



Use of a non-thermal plasma technique to increase the number of chlorine active sites on biochar for improved mercury removal



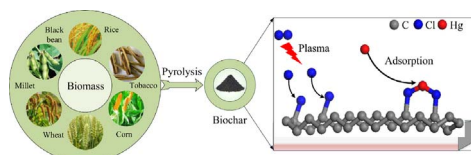
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GRAPHICAL ABSTRACT



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ABSTRACT

Biochar, known as a byproduct of biomass pyrolysis, was prepared from rice straw (R6), tobacco straw (T6), corn straw (C6), wheat straw (W6), millet straw (M6), and black bean straw (B6) in high purity nitrogen at 600 °C. Chlorine (Cl) non-thermal plasma was used to increase Cl active sites on biochar to promote the mercury removal efficiency. The physio-chemical properties of biochar were characterized by proximate analysis, ultimate analysis, BET, SEM, TGA, FTIR, and XPS. Modification by chlorine plasma increased the Hg⁰ removal efficiency of the biochar from around 8.0% to 80.0%. The Hg⁰ adsorption capacity of T6 was 36 times higher after Cl₂ plasma modification. Plasma caused the biochar surface to become porous and promoted the thermal stability of the biochar. Sulfur (S) content remained in the range of 0.5–0.7%, elemental/organic sulfur and sulfide were converted to sulfate during plasma treatment. The relative intensity of the oxygen functional groups (C–O, C=O and C(O)–O–C) were enhanced, while the content of oxygen (O) in biochar decreased. The main reason for the improved mercury removal efficiency by modified biochars was attributed to the increased number of C–Cl groups on the surface of the biochars induced by Cl₂ plasma. The C–Cl groups functioned as activated sites and promoted the Hg⁰ removal efficiency.

1. Introduction

Mercury has received more and more attention because it is a human health hazard and because it can bioaccumulate in the ecosystem. There are three main forms of mercury [1]: elemental mercury (Hg⁰), particulate-bound mercury (Hg^p), and oxidized mercury (Hg²⁺). Hg⁰ is of high concern owing to its low reactivity, low melting point and low water solubility. Numerous methods have been developed to control Hg⁰ emission including photochemical oxidation [2,3], sorbent

adsorption [4–6], and non-thermal plasma [7–9]. Activated carbon (AC) sorbents have been used for capturing Hg⁰ in coal-fired power plants [10], but its high cost limits full-scale applications. Biochar, made from pyrolyzed agricultural waste in an oxygen-free environment, is a byproduct of biomass pyrolysis. Biochar costs less and is relatively simple to prepare, so it an attractive alternative sorbent. Previous research indicates that the Hg⁰ removal efficiency of raw biochar is only 1.2% [11]. The adsorption capacity of Hg⁰ to commercial activated carbons is approximately 2–3 orders of magnitude stronger than

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unactivated biochar [12]. Therefore, many researchers aim to improve the adsorption capacity of biochar by physical or chemical modification techniques.

The physical modification technique mainly changes the pore structure such as specific surface area, pore volume and pore size of the biochar by heating [4,12,13], microwave [14,15], and ultrasonic [16]. Shu et al. [4] reported that steam heating activation increased the specific surface area and pore volume, enhancing mercury adsorption capacity from 5.07 to 8.76 $\mu\text{g/g}$. Li et al. [14] showed that the initial Hg^0 removal efficiency of biochar increased from 35.1% to 50.2% after microwave activation.

Chemical modification techniques mainly include acid [17–20], alkali [21,22], sulfur (S) [22,23], and halogen (Cl, Br, I) [24–27] modification. Chemical modification increases active functional groups on the surface of biochar, improving the chemical adsorption of mercury. It was reported that Hg^0 adsorption capacity reached 6067 $\mu\text{g/g}$ in 700 h [18] and removal efficiency was more than 95% [19] using hydrochloric acid-modified biochar. Hg^0 adsorption capacity increased from 730 $\mu\text{g/g}$ to 956 $\mu\text{g/g}$ after NaOH activation [21]. Mercury removal efficiency of KOH and Na_2S modified biochar also increased by 32% and 77% [22], respectively. Tan et al. [20,26,27] also discussed the effect of H_2O_2 , ZnCl_2 , FeCl_3 , NH_3 , H_2O , and HNO_3 modification on Hg^0 adsorption by biochar. Li et al. [14] demonstrated that Hg^0 removal efficiency of chemically modified biochar was about 2–3 times higher than physically modified biochar. However, chemical modification is complex, time-consuming, and the added element could leach from the biochar and cause a pollution problem. The modification process will be more feasible if a simple, time-saving and efficient method is developed.

Non-thermal plasma produces energetic electrons, ions and active radicals that improve the pore structure of sorbent and increase the active functional groups on the surface of sorbent [28–31]. Zhang et al. [32,33] indicated that the removal efficiency of mercury with original AC was 56.3%. While the removal efficiency of mercury with air plasma-modified AC and Cl_2 plasma-modified AC was 80% and 96%, respectively. Pure N_2 plasma modification, however, decreased the mercury removal performance. Zhang et al. [34] found that the average Hg^0 removal efficiency of modified sorbent with O_2 plasma was about 2–3 times higher than that of raw sorbent. However, few studies have used non-thermal plasma techniques to increase the chlorine active sites on biochar to improve mercury removal.

