Mechanism identification of temperature influence on mercury adsorption capacity of different halides modified bio-chars

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Abstract

Bio-chars as mercury sorbent were derived from cotton straw via pyrolysis carbonization, microwave/steam activation and ammonium halides impregnation. Mercury adsorption capacity of various impregnated bio-chars was tested at different temperatures. Rising temperature improved the adsorption capacity of bio-chars modified with NH_4Br and NH_4I yet inhibited that of bio-char modified with NH_4Cl . Kinetic model analysis indicated that the changes of mercury adsorption capacity were related to the difference of enthalpy change for various bio-chars. In temperature programmed desorption technic (TPDT) analysis, high desorption energy ($80.9\text{--}82.1 \text{ kJ}\cdot\text{mol}^{-1}$) proved that mercury adsorption mainly depended on chemisorption for halide modified bio-chars. Modification effect of ammonium halides on mercury adsorption capacity followed the order: $\text{NH}_4\text{I} (7643.1 \text{ }\mu\text{g}\cdot\text{g}^{-1}) > \text{NH}_4\text{Br} (842.0 \text{ }\mu\text{g}\cdot\text{g}^{-1}) > \text{NH}_4\text{Cl} (365.3 \text{ }\mu\text{g}\cdot\text{g}^{-1})$. X-ray photoelectron spectroscopy (XPS) analysis proved that C-X groups served as mercury adsorption sites and determined the mercury removal capacity of bio-chars. This study explained the mechanism of temperature effects and halides modification as well as proposed useful suggestion on mercury sorbent preparation and application.

Keyword: bio-char; mercury adsorption; kinetic model; desorption energy

1. Introduction

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The fossil fuel combustion is an important anthropogenic source for mercury emission [1]. The mercury from combustion flue gas exists in three forms: particle-bound mercury (Hg^{P}), oxidized mercury (Hg^{2+}) and elemental mercury (Hg^0). Hg^{2+} and Hg^{P} can be captured by synergic Hg removal techniques, such as flue gas desulfurization (FGD) system and dust collectors [2, 3]. Conversely, elemental mercury is very difficult to be removed because of its high vapor pressure and low water solubility [4]. Therefore, people pay much attention to the emission of Hg^0 due to its volatility, high toxicity, bioaccumulation in the environment [5]. The technology of activated carbon (AC) injection has been commercially applied to reducing Hg^0 emissions from coal combustion system. However, the high cost for AC injection is the main obstacle to prevent its further popular application [6, 7]. Consequently, various low-cost carbonaceous sorbent materials as AC alternatives were extensively studied, such as mulberry twig [8], bamboo [9], coconut shells [10] and coke [11].

Original pyrolysis products performed a poor mercury adsorption capacity and hence various physical and chemical modification methods were used to improve their adsorption property. The halides were usually selected and considered as effective modification reagent in previous studies [8, 12-14]. Various halides modified AC and bio-chars have widely used in the coal-fired power plants. The sorbent injection point usually contains two positions: before electrostatic precipitation (ESP) and after ESP (TOXECON Technology). The sorbent injection position is often placed between Selective Catalytic Reduction (SCR) and ESP equipment. The flue gas temperature from injection point to ESP outlet is in the range of 200-130 °C. TOXECON Technology added a fabric filter (FF) after ESP, which can effectively separate carbon-based sorbents from ash and reduce sorbent negative influence on ash recycling. The flue gas temperature further decreases with the flue gas flow. For TOXECON Technology, the flue gas temperature from AC injection point to FF outlet is in the range of 110-80 °C. Therefore, the flue gas temperature of sorbent injection point shows obvious difference between two technologies, which possibly plays an important role on mercury adsorption capacity of carbon-based sorbents [15]. However, few studies had comprehensively considered and researched the influence of flue gas

temperature on halides modified sorbents in practical application. Moreover, the adsorption mechanism of testing temperature influence on halides modified bio-chars was still inconsistent and ambiguous. It is known that the increase of temperature improves chemisorption yet inhabits physisorption since high temperature helps to reach chemisorption reaction energy and low temperature makes for mercury condensation. This was proved in Cai's and De's studies, that is, high temperature (180-195 °C) improved the mercury adsorption performance of halides modified sorbents [12, 13]. However, some studies suggested that rising the temperature in the range of 80-160 °C could decrease the mercury adsorption efficiency and adsorption capacity of chloride modified bio-char [14], which confirms to physisorption property. Thereby, whether physisorption or chemisorption determines the adsorption performance of halide modified bio-chars at various reaction temperatures is still unclear and needs to be explored.

