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Full Length Article

Removal of elemental mercury from flue gas using sargassum chars modified by NH_4Br reagent

Wei Yang, Ziyang Liu, Wen Xu, Yangxian Liu*

School of Energy and Power Engineering, Jiangsu University, Zhenjiang, Jiangsu 212013, China

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ABSTRACT

Ocean contains huge biomass resources. Actively developing marine biomass resources has great significance to human development. In this work, a kind of seaweed, sargassum, is used to prepare chars by pyrolysis. The sargassum chars are modified by NH_4Br reagents using a simple impregnation method, and are applied to capture Hg^0 from flue gas. The physicochemical properties of the samples are investigated using scanning electron microscopy (SEM), proximate and ultimate analysis, X-ray photoelectron spectroscopy (XPS) and Brunauer-Emmett-Teller (BET), respectively. The effects of pyrolysis temperature, reaction temperatures, loading values and the components of flue gas such as O_2, water vapor, NO and SO_2 on mercury removal efficiency are studied. Mercury removal mechanism, kinetics and thermodynamics are also investigated. The results show that increasing pyrolysis temperature, reaction temperature, loading value, O_2 concentration and NO concentration enhances mercury removal. Low concentrations of SO_2 and H_2O are beneficial to mercury removal, and high concentrations of SO_2 and H_2O inhibit mercury removal. C-Br and C=O covalent groups are the major chemisorption sites for Hg^0 removal. Finally, the kinetic and thermodynamic parameters of mercury removal are also obtained.

1. Introduction

Mercury emissions have caused worldwide attention because of its significant impact on the human health and ecological environment [1]. And the total amount of anthropogenic mercury emissions is more than 1000 tons each year [2]. The combustion of fossil fuel has become the main anthropogenic mercury emissions source, which accounts for about 30 percent of anthropogenic mercury emissions [3]. The mercury from the typical flue gas consists of particulate bounded mercury (Hg^p), elemental mercury (Hg^0) and oxidized mercury (Hg^{2+}) [4]. Since the divalent mercury (Hg^{2+}) from the flue gas has a high water solubility, it can be effectively removed using a WFGD system (wet flue gas desulfurization). The Hg^p from flue gas can also be easily collected by the electrostatic precipitator (ESP) and the fabric filter (FF) [5]. However, compared with Hg^{2+}, elemental mercury (Hg^0) from flue gas is very hard to be captured due to its low water solubility and high volatility. To reduce Hg^0 emission, lots of technologies have been developed, including catalytic oxidation [6], adsorption removal [7], advanced oxidation [8], etc. Activated carbon injection (ACI) technology is one of the effective ways to remove mercury due to its simple process and device, but the high operating costs limit its application [9,10]. In order to develop low-cost and effective sorbents, some scholars have studied a lot of inexpensive biomass-based sorbent materials as alternatives to activated carbon, such as bamboo [11], tea [12], mulberry branches [13], coconut shells [14], medicinal residues [15], agricultural wastes [16,17], etc.

Ocean contains huge biomass resources. Actively developing marine biomass resources has great significance to human development. Sargassum is a kind of abundant seaweed in ocean with high reproduction rate, strong adaptability and high photosynthetic efficiency [18]. Compared with terrestrial crops, sargassum is very easily cultivated or planted in sea/beach on a large scale with low costs (being able to grow naturally), and has less competition with any arable land [18]. In China, sargassum has been used to prepare chemicals and fuels by pyrolysis, and as a biomass fuel for direct combustion [18,19]. In the pyrolysis process of sargassum for preparation of bio-oil, a large amount of sargassum chars will be produced. To further utilize the pyrolysis byproducts, and avoid solid waste pollution, we for the first time propose to use sargassum chars as low-cost adsorbents to remove Hg^0 from flue gas. In the previous studies [20–24], the halogens (especially NH_4Cl, NH_4Br and NH_4I) are considered to be effective modified reagents for Hg^0 removal of from flue gas by bio-char sorbents. Among them, NH_4Br often has a better performance than NH_4Cl, and a much lower price than NH_4I [25–28]. Thus, in this article, NH_4Br modified

* Corresponding author.
E-mail address: liuyx1984@126.com (Y. Liu).

