



Mercury sorption study of halides modified bio-chars derived from cotton straw



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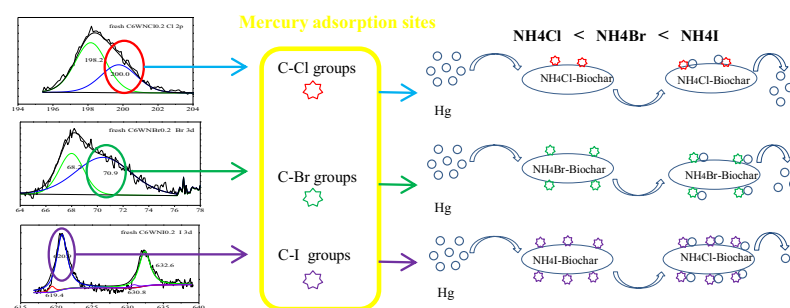
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HIGHLIGHTS

- The C-X (Cl, Br and I) groups sever as chemisorption sites for elemental mercury.
- The different ratio of C-X groups explains the result that halide modified effect follows the order: I > Br > Cl.
- The formation of C-X groups depended on the reducibility and size of halide ions.

GRAPHICAL ABSTRACT



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ABSTRACT

The mechanism of three halides (chloride, bromide and iodide) modification and reason for their modified effect difference was investigated in this study. Bio-chars derived from cotton straw were further activated and modified with microwave/steam and halides impregnation. Modified bio-chars serving as mercury sorbent was measured via BET, SEM and XPS analyses. The chemisorption site was identified as crucial factor for mercury adsorption performance via pore structure, SEM analysis and adsorption testing study. Based on XPS analysis of bio-char prior to and after adsorption testing, carbon-halide functional groups (C-X) were dominant chemisorption sites oxidizing Hg⁰ into mercury halide (HgCl₂, HgBr₂ and HgI₂). The amount of C-X groups possibly decided halide modification effect order: I⁻ > Br⁻ > Cl⁻. The formation of C-X groups depended on the reducibility and size of halide ions. In order to verify the adsorption mechanism, the molecular sieve (MCM-22) as non-carbon carrier was used to compare with bio-char. Results suggested that the lack of C-X groups decreased mercury removal performance in experimental condition. This paper firstly explained the reason for modified difference of three halides in term of chemisorption site formation mechanism.

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1. Introduction

Global mercury emissions have caused attention in the past decade due to the high toxicity and bioaccumulation of mercury

in the environment. To prevent its further impact on environmental and human health, the Minamata Convention on Mercury was passed, where coal combustion was one of the most significant regulated emission sources.

Coal combustion has emitted 474 t of atmospheric Hg in 2010, accounting for 24.2% of global anthropogenic mercury emissions [1]. The particle-bound mercury (Hg^p), oxidized mercury (Hg²⁺) and elemental mercury (Hg⁰) were three forms in the coal-fired

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flue gas. The Hg^{2+} and Hg^0 can be easily captured by wet flue gas desulfurization (WFGD) system and dust control devices, respectively [2,3]. However, Hg^0 is difficult to remove by current technologies because of its volatility and insolubility. Therefore, Hg^0 in atmosphere has a long residence time ranging from 0.5 to 2 year and can be transported and deposited to remote places even 1000 km away from emission source [4]. Activated carbon (AC) has been commercially used to reduce Hg^0 emission from coal combustion system. But the high cost hinders further popular application of activated carbon. So many studies aimed to research and develop various low-cost carbonaceous absorbent materials as AC alternatives, such as mulberry twig [5], bamboo [6], coconut shells [7] and coke [8].

Original pyrolysis products existed a general application problem that they had a poor adsorption performance for elemental mercury. Hence, various modification methods were used to improve the adsorption capacity of original products. The halides have been proved to be an effective modified reagent in previous studies [5,9–12]. Modification effect showed obvious difference among chloride, bromide and iodide. Previous studies had indicated that halides modification effect followed the order: iodide > bromide > chloride [9–12]. Previous studies only explained this phenomenon in term of physical property difference of halide ions, the mechanism was not investigated deeply. Mahuy et al. and Cai et al. attributed this modification difference to their atomic diameter since the big size of iodine ion improved the exposure to mercury [9,10]. However, mercury adsorption capacity via the halide impregnation was generally ascribed to the formation of chemical adsorption sites. As a result, the impact of chemical sites on bio-chars modified with various halides was also possibly an important reason for their performance. This aspect was necessary to further deeply explore yet usually neglected in previous studies.

In this study, the cotton straw and ammonium halides were chosen to be the raw material and modified reagents. Chloride, bromide and iodide modification effect on bio-char was compared and investigated. The influence of loading was also explored on the mercury removal. In order to investigate the mechanism of mercury adsorption on halides modified bio-chars, the potassium halides as modification reagents and molecular sieves as carrier was used to compare with ammonium halide modified bio-chars. In addition, the proximate and ultimate analysis, pore analysis, SEM and XPS characterization was used to measure the property of bio-chars.

