Chemical Engineering Journal 263 (2015) 1–8

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Increasing oxygen functional groups of activated carbon with non-thermal plasma to enhance mercury removal efficiency for flue gases

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HIGHLIGHTS

- Activated carbon treated with non-thermal plasma has higher mercury removal efficiency.
- Non-thermal plasma can increase the amount of carbonyl groups and ester groups of activated carbon.
- Ester groups dominated mercury removal efficiency at higher temperature.
- Mercury desorption peak of carbonyl groups and ester groups occur at 230 °C and 320 °C, respectively.

ARTICLE INFO

Article history:
Received 31 July 2014
Received in revised form 16 October 2014
Accepted 26 October 2014
Available online 1 November 2014

Keywords:
Activated carbon
Mercury
Flue gas
Functional group
Non-thermal plasma
Temperature programmed desorption

ABSTRACT

To improve mercury removal efficiency of activated carbon (AC), a simple and efficient non-chemical treatment method was proposed: AC was treated by non-thermal plasma in air environment and characterized with ultimate analysis, Brunauer–Emmett–Teller (BET) surface area and X-ray photoelectron spectroscopy (XPS) technique. Mercury removal performance of AC was tested in a bench-scale quartz tube reactor. AC samples with different treatments were used as contrast sorbents for adsorption and desorption experiments. The results showed that AC treated with non-thermal plasma had higher mercury removal efficiency than others, and longer treatment time resulted in higher efficiency, the main reason was that non-thermal plasma treatment increased active sites, carbonyl groups (C═O) and ester groups (C(O)—O—C) of AC, which played an important role in mercury absorption. By further analysis, it was found that increasing the active sites of AC was more effective than increasing the surface area for improving the mercury removal efficiency. And ester groups dominated mercury removal efficiency at higher temperature. Moreover, the results of the temperature programmed desorption (TPD) experiments indicated that the mercury desorption peak of carbonyl groups and ester groups should occur at 230 °C and 320 °C, respectively. By removing the functional groups of AC, mercury desorption peak desorbed by sorbent's pore at 130 °C was found. The non-thermal plasma treatment is a potential method for improving the mercury adsorption performance of sorbents.

1. Introduction

Mercury has attracted wide attention due to its high toxicity to human and other organisms [1]. The major anthropogenic sources of mercury are coal-fired power plants [2]. In flue gases, mercury usually exists in three forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and particle-bound mercury (Hg^p) [3]. Compared with Hg^{2+} and Hg^p, it is hard to remove Hg^0 from flue gases because of its volatility and indissolubility [4].

Activated carbon (AC) injection technique has been proved to be one of the most promising methods to remove mercury from flue gases [5]. However, its high cost and poor efficiency tremendously inhibits its application; hence, many researchers put forward various chemical treatment methods for AC to improve its performance [6]. The introduction of various impregnants (such as sulfur, iodine, chlorine, bromine) as precursors of new active sites, and the chemical treatment methods to increase active sites of AC have been proved good methods [7–11]. Although the impregnants

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http://dx.doi.org/10.1016/j.cej.2014.10.090
1385-8947/

can improve the mercury removal efficiency and reduce the sorbent dosage, the chemical impregnation procedure is too complex and time-consuming, and the cost of impregnants is relatively high. Nowadays, lots of coal-fired power plants in USA use modified ACs to control the mercury emission, while the ACs are provided by commercial company. If a new way which is simple and time-saving consumed can be found, it will reduce the cost.

Plasma has been widely studied and used in a variety of fields during the last two decades [12,13]. It has been used to modify adsorbent or catalyst to achieve better performance. The mechanism of plasma treatment is producing chemical active species to change the properties of adsorbent surface. Under different gas environments, plasma can generate different functional groups on adsorbent surface by oxidative, reductive, or inactive reaction [14–16]. Because the plasma treatment does not need chemical solution, it is simpler than chemical treatment. Although plasma treatment for AC is a promising method, few researchers have tried to apply it to mercury removal. Therefore, this paper firstly introduced non-thermal plasma treatment for AC to better capture mercury from flue gases of coal-fired power plants.

It has been proved that the oxygen plasma can increase the amount of oxygen functional groups [17,18]. And some researches indicated that oxygen functional groups could enhance the mercury removal efficiency of AC [19,20]. In this work, AC was treated with dielectric barrier discharge (DBD) non-thermal plasma in air to check whether this treatment is suitable for removing mercury. AC samples with different treatment times, different thermal treatments and different gas environments were used for contrast test. The tests of mercury removal performance were conducted in a fixed bed at two different temperatures, 30 °C and 130 °C. To get a better understanding of different functional groups' effects on mercury removal, temperature programmed desorption (TPD) tests were also conducted. According to the results, the correlation between sorbents' physical and chemical properties and the mechanism of mercury adsorption were discussed.

2. Experimental procedures

2.1. Sample treatment

AC was washed with deionized water to remove ultrafine particles and then dried at 105 °C in oven for 24 h. Afterwards, it was ground and sieved to obtain particles in a range of 0.2–0.3 mm diameter.