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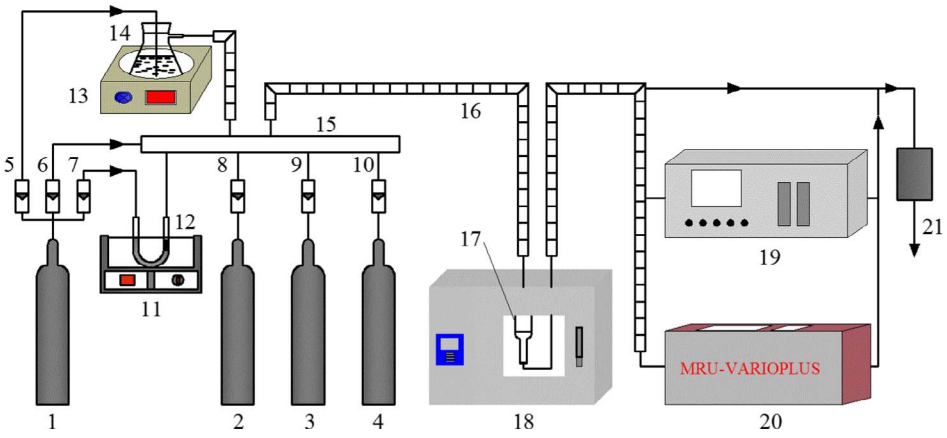

Fig. 1. The experimental system for Hg^0 removal tests of sorbents. (1–4) $N_2/SO_2/NO/O_2$ cylinders; (5–1 0) Flowmeters; (11) Thermostat water bath; (12) Mercury vapor generator; (13–14) Generator of water vapor (combination of thermostat water bath 13 and conical flask 14); (15) Gas mixer; (16) Heating tape; (17) Quartz fixed bed reactor; (18) Thermostat drying oven; (19) Hg^0 analyzer; (20) Flue gas analyzer; (21) Exhaust gas treatment pipe.

sargassum chars are prepared by an impregnation method, and are applied to capture Hg^0 from flue gas. And the physicochemical properties of the sobents are characterized using scanning electron microscopy (SEM), proximate and ultimate analysis, X-ray photoelectron spectroscopy (XPS) and Brunauer-Emmett-Teller (BET), respectively. The effects of pyrolysis temperature, reaction temperatures, loading values and the components of flue gas such as O_2, water vapor, NO and SO_2 on Hg^0 removal are studied. The mechanism, kinetics, thermodynamics of Hg^0 removal are also analyzed based on the characterization analysis and experimental results. These experimental results are very important for the large-scale development and application of this technology.

2. Experimental

2.1. Preparation of samples

The sargassum materials (from Weihai of Shandong province, China) are dried, crushed and sieved into the particles smaller than 50 mesh (< 300 μm). The raw sargassum particles are pyrolyzed at required temperature (400, 600 and 800 °C) for 20 min under a nitrogen (N_2) atmosphere (250 mL/min). The sargassum chars pyrolyzed at 400, 600 and 800 °C are denoted as S4, S6 and S8, respectively. The S8 biochar samples are further impregnated with NH_4Br solution. In addition, the weight ratios of NH_4Br to S8 sargassum chars are 1, 5 and 9 wt%, respectively, and the mixing ratio of S8 to impregnated NH_4Br solution is 1 g: 10 mL. The mixtures are stirred for 60 min at room temperature and then dried for 12 h at 90 °C. The final products are denoted as S8Br1, S8Br5 and S8Br9, which corresponds to the weight ratios of NH_4Br to S8 bio-chars (1, 5 and 9 wt%), respectively.

