are named as MT873-A-H1 and MT873-A-H3, respectively.

(2) ZnCl₂-impregnated mulberry twig chars: A certain amount of MT873-A sample were put into ZnCl₂/HNO₃ solution, in which, HNO₃ concentration is 2 mol L⁻¹, ZnCl₂ concentration is 1%, 3% and 5%, respectively, and each gram MT873-A sample was mixed with 1.0 mL ZnCl₂/HNO₃ solution. The impregnated samples were hold at room temperature for 24 h after stirring fully and air-dried at 363 K for 30 h. The ZnCl₂-impregnated MT chars are named as MT873-A-Z1, MT873-A-Z3 and MT873-A-Z5, respectively.

(3) The preparation of NaCl-impregnated mulberry twig char (named as MT873-A-N3) was similar to the corresponding ZnCl₂-impregnated MT chars. 3% ZnCl₂/HNO₃ solution was replaced by 3% NaCl/HNO₃ solution, and each gram MT873-A sample was mixed with 0.85 mL NaCl/HNO₃ solution to guarantee the same chlorine content in the samples of MT873-A-Z3 and MT873-A-N3.

2.2. Characterization of samples

The characterization of samples was carried out by N₂ adsorption at 77 K with relative pressures (P/P_0) up to 0.995 using a surface area and pore size analyzer (Quantachrome Nova-1000e) to assess the pore morphology of the produced MT chars. The samples were outgassed at 393 K for 24 h before N₂ adsorption of the samples. The surface areas of samples were determined at $P/P_0 = 0.05$ – 0.30 according to the Brunauer–Emmett–Teller (BET) method (Azevedo et al., 2007). The total pore volumes were directly measured at the highest relative pressure ($P/P_0 = 0.995$) and average pore widths were calculated based on the total pore volume and surface area. Adsorption data were also analyzed by the Dubinin–Radushkevich equation to assess the DR surface area and DR micropore volume (Arami-Niya et al., 2011). Fourier transform infrared spectroscopy (FTIR) was utilized to qualitatively identify the functional groups. The spectra were measured from 4000 to 400 cm⁻¹ and recorded on a Nicolet Nexus 670 FTIR spectrometer (Thermo electron corporation, USA) using the KBr pellets containing 1% of MT char samples (Wen et al., 2011).

2.3. Mercury adsorption

The fixed-bed mercury adsorption experimental setup is shown in Fig. 1, which consists of an elemental mercury generator, a vertical temperature-controlled electrical furnace, a quartz tube fixed-bed adsorber, a simulated flue gas supplying system, an online mercury analyzer and a flue gas cleaner. The efficient heating height of the vertical furnace (manufactured by Southeast University, China) is 300 mm. A vertical quartz tube absorber (900 mm in height with an outer diameter of 56 mm and an inner diameter of 50 mm) with a inside porous quartz plate and several glass fiber filters was placed inside the vertical electric heating furnace to support the tested sorbents. Elemental mercury generator consists of a numerical control thermostatic water bath, a mercury permeation tube (VICI Metronics, Inc., Poughkeepsie, NY, USA) and a U-shaped quartz tube. The U-shaped quartz tube loaded a mercury permeation tube was immersed in the thermostatic water bath. A flow of 100 mL min⁻¹ high-purity N₂ (99.999%) passed the permeation tube to carry elemental mercury into a mixing container, and mixed with components of N₂, NO and SO₂ to yield stable Hg⁰-laden simulated flue gases.

During the test, 350 mg of each mulberry twig chars was put on the filter of the fixed bed adsorber. A temperature control device is employed to keep the absorber temperature (T_a) at 363 K. Once

Table 1
Proximate and ultimate analyses of raw mulberry twig (as-received basis).

Proximate analysis (wt.%)				Ultimate analysis (wt.%)				
M _{ar}	A _{ar}	FC _{ar}	V _{ar}	C _{ar}	H _{ar}	N _{ar}	S _{ar}	O _{ar} ^a
10.83	2.55	18.46	68.16	38.86	9.41	2.34	0.15	35.86

^aBy difference.

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