In this study, the cotton straw and ammonium halides were selected as the raw material and modified reagents, respectively, since the cotton straw and ammonium halides were proven to be an optimal selection from three raw materials (municipal solid wastes, industrial wastes, and cotton straw) and three modified reagents (NH_4Cl , HCl , and ZnCl_2) in our previous studies [16, 17]. The effect of different halides modification, loading and testing temperature was further investigated on the mercury capture experiment. The proximate and ultimate analyses, pore analysis, SEM, TPDT and XPS characterization were conducted to analyze the property and adsorption mechanism of bio-chars. Kinetic model and thermodynamic parameters were calculated to further investigate the reaction mechanism of halides modified bio-chars under various testing temperatures.

2. Materials and Methods

2.1. Sample preparation

After natural drying, the raw materials (cotton straw) was shredded and crushed to a size of 8.0-10.0 mm. The cotton straw chipping was placed in 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 reactor was steadily heated to desired pyrolysis temperature of 600 °C at 20

$^{\circ}\text{C}\cdot\text{min}^{-1}$ and remained for 60 min. Then, the pyrolysis reactor was cooled to room temperature under the oxygen-free environment. The derived bio-char was denoted as C6.

The microwave and steam activation can remove the ash and improve the pore structure of bio-char. The pore development is beneficial to mercury physisorption and offering adsorption sites for modification reagents [16]. The above-mentioned bio-char (2.0 g) was placed in a quartz bottle reactor (50 cm^3) under oxygen-free atmosphere with a constant flow of N_2 ($80\text{ mL}\cdot\text{min}^{-1}$). Deionized water was injected into the bottle reactor to generate steam under the control of the peristaltic pump. The whole bottle reactor was placed in a microwave oven (power: 950 W). The bio-char C6 was activated by the microwave and steam for 4 h. The derived bio-char was denoted as C6W.

The bio-char C6W was impregnated with various additives solutions of uniform concentration of $0.05\text{ mol}\cdot\text{L}^{-1}$, including NH_4Cl , NH_4Br and NH_4I . Two liquid-solid ratios ($4\text{ mL}\cdot\text{g}^{-1}$ 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 mol% of bio-chars. Various liquid-solid 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 $105\text{ }^{\circ}\text{C}$. The following abbreviation was used to introduce different additives modified bio-chars: C6WNXY. The X represents the species of ammonium halides (X: Cl, Br and I) and Y represents the molar loading (0.2 and 1.0 mol%) of halides (Y: 0.2 and 1). Therefore, the derived bio-chars modified various additives were denoted as C6WNCI0.2, C6WNCI1, C6WNBBr0.2, C6WNBBr1, C6WNI0.2 and C6WNI1, respectively.

2.2. Characterization techniques

The proximate analysis of cotton straw was measured according to the method of Chinese National standards (GB/T 212-2008). Elementar EA3000 (LEEMAN, China) was used to measure the ultimate analysis of cotton straw. Specific surface area (S_{BET}), micropore specific surface area (S_{BETmicro}), the ratio of S_{BETmicro} to S_{BET} (S%), pore volume (V_{total}), micropore volume (V_{micro}), the ratio of V_{micro} to V_{total} (V%) and pore diameters (D), were measured by N_2 adsorption at $-196\text{ }^{\circ}\text{C}$ on a ASAP 2020

automated gas adsorption system (Micromeritics, USA). The surface morphology of bio-chars was analyzed by the Scanning electron microscope SSX-550 (SHIMADZU CO. Ltd, Japan). The element (Cl, Br, I and Hg) valence state on the surface of bio-chars was analyzed by X-ray photoelectron spectroscopy (XPS) using Axis Ultra DLD (Kratos Analytical Ltd, Britain) with Mg X-ray source. All binding energies were calibrated by the C 1s peak at 284.6 eV. The temperature programmed desorption technic (TPDT) was used to analyze the desorption energy of mercury adsorbed on various bio-char. The TPDT schematic and operation detail was shown in Fig. S1.

2.3. Mercury adsorption testing

The setup of the mercury adsorption testing used to evaluate the mercury adsorption performance of various bio-chars 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 gas flue cleaner. The mercury vapor was generated from Hg^0 permeation tube when an N_2 flow, serving as carrier gas, passed through the permeation tube within a U-type glass tube. The U-type glass tube was placed in a temperature-controlled thermostat water bath to remain Hg^0 concentration at $29.0 \pm 1 \mu\text{g}\cdot\text{m}^{-3}$. In order to avoid the oxidation influence of acid and oxidizing gases, only the N_2 served as the balance gas to keep the total inlet gas flow at $850 \text{ mL}\cdot\text{min}^{-1}$. The quartz fixed bed was heated by electricity controlled at 60, 120 and 180°C . 5.0 mg char was mixed with 0.5 mL silica sand and then placed the mixture in the adsorption zone of reactor. The space velocity was $100,000 \text{ h}^{-1}$, which is similar to those used in industries. The whole gas line was kept warm to avoid Hg^0 condensation. The elemental mercury concentration at the inlet and outlet of the reactor was online measured by the H11-QM201H cold vapor atomic analyzer (Jiangsu, China). The mercury adsorption testing was stopped until the bio-chars reached the adsorption equilibrium or the testing time reached 1600 min.