Three sets of AC samples were treated by non-thermal plasma in air for 7 min (named as AC-A7), 15 min (AC-A15) and 30 min (AC-A30), respectively. Plasma treatment in N_2 for 30 min (AC-N30) as a comparative experiment was done. To better understand the effects of functional groups on mercury removal, another two sets of AC samples were treated in different ways: thermal treatment at 900 °C in N_2 (AC-T) for 30 min to remove the most functional groups of AC [21], thermal treatment at 900 °C in N_2 for 30 min + plasma treatment in air for 30 min (AC-T-A30).

Fig. 1(a) presents the experimental setup of non-thermal plasma treatment. A DBD plasma reactor (DBD-100A, Suman Corporation, China) was used for non-thermal plasma treatment of AC. Two quartz circular plates are barrier materials and stainless steel for the electrodes. The quartz plate is 70 mm in diameter, 3.0 mm in barrier thickness, and 8.0 mm in barrier-to-barrier gap. 2.0 g of AC sample was loaded in the reactor and the pressure during the plasma treatment was 1 atm and the thickness of sample is 3 mm. And all samples which were put in the DBD reactor could be treated by non-thermal plasma. The power supply of the DBD was an alternating current with a 10 kHz audio-frequency and 3 kV peak voltage. A digital oscilloscope was used to measure

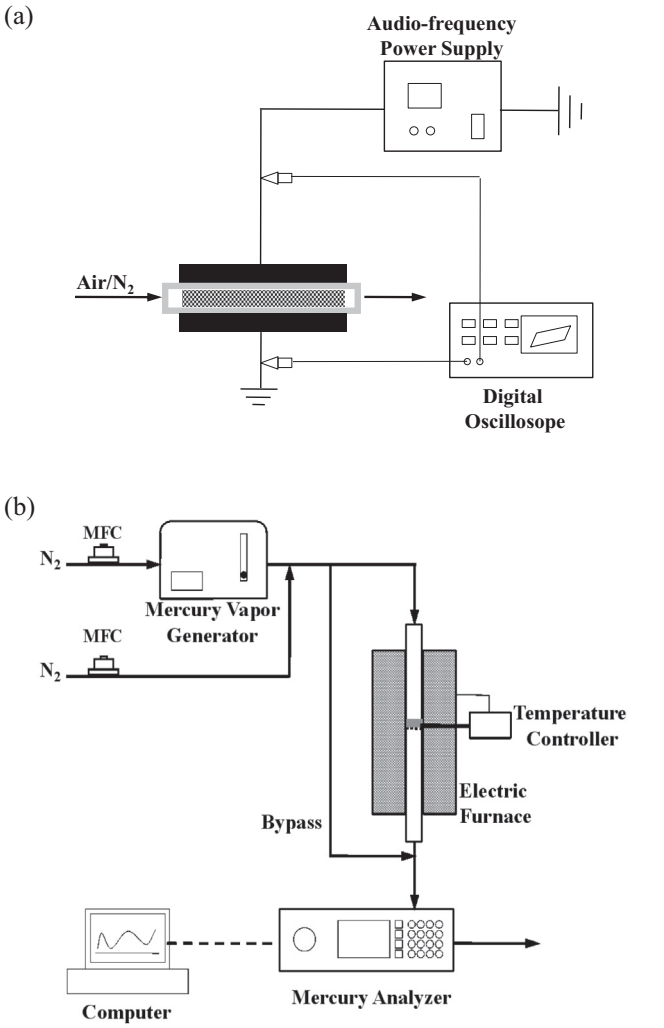

Fig. 1. Schematic of the experimental set up of non-thermal plasma treatment (a) and mercury adsorption test (b).

the input power that was delivered to plasma reactor by detecting the Lissajous diagrams [22]. The specific energy input (SEI) of the plasma was 45 J/s. The weight loss of all samples after plasma treatment was less than 0.5%, which was negligible.

2.2. Sample characterization

Vario Microcube elemental analyzer (Elementar Company, Germany) was used to obtain ultimate analysis of sorbents. The Brunauer–Emmett–Teller (BET) surface area and pore size distribution were calculated from the nitrogen adsorption at 77 K using a Micromeritics ASAP 2020. Fourier transform infrared spectroscopy (FT-IR) was used to qualitatively measure the surface functional groups of sorbents. 1 mg of the sample with 100 mg of KBr was pestled in an agate mortar to make sample discs. The sample discs were scanned in a range from 4000 to 400 cm^{-1} by Nicolet 4700 FT-IR spectrometer (VERTEX 70, Bruker Corporation). XPS technique was employed to characterize the surface binding by VG Multilab 2000, with the surface excitation by an Mg X-ray source (hv = 1253 eV).

2.3. Mercury adsorption experiment

The experimental setup of mercury adsorption test is presented in Fig. 1(b). Mercury removal performance of AC was tested in a