2.2. Characterization of samples

The ultimate analysis of sargassum is determined by Flash 2000 (Thermo Fisher, USA). The Chinese National Standards (GB/T 212-2008) can be applied to calculate the proximate analysis of sargassum. The moisture, ash and volatile are measured at the temperatures of 110, 815 and 900 °C, respectively. The Micromeritics Tristar II 3020 analyzer [SPS]code = "OT" instruction = "Others"[/SPS]– > analyzer (Micromeritics Instrument Crop., USA) is applied to measure the pore volume and specific surface area of the sargassum chars. The pore characteristics of samples are analyzed by nitrogen (N_2) adsorption isotherms at −196 °C. The specific surface area of samples are carried out by the BET (Brunauer-Emmett-Teller) equation. The SEM micrographs of samples are analyzed by the Scanning Electron Microscopy (JSM-7500F). The K-Alpha X-ray photoelectron spectrometer (XPS, Thermo Fisher, USA) is used to analyze the elements chemistry valence states on the surface of the S8Br5 sample.

2.3. Experimental apparatus and procedure

As shown in Fig. 1, the experimental system consists essentially of four parts: simulated flue gas system, reaction system, temperature adjusting system and measurement/tail gas treatment device. The simulated flue gas system consists essentially of four cylinder gases (1–4), six flowmeters (5–10), a mercury vapor generator (11–12) (VICI Metronics, USA), a water vapor generator (13–14) and a gas mixer (15). The temperature adjusting system consists of two thermostat water baths (11, 13) and a heating tape (16). The reaction system mainly includes a quartz fixed bed reactor (17) (inner diameter, 35 mm; length, 50 mm) and a thermostat drying oven (18). The measurement/tail gas treatment system mainly includes a Hg^0 analysis device (19) (QM201H, Suzhou Qingan Instrument Co., Ltd, China), a flue gas analysis device (20) (MRU-VARIOPLUS, Germany) and an exhaust gas absorption pipe (21).

All individual flue gas components are produced by O_2, SO_2, NO and N_2 cylinders, and are regulated by the flowmeters, with the total gas flow rate of 900 mL/min. At the same time, the gas hourly space velocity (GHSV) is 21,000 h^{-1}. Hg^0 vapor is generated using a Hg^0 vapor permeation device. A water vapor generator is used to provide a certain concentration of water vapor. The inlet concentrations of NO, SO_2, O_2 and Hg^0 are measured by the flue gas analysis device (MRU-VARIOPLUS, Germany) and the Hg^0 analysis device (QM201H, Suzhou Qingan Instrument Co., Ltd, China). All of the gas lines are heated by a heating tape in order to prevent the condensation of mercury vapor and water vapor. The simulated flue gas mainly consists of 400 ppm NO, 600 ppm SO_2, 5% O_2, 1% (vol) water vapor, 60 μg/m^3 Hg^0 and balanced N_2. In each experiment, a mixture of 0.25 g sample and 1.5 g quartz sand is placed in a quartz fixed bed reactor. After each experiment, the exhaust gas is firstly treated by the tail gas treatment device and then is discharged into the atmosphere. The Hg^0 removal performance can be evaluated by the Eq. (1).

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

where η denotes the efficiency of Hg^0 removal (%); C_{in} denotes the inlet concentration of Hg^0 in gas (μg/m^3); C_{out} denotes the outlet concentration of Hg^0 in gas (μg/m^3).

The mercury accumulative adsorption amount per gram of sorbent can be calculated by the Eq. (2).

$$q = \frac{Q}{M} \int_0^t (C_{in} - C_{out}) dt \quad (2)$$

where Q represents total gas flow rate, m^3/min; M represents the sorbent mass, g; t represents the adsorption time of sorbent, min; q represents the mercury accumulative adsorption amount per gram of sorbent, μg/g.