The efficiency (η) of the sorbent was calculated according to Eq. (1).

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

where, η is Hg^0 removal efficiency, which is the average of two parallel experimental data and the relative error of all parallel experimental data is less than 8%. C_{in} and C_{out} ($\mu\text{g}\cdot\text{Nm}^{-3}$) are Hg^0 concentrations at the inlet and outlet of the fixed-bed reactor, respectively.

The activity of the sorbent was determined by Hg^0 adsorptive capacity q_t ($\mu\text{g}\cdot\text{g}^{-1}$) according to Eq. (2).

$$q_t = \frac{F \times C_{in} \times \int_0^t \eta dt}{W} \quad \text{Eq. (2)}$$

where, F is the gas flow rate ($\text{Nm}^3\cdot\text{min}^{-1}$), W is the mass of sorbent (g) and t is the adsorption time.

3. Results and Discussion

3.1 Sample characterization

3.1.1 Proximate and ultimate analysis

The result of proximate and ultimate analysis for cotton straw was shown in Table 1. According to the proximate analysis, the content of moisture was only 0.2%, which was possibly attributed to prior natural drying. The ash content of cotton straw was also relatively low while the volatile and fixed carbon (FC) was relatively high, compared with other materials, such as coal [18]. Our previous study has proved that low ash and high volatile content are beneficial to the development of pore structure of the char during pyrolysis process [16]. As shown in ultimate analysis, the H and N content were very small, but the content of C and O element was relatively high in cotton straw. The high C and O content contributed to the growth of oxygen-containing functional groups, which made for Hg^0 adsorption [19].

3.1.2 Pore analysis

As shown in Table 2, the microwave activation and chemical impregnation played an important role on the pore parameter of bio-chars. The original bio-char C6 presented a good performance in the pore structure, indicating that good property of cotton straw facilitated the development of pore structure during pyrolysis as shown

in Table 1. Furthermore, the microwave and steam activation further improved the pore property. The ash removal by microwave action increased the pore volume and specific surface area of bio-chars [20, 21]. On the contrary, the loading of ammonium halides inhabited pore property of bio-chars. The NH_4I and NH_4Cl loading decreased the specific surface area in the range of $65.5\text{-}294.9\text{ m}^2\cdot\text{g}^{-1}$ and $29.4\text{-}269.1\text{ m}^2\cdot\text{g}^{-1}$, respectively.” Similarly, the increase of NH_4Br impregnation decreased the specific surface area in the range of $4.2\text{-}234.9\text{ m}^2\cdot\text{g}^{-1}$. The similar phenomenon was also seen in the micropore area, pore volume and micro volume. In addition, after the halide modification, the ratio (S%) of S_{BETmicro} to S_{BET} and the ratio (V%) of V_{micro} to V_{total} obviously declined and the diameter evidently rose compared with that of the bio-char C6W. It indicated that ammonium halides impregnation possibly concentrated on the micropore region, resulting in increasing the pore diameters and declining the S% and V%.

In order to further analyze the influence of ammonium halides on the pore structure, the pore distribution of C6, C6W, C6WNI0.2 and C6WNI1 was shown in Fig. 1. To reduce the influence of the fictitious bottle in the desorption branch caused by the tensile strength effect (TSE) of mesopores, the pore distribution was calculated on the basis of the adsorption branch [22]. The inset of pore distribution in the range of $0\text{-}0.003\text{ cm}^3\cdot\text{g}^{-1}$ was inserted into Fig. 1 to further exhibit the pore character in mesopore and macropore. As shown in the inset of Fig. 1, the pores of C6 were well-balanced and distributed in the micropore, mesopore and macropore regions. But after microwave and steam action, the distribution plot of bio-char C6W became steep over the micropore and flat over the mesopore and macropore, indicating the pore volume concentrated on the micropore region. Nevertheless, after the halide impregnation, the curve of C6WNI0.2 showed a relatively mild climb over micropore region and that of C6WNI1 expressed a milder climb over micropore region, indicating that chemical reagent intensively blocked the micropore region of bio-char. This result verified the conclusion that ammonium halides impregnation focused on the reduction of the micropore volume.

3.1.3 SEM analysis

The SEM images of prior and after NH_4I impregnated bio-chars were shown in Fig. 2(A-C) to further investigate the surface structure of bio-chars. Fig. 2A indicates that the surface of C6W has excellent pore structure after the microwave activation. In contrast, there were particulate matters aggregating on the surface of C6WNI0.2 and partially blocking pore structure, as shown in Fig. 2B. When the loading further increased, a layer of dense NH_4I reagent absolutely covered all pore structure on the surface of bio-chars in Fig. 2C. This is supported by the EDS analysis in Fig. S3 and Table S1. The result of SEM analysis confirms to the conclusion in pore analysis that the increase of impregnation loading could block the pore structure and reduce the pore volume.