2. Materials and Methods

2.1. Sample preparation

In our previous study, the agricultural waste (cotton straw), industrial wastes (medicinal residues) and municipal solid wastes, were pyrolyzed to generate bio-chars for Hg^0 adsorption [13]. And the result manifested that the bio-char from cotton straw had the best performance for the mercury adsorption since it possessed the good pore property and more oxygen-containing functional groups. In our another study, a series of chlorides (NH_4Cl , HCl and ZnCl_2) were used to modify bio-chars and the results indicated that the NH_4Cl was an optimal modification method due to its high efficiency and low price [14]. Based on above studies, the cotton straw and ammonium halides were chosen to be the raw material and modified reagents in this study.

The raw materials (cotton straw), after undergoing natural drying, was crushed to size of 8.0–10.0 mm. The pyrolysis reactor was a quartz reactor (160 mm in diameter and 400 mm in depth) under a N_2 atmosphere with $200 \text{ mL} \cdot \text{min}^{-1}$. The cotton straw chipping was placed in pyrolysis zone and steadily heated to $600 \text{ }^\circ\text{C}$ at

$20 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$, and then remained for 60 min. Under the oxygen-free environment, the pyrolysis reactor was cooled to room temperature. The yield ratio of carbonization of cotton straw was 37.1%. The derived bio-char was denoted as C6. The schematic of pyrolysis system was shown in Fig. S1.

The 2.0 g above bio-char was placed in a quartz bottle activation reactor (50 cm^3) under oxygen-free atmosphere with a constant flow of N_2 ($80 \text{ mL} \cdot \text{min}^{-1}$). Under the control of the peristaltic pump, deionized water was injected with a flow rate of $4 \text{ mL} \cdot \text{h}^{-1}$ into the activation reactor to generate steam. The whole activation reactor was placed in a microwave oven (950 W). The bio-char C6 was activated by the microwave and steam for 4 h. The yield ratio of microwave activation of C6 was 89.2%. The derived bio-char was denoted as C6W.

The bio-char C6W was impregnated with various precursor solutions of same concentration of $0.05 \text{ mol} \cdot \text{L}^{-1}$, including NH_4Cl , NH_4Br , NH_4I , KCl , KBr and KI . The liquid–solid ratios of $4 \text{ mL} \cdot \text{g}^{-1}$ and $20 \text{ mL} \cdot \text{g}^{-1}$ were adopted to obtain the molar loading of halides in the range of 0.2 – $1.0 \text{ mol} \cdot \text{g}^{-1}$ of bio-chars. Various mixtures were stirred for 12 h and then dried at a water bath at $80 \text{ }^\circ\text{C}$. The mixtures were further dried at an oven for 12 h at $105 \text{ }^\circ\text{C}$. In order to contrast with the bio-char, the molecular sieve (MCM-22) was also impregnated with NH_4Cl , NH_4Br and NH_4I . The impregnation and drying method was same as above. Different additives modified sorbents were introduced with following abbreviation: X6WYZH. The X represents the species of carriers (X: C for bio-char and M for MCM-22). The Y represents the species of positive ion (Y: K for K^+ and N for NH_4^+). The Z represents the species of halides (Z: Cl, Br and I) and H represents the molar loading (0.2 and $1.0 \text{ mol} \cdot \text{g}^{-1}$) of halides (H: 0.2 and 1). Therefore, the derived bio-chars modified various additives were denoted as C6WNCI0.2, C6WNCI1, C6WNBRO.2, C6WNBRI, C6WNI0.2, C6WNI1, C6WKCI0.2, C6WKCI1, C6WKBR0.2, C6WKBR1, C6WKIO.2, C6WKI1, M6NCI0.2, M6NBRO.2 and M6NIO.2, respectively. The detailed information of various sorbents was listed in Table S1.

2.2. Characterization techniques

The proximate analysis of cotton straw was measured according to the method of Chinese National standards (GB/212-2008). Elemental EA3000 (LEEMAN, China) was used to measure the ultimate analysis of cotton straw. The specific surface area (S_{BET}), micropore ($2 < \text{nm}$) surface area (S_{BETmicro}), mesopore (2 – 50 nm) surface area (S_{BETmeso}), pore volume (V_{total}), micropore volume (V_{micro}) and mesopore volume (V_{meso}) were determined by N_2 adsorption at $-196 \text{ }^\circ\text{C}$ on a ASAP 2020 automated gas adsorption system (Micromeritics, USA). The N_2 isotherms were employed to calculate the S_{BET} according to the Brunauer–Emmett–Teller (BET) model at a relative pressure ranging from 0.05 to 0.35, and the V_{total} at a relative pressure of 0.98. The S_{BETmicro} and V_{micro} were estimated on the basis of t-plot method [15]. The D was based on the differential pore volumes of Barrett–Joyner–Halenda (BJH) desorption branch. The Scanning electron microscope SSX-550 (SHIMADZU CO. Ltd, Japan) was used to analyze the surface morphology of bio-chars. The element (Cl, Br, I and Hg) valence state was analyzed by X-ray photoelectron spectroscopy (XPS) by Axis Ultra DLD (Kratos Analytical Ltd, Britain) with Mg X-ray source. All binding energies were calibrated with the C 1s peak at 284.6 eV .

2.3. Mercury adsorption testing

The scheme of the mercury adsorption testing used to evaluate the performance of various sorbents for mercury adsorption was shown in Fig. S2. The testing devices contain an elemental mercury generator, a fixed-bed reactor, temperature-controlled heating equipment, an online mercury analyzer and a flue gas cleaner. An

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