In this paper, six raw materials, rice straw, tobacco straw, corn straw, wheat straw, millet straw, and black bean straw were pyrolyzed in high purity nitrogen to produce biochar. Dielectric barrier discharge (DBD) plasma was used to modify biochar in chlorine gas (Cl_2), and the effect of Cl_2 plasma modification on Hg^0 removal by different biochars were investigated. Proximate analysis, ultimate analysis, Brunauer–Emmett–Teller (BET), scanning electron microscope (SEM), thermogravimetric analysis (TGA), fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were conducted to reveal possible Hg^0 adsorption properties and mechanisms using modified biochar.

2. Materials and methods

2.1. Preparation of biochar

The raw materials for the biochar come from different regions in China. Corn straw, millet straw, wheat straw, and black bean straw were collected from the Shaanxi province. Rice straw was from the Anhui province and the tobacco straw came from the Henan province. The straws were washed by deionized water 3 times to remove impurities, and then dried at 110 $^\circ\text{C}$ for 24 h. The washed samples were ground using a ball mill and sieved between 100 and 200 mesh. The preparation process is shown in Fig. 1. Ten grams samples were wrapped in a copper mesh (200 mesh) and placed in the center of

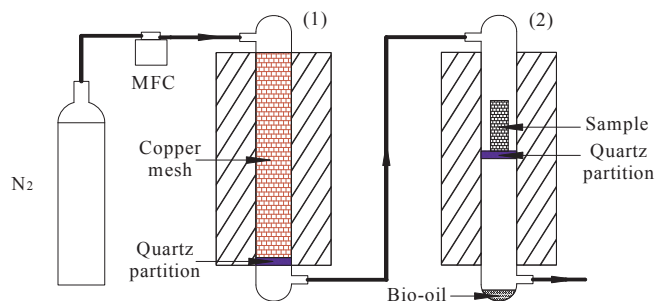


Fig. 1. Schematic diagram for preparation of biochar.

reactor 2 then heated by an electrical furnace. The length of the heating element was 50 cm, to minimize axial temperature differences in samples. In reactor 1, the copper mesh was used to remove the trace oxygen in the high purity nitrogen at 500 $^\circ\text{C}$, ensuring the purity of the biochar [16]. The flow rate of N_2 was controlled at 300 mL/min by mass flow controllers (MFCs). Furnace 2 was set to 600 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$ and held for 1 h, then naturally cooled down to room temperature in high purity nitrogen. After the pyrolysis process, the biochars of rice straw, tobacco straw, corn straw, wheat straw, millet straw, and black bean straw were denoted as R6, T6, C6, W6, M6, and B6, respectively.

2.2. Modification of biochar by plasma

As shown in Fig. 2, 0.3 g biochar was loaded in a DBD plasma reactor and that was sealed with high-vacuum silicon grease. One percent Cl_2 (N_2 as balance) was introduced into the reactor at 100 mL/min and the biochar was modified by Cl_2 plasma for 5 min. Nitrogen was introduced into reactor to purge the residual Cl_2 at 600 mL/min for 5 min after plasma modification. The modified biochars were named as R6Cl and T6Cl, C6Cl, W6Cl, M6Cl and B6Cl, respectively. The DBD reactor consisted of two quartz plates with a thickness of 3 mm and a diameter of 70 mm. The electrodes were stainless steel with a diameter of 50 mm. The gas gap between the two quartz plates is 8 mm. The plasma was created by an alternating power current with a frequency of 10 kHz. The peak voltage was within 0–30 kV and the measured capacitance was 0.14 μF . An oscilloscope (Rigol DS1202CA) was used to determine the discharge power that was calculated from Lissajous figure. The discharge power of modification was 23 W.

2.3. Mercury adsorption experiment

The Hg^0 adsorption apparatus is shown in Fig. 3. It consists of a mercury vapor generating system, a fixed-bed adsorption system and a

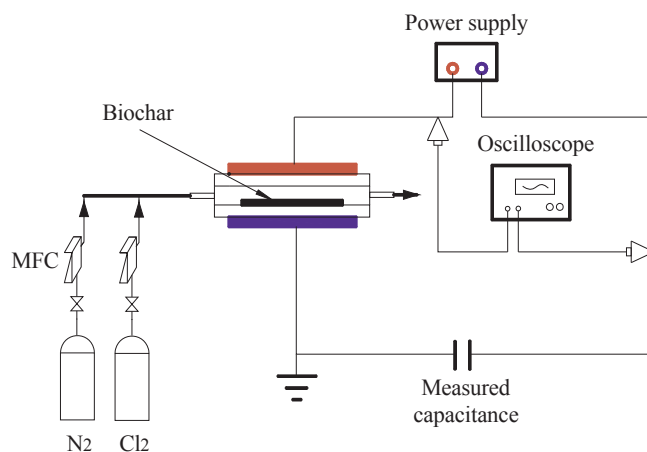


Fig. 2. Schematic of non-thermal plasma modification.

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