3.2 Mercury adsorption testing

3.2.1 Effect of halides modification on Hg^0 adsorption

To compare modification effect of bio-chars impregnated by three ammonium halides, their mercury adsorption performance was shown in Fig. 3. In general, the adsorption capacity for three modified bio-chars all enhanced obviously compared to 7.5 and 30.0 $\mu\text{g}\cdot\text{g}^{-1}$ for C6 and C6W [16], suggesting that chemical modification greatly improved the mercury adsorption capacity of bio-chars. The equilibrium adsorption capacity of C6WNCI0.2 reached 365.3 $\mu\text{g}\cdot\text{g}^{-1}$ and that of C6WNBBr0.2 reached 842.0 $\mu\text{g}\cdot\text{g}^{-1}$. Moreover, the bio-char C6WNI0.2 did not reached adsorption equilibrium and its mercury adsorption efficiency surpassed 90% at whole adsorption testing (1600 min). The adsorption capacity of C6WNI0.2 reached 7643.1 $\mu\text{g}\cdot\text{g}^{-1}$ at the end of adsorption testing. The bio-char C6WNI0.2 with a poor pore structure showed a better adsorption capacity than the C6WNCI0.2 and C6WNBBr0.2. The pore structure seems not a key factor affecting the mercury adsorption of halides modified bio-char. Moreover, these testing results indicated that mercury adsorption capacity of bio-chars mainly depended on modification halide species. Their modified effect followed the order: $\text{NH}_4\text{I} > \text{NH}_4\text{Br} > \text{NH}_4\text{Cl}$. Previous study suggested that excellent performance of iodide-modification was attributed to its bigger atomic radius

resulting in higher surface exposure to mercury, which increased the reaction probability of Hg atom and Γ ion [13]. However, the difference value of ion radius between Cl^- (1.81 Å), Br^- (1.96 Å) and I^- (2.20 Å) was only 0.39 and 0.24 Å, respectively, which might not have much influence on their adsorption capacity. As a result, the mercury adsorption mechanism was necessary to further discussed at other aspects.

3.2.2 Effect of the loading on Hg^0 adsorption

In order to further investigate the effect of different loading on the adsorption performance, the adsorption capacity of bio-chars modified by three ammonium halides was shown in Fig. 4. As shown in Fig. 4, the loading increase of three ammonium halides all evidently improved mercury adsorption capacity of bio-chars. The bio-chars C6WNC11 and C6WNB1 possessed greater equilibrium adsorption capacity ($1239.2 \mu\text{g}\cdot\text{g}^{-1}$ and $2781.9 \mu\text{g}\cdot\text{g}^{-1}$, respectively) than the C6WNC10.2 and C6WNB0.2. The mercury adsorption capacity of C6WNI0.2 and C6WNI1 were not significantly different since their mercury adsorption efficiency was similar at the whole testing procedure. It should be noted that rising loading decreased the pore property but increased the mercury adsorption capacity. These results suggested that the loading increase possibly could offer more chemical sites for elemental mercury adsorption.

3.2.3 Effect of testing temperature on Hg^0 adsorption

Fig. 5 showed different effect of testing temperature on Hg^0 adsorption capacity of bio-chars modified by various halides. In Fig. 5B and Fig. 5C, the mercury adsorption performance of C6WNB0.2 and C6WNI0.2 was similar and obviously went up from 60 °C to 180 °C. In the range of 60-180 °C, the adsorption capacity increased from $631.7 \mu\text{g}\cdot\text{g}^{-1}$ to $3089.4 \mu\text{g}\cdot\text{g}^{-1}$ for C6WNB0.2 and from $5337.6 \mu\text{g}\cdot\text{g}^{-1}$ to $7752.0 \mu\text{g}\cdot\text{g}^{-1}$ for C6WNI0.2. This result was consistent with common theory that rising temperature in the range of 20-180 °C was beneficial to the chemisorption of mercury since high temperature easily met the reaction energy of chemisorption [9, 14]. On the contrary,

the mercury adsorption capacity of C6WNC10.2, as shown in Fig. 5A, decreased from 1118.9 $\mu\text{g}\cdot\text{g}^{-1}$ to 335.2 $\mu\text{g}\cdot\text{g}^{-1}$ at the range of 60-180 °C. It was opposite to above theory that the temperature rising promoted chemisorption reaction. According to above testing results, the halide modified bio-chars seemed to adsorb elemental mercury on the basis of different adsorption mechanism. In order to further investigate and verify the adsorption mechanism, the kinetic models were used to further analyze.

3.3 Kinetic model analysis

Diversified kinetic models, such as pseudo-first order model, intra-particle diffusion equation, pseudo-second order model and Elovich kinetic equation, had been used to explore and determine the mechanism of the mercury adsorption process [23, 24]. The pseudo-first order model and intra-particle diffusion model concentrated on the mechanism study of mass transfer and inter diffusion process, respectively [23]. The pseudo-second order and Elovich models investigated the process of surface reaction and catalytic reaction. Therefore, the Hg^0 mass transfer process from gas phase to adsorption sites was more likely to match with the pseudo-first order model while the chemisorption for Hg^0 was in accord with pseudo-second order model [23-25]. Considering the purpose of this study to distinguish and ascertain the main adsorption mechanism of modified bio-chars, the pseudo-first and pseudo-second order models were used to simulate the mercury adsorption process and determine the adsorption mechanism.

The pseudo-first order equation can be described by Eq. (3) [23].

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303} t \quad \text{Eq. (3)}$$

where, q_t and q_e represent the amount of adsorbate ($\mu\text{g}\cdot\text{g}^{-1}$) at time t and at equilibrium time, respectively, and k_1 represents the rate constant of first order equation (min^{-1}).

The kinetic rate equation for the pseudo-second order was expressed by Eq. (4).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{Eq. (4)}$$

where, q_t and q_e have the same meaning as those in Eq.(3), and k_2 represents the adsorption reaction rate constant ($\text{g} \cdot \mu\text{g}^{-1} \cdot \text{min}^{-1}$).

The experimental data of three bio-chars in different temperature was fitted with the pseudo-first and pseudo-second order models. The result was shown in Fig. 6 and specific fitting correlation coefficient (R^2) was listed in Table 3.

As shown in Fig. 6, three bio-char modified by various halides had much difference in the fitting result of pseudo-first and pseudo-second order models. In Table 3, for three modified bio-chars, the correlation coefficient of pseudo-second was all over 0.96. Moreover, combining Table 3 with Fig. 6, it was noteworthy that when the correlation coefficient of pseudo-second rose, mercury adsorption capacity for all bio-chars increased accordingly. These results illustrated that the mercury adsorption capacity of bio-chars possibly depended on the chemisorption. However, the temperature rising had different influence on the fitting result and adsorption capacity. The high temperature improved fitting correlation coefficient of pseudo-second for C6WNB0.2 and C6WNI0.2 yet decreased that for C6WNCI0.2. In addition, the temperature change also played different role on the fitting correlation coefficient of pseudo-first order model. The high temperature lowered the R^2 of pseudo-first order model of C6WNB0.2 and C6WNI0.2 since the temperature rising inhabited the physisorption occurrence. However, for C6WNCI0.2, the fitting correlation coefficient of pseudo-first order model reached lowest point (0.63) at 60 °C. These results implied that the chemisorption mechanism for the temperature change was different between C6WNB0.2, C6WNI0.2 and C6WNCI0.2. According to previous study, the thermodynamic property possibly affected the adsorption reaction [14, 26]. In order to further investigate the adsorption mechanism of different bio-chars, the enthalpy change (ΔH°) was calculated to reflect the effect of temperature change.

The enthalpy change (ΔH°) could be obtained using the data from pseudo-second order model according to Eq. (5).

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \text{Eq. (5)}$$

where K_D represents the distribution coefficient of sorbent, which is equal to $q_e \cdot C_e^{-1}$; C_e represents the initial concentration of elemental mercury; ΔS° represents standard entropy ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$); ΔH° represents standard enthalpy ($\text{kJ} \cdot \text{mol}^{-1}$); R represents the gas constant which is equal to $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; T (K) represents the operated temperature. According to the Eq. (5), the fitting result of different bio-chars was shown in Fig. S4 and Table 4.

As shown in Fig. S4, the data of three bio-chars all expressed good linear relation. According to Fig. S4, the Enthalpy change (ΔH°) was calculated and listed in Table 4. The positive ΔH° represented endothermic nature of chemical reaction, indicating that rising temperature promoted the occurrence of chemisorption. The ΔH° of C6WNB0.2 and C6WNI0.2 was 16.5 and 40.5 $\text{kJ} \cdot \text{mol}^{-1}$, respectively. Therefore, rising testing temperature increased the chemisorption and adsorption capacity of C6WNB0.2 and C6WNI0.2. On the contrary, the negative ΔH° stood for exothermic nature of chemisorption, suggested that rising temperature inhabited the chemisorption occurrence and decreased the chemical adsorption. The ΔH° of C6WNCI0.2 was $-16.2 \text{ kJ} \cdot \text{mol}^{-1}$, and hence it showed higher chemisorption character at low temperature. Though the temperature decreasing facilitated both physisorption and chemisorption for C6WNCI0.2, the facilitation for chemisorption was possibly more than for physisorption. Therefore, the C6WNCI0.2 showed high R^2 for pseudo-second order model and low R^2 for pseudo-first order model at low temperature.

Various halides modified AC and bio-chars have widely used in the coal-fired power plants. As discussed in introduction, the injection point usually contains two positions: before ESP and after ESP (TOXECON Technology). The process flow diagram of two AC injection technologies was shown in Fig. S5. The flue gas temperature from AC injection point to ESP outlet is in the range of 200-130 °C. For TOXECON Technology, the flue gas temperature from AC injection point to FF outlet is in the range of 110-80 °C. According to Fig 5, the temperature change has opposite influence on different halides modified bio-chars. The Br and I modified bio-chars are

more geared to inject before ESP because high temperature (200-130 °C) can promote their mercury adsorption capacity. In contrast, the Cl modified bio-char is more suitable for TOXECON Technology. The relatively low temperature makes Cl modified bio-char adsorb more mercury. However, the Cl modified sorbent is often injected into before ESP in practice. These cases possibly cause resource and economic waste. As shown in Fig. 5A, the mercury adsorption capacity of C6WNCI0.2 is only 335.2 $\mu\text{g}\cdot\text{g}^{-1}$ at 180 °C but 1118.9 $\mu\text{g}\cdot\text{g}^{-1}$ at 60 °C. The former value is only 30% of the latter one. The similar result is also seen in Br and I modified bio-chars. In Fig. 5B, the mercury adsorption capacity of C6WNBr0.2 is only 631.7 $\mu\text{g}\cdot\text{g}^{-1}$ at 60 °C yet 3089.4 $\mu\text{g}\cdot\text{g}^{-1}$ at 180 °C. The former value is only 20% of the latter one. This result indicates that improper application condition could result in invalidation of 70-80% adsorption capacity of sorbents. On the contrary, the correct AC injection position possibly reduces over half sorbent application. Andrew's study indicated that the cost of mercury control ranged from 3810-166000 dollars per pound of mercury removed [7]. Therefore, the correct injection way will save huge costs of mercury pollution control. As for this point, this research result has an important guidance significance for the application of halide modified sorbent in the future.

3.4 The TPDT study

According to above testing and modeling analyses, the mercury capture of halide modified bio-chars mainly depended on chemisorption. The temperature program desorption technic (TPDT) is widely used to analyze adsorption state of adsorbate since desorption process is related to the adsorption energy. Chemical adsorption is controlled by strong chemical bonds formed between the adsorbate and chemisorption sites. Thereby, the breaking of chemical bonds usually require more energy under high desorption temperature. On the contrary, the desorption of physisorbed mercury needs relatively lower temperature because bonds are weak for physical adsorption based on van der Waals' force. In this study, the TPDT result was used to judge adsorption mechanism via analyzing desorption energy of mercury on various bio-chars after adsorption experiment. The energy of mercury desorption from

bio-chars was calculated via desorption rate ($-d\theta/dT$), which is described as follows [27, 28]:

$$-\frac{d\theta}{dT} = \frac{\nu}{\beta} \theta^n \exp\left(-\frac{E_d(1-\alpha\theta)}{RT}\right) \quad \text{Eq. (6)}$$

Where ν is the pre-exponential factor; θ is the adsorbate coverage at temperature T ; β is the heating rate (dT/dt); n is the order of desorption process; E_d is the desorption energy; and α is the intermolecular parameter, negative value of α represents attractive intermolecular interactions and positive one represents repulsive intermolecular interactions. The desorption experiment data of various bio-chars was fitted with Eq. (6) via Matlab software. This fitting procedure used ν , E_d and α as free parameters that were allowed to vary to optimize fitting result. All desorption experiments was consider as one order of desorption process ($n=1$). The fitting result reflected that the ν was in the range of $10^{8.8} \sim 10^{9.2}$ and α in the range of 0.018~0.021. The calculated desorption energy of various bio-chars was shown in Table 5.

As shown in Fig. 7, the TPD spectra of different bio-chars distributed over a wide temperature range, indicating the mercury adsorbed on bio-chars involved different types of adsorption sites. In case of C6W, two characteristic peak of mercury desorption appeared at temperature around 205 °C and 287 °C in Fig. 7A. The Hg^0 desorbed at two temperatures, indicating that it seems to exist two different adsorption states at least. However, the bio-chars of C6WNCI0.2, C6WNBBr0.2 and C6WNI0.2 showed only one peak at 377, 360 and 353 °C, respectively. The calculated desorption energy of C6W, C6WNCI0.2, C6WNBBr0.2 and C6WNI0.2 was listed in Table 5. The desorption energy calculated from first peak of C6W was $32.5 \text{ kJ}\cdot\text{mol}^{-1}$, indicating that it was related with weakly adsorbed or physisorbed mercury. The desorption energy of second desorption peak at 287 °C was $60.2 \text{ kJ}\cdot\text{mol}^{-1}$. This implied a stronger adsorbed mercury compound, which was possibly caused by oxygen-containing functional groups. The area of first peak was bigger than second peak. This result suggested that physical adsorption was more important than functional group adsorption for C6W. The desorption energy of C6WNCI0.2, C6WNBBr0.2 and

C6WNI0.2 was 82.1, 81.7 and 80.9 kJ·mol⁻¹, respectively, which was higher than C6W. This result implied that ammonia halide modified bio-chars captured mercury via chemisorption. Therefore, halide modification changed mercury capture pattern from physisorption to chemisorption. Combining with mercury adsorption capacity of modified bio-chars and C6W, it inferred that the chemisorption was more important than physisorption for mercury removal.

3.5 XPS analysis and chemisorption mechanism exploration

To explore chemical reaction mechanism of mercury adsorption, the XPS was applied to investigating the valence state change of Cl, Br, I and Hg on the bio-chars. The analysis result was shown in Fig. 8. In Fig. 8A, two peaks appeared on the XPS spectrum of fresh and used C6WNCI0.2 at Cl 2p, which belonged to the ionic Cl⁻ (198.2 eV) and C-Cl groups (200.0 eV), respectively [29]. In Fig. 8B, there were also two peaks appearing at the 68.2 eV (Br⁻) and 70.9 eV (C-Br) on the surface of fresh and used C6WNB0.2 [30-32]. The spectrum of fresh and used C6WNI0.2 had four peaks in Fig. 8C. The peaks at 620.9 eV and 532.6 eV both stood for the C-I groups and the peaks at 619.4 eV and 630.8 eV belonged to the ionic I⁻ groups [32]. As shown in Fig. 8D, there was no obvious peak at Hg 4f on the spectrum of fresh C6WNI0.2. However, after mercury adsorption testing, two peaks representing Hg²⁺ centered at 100.6 eV and 104.6 eV, indicating that the adsorbed mercury existed in the form of oxidation on the bio-chars [30, 33]. The similar result is found in bio-chars C6WNB0.2 and C6WNCI0.2 in Fig. S6. The peak area ratio of different valence state halides was listed on the Table 6 to further investigate the mercury adsorption mechanism.

As shown in Table 6, via contrasting three bio-chars prior to and after the adsorption testing, three halide modified bio-chars got a uniform principle: covalent halides group ratio all decreased and ionic group ratio ascended after adsorption testing. This indicated that some covalent halides groups translated into the ionic groups during the adsorption process. Combining the existence form of oxidation state mercury, it could be proved that the covalent halide groups oxidized elemental

mercury into mercuric halides, such as HgCl_2 , HgBr_2 and HgI_2 . Therefore, the covalent halide groups were considered to be chemical adsorption sites of elemental mercury. In term of this point, the higher ratio of covalent halide groups possibly represented the more mercury adsorption sites and better adsorption capacity. Thereby, according to Table 6, the mercury adsorption performance of three modified bio-chars followed the order: $\text{C6WNI0.2} > \text{C6WNB0.2} > \text{C6WNCI0.2}$.

The amount of C-X groups determine the mercury removal performance of various modified bio-chars. The reason for different covalent halide group ratio of three bio-chars was possibly attributed to two aspects. On one hand, the halide ions expressed different reducibility ($\text{I}^- > \text{Br}^- > \text{Cl}^-$). The halide ion with higher reducibility was easier to donate electron and form covalent bonds with carbon atom. Hence, on the basis of the reducibility of halide ions, covalent group ratio should follow the order: $\text{I}^- > \text{Br}^- > \text{Cl}^-$. On the other hand, the halide ion with bigger size possibly provided more chance to react with carbon atom and form covalent bonds. In term of this point, the covalent group ratio of halides modified bio-chars should also follow above order: $\text{I}^- > \text{Br}^- > \text{Cl}^-$. Moreover, according to Table 6, the result of halide covalent group ratio ($\text{C6WNI0.2} > \text{C6WNB0.2} > \text{C6WNCI0.2}$) supported above two inference.

This discovery possibly explained different adsorption performance of halides modified bio-chars from chemical property aspect. According to above analysis and previous studies, the mechanism of halide modified bio-chars could be described as follow: (1) the halide ions reacted with carbon atom to form the halide covalent bonds; (2) the elemental mercury transferred from gas phase to the surface of bio-chars; (3) the halide covalent groups oxidized elemental mercury into mercury halides. The mechanism of halide modified bio-chars could be described as follow (X represents the Cl, Br, and I) [14, 34]:

This result indicates that the effective groups are the key factor deciding the mercury adsorption capacity of halide modified bio-chars. The preparation process of mercury sorbent should focus on improving the formation of C-X groups. Therefore, the carbon-based carrier materials are better option for mercury adsorption sorbents [35].

4. Conclusion

This study investigated the mercury adsorption capacity of bio-chars modified with ammonium halides and judged the relative importance of physisorption and chemisorption. According to the kinetic modeling, the difference of enthalpy change determined that high testing temperature improved adsorption capacity of C6WNI0.2 and C6WNB0.2 yet lowered that of C6WNCI0.2. Halides modification increased desorption energy of adsorbed halide mercury from 32.5 to 80.9-82.1 kJ·mol⁻¹ since adsorption mechanism changed from physisorption to chemisorption. The amount difference of C-X groups serving as chemisorption sites decided halide modification effect order, which is NH₄I > NH₄Br > NH₄Cl. This study offers a guidance for application and preparation of mercury sorbents. This study indicates that proper application condition could increase 70-80% adsorption capacity of sorbents and hence correct injection position possibly reduces over half sorbent application.

Acknowledgements

This work was sponsored by the Major State Basic Research Development Program of China (973 Program) (No. 2013CB430000) and National Science Foundation of China (21521064). We are grateful to the great help offered by professor Boxiong Shen.

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Fig. 1 Pore distribution of bio-chars (Inset: pore distribution in mesopore and macropore)

Fig. 2 SEM images of bio-chars, A: C6W; B: C6WNI0.2; C: C6WNI1

Fig. 3 Effect of three halides on Hg^0 adsorption at 120 °C

Fig. 4 Effect of loading on Hg^0 adsorption at 120 °C

A: NH_4Cl ; B: NH_4Br ; C: NH_4I

Fig. 5 Effect of testing temperature on Hg^0 adsorption

A: C6WNCI0.2; B: C6WNBBr0.2; C: C6WNI0.2

Fig. 6 Kinetic analysis of bio-chars by pseudo-first order model and pseudo-second order model

A: C6WNCI0.2; B: C6WNBBr0.2; C: C6WNI0.2

Fig. 7 The TPD experimental data and fitting analysis of various bio-chars, (A) C6W; (B) C6WNCI0.2; (C) C6WNB0.2; (D) C6WNI0.2

Fig. 8 XPS analysis of bio-chars

Table 1 Proximate and ultimate analysis of raw materials

Sample	Proximate analysis (wt. %)				Ultimate analysis (wt.%)			
	Moisture	Volatile	Ash	FC	C	H	O	N
Cotton straw	0.2	63.0	8.3	28.5	43.6	5.8	49.8	0.8

Table 2 Pore structural parameters of samples

Sample	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	S_{BETmicro} ($\text{m}^2 \cdot \text{g}^{-1}$)	S% (%)	V_{total} ($\text{cm}^3 \cdot \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \cdot \text{g}^{-1}$)	V% (%)	D (Å)
C6	226.4	125.8	55.6%	0.145	0.026	20.8%	39.1
C6W	453.5	294.2	64.9%	0.222	0.136	61.3%	20.0
C6WNI0.2	388.0	194.5	50.1%	0.208	0.088	42.3%	30.8
C6WNI1	158.6	78.3	49.4%	0.084	0.033	39.3%	31.4
C6WNB0.2	449.3	239.9	53.4%	0.221	0.121	54.8%	23.0
C6WNB1	218.6	117.0	53.5%	0.115	0.053	46.1%	27.5
C6WNCI0.2	424.1	224.3	52.9%	0.210	0.095	45.2%	24.1
C6WNCI1	184.4	94.3	51.1%	0.099	0.041	41.4%	29.4

Table 3 Fitting correlation coefficient of pseudo-first and pseudo-second order model

Sample	Pseudo-first order (R^2)			Pseudo-second order (R^2)		
	60 °C	120 °C	180 °C	60 °C	120 °C	180 °C
C6WNCI0.2	0.63	0.94	0.93	0.99	0.97	0.96
C6WNBBr0.2	0.93	0.89	0.88	0.96	0.97	0.98
C6WNI0.2	0.90	0.88	0.85	0.96	0.99	1.00

Table 4 Enthalpy change (ΔH°) of mercury adsorption reaction for three bio-chars

Sample	C6WNCI0.2	C6WNBBr0.2	C6WNI0.2
ΔH° (kJ·mol ⁻¹)	-16.2	16.5	40.5

Table 5 The calculated desorption energy

Sample	Desorption temperature (°C)	Desorption energy E_d (kJ·mol ⁻¹)
C6W (first peak)	205	32.5
C6W (second peak)	287	60.2
C6WNCI0.2	377	82.1
C6WNB0.2	360	81.7
C6WNI0.2	353	80.9

Table 6 Peak area ratio of different valence state halides

Groups	Position (eV)	C6WNCI0.2		C6WNBBr0.2		C6WNI0.2	
		fresh	used	fresh	used	fresh	used
C-Cl	200.2±0.3	39.1%	23.5%	-	-	-	-
Cl ⁻	198.3±0.3	60.9%	76.5%	-	-	-	-
C-Br	70.6±0.3	-	-	67.1%	37.9%	-	-
Br ⁻	68.4±0.2	-	-	32.9%	62.1%	-	-
C-I	621.0±0.1	-	-	-	-	94.5%	39.5%
I ⁻	619.3±0.1	-	-	-	-	5.5%	60.5%