Role of inherent active constituents on mercury adsorption capacity of chars from four solid wastes

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Abstract

Many raw materials have active constituents for mercury removal, such as the elements oxygen (O), sulfur (S) and chloride (Cl), but these constituents are frequently neglected during the preparation process of mercury adsorbents. This study investigated the effect of various inherent active constituents of four solid wastes (waste tire, cotton straw, Chinese medicinal residue and municipal solid waste) on the mercury removal performance of their derived chars. Modification methods (chemical impregnation and physical activation) were used to clarify modification influence on inherent active constituents and mercury removal performance of chars. Brunauer–Emmett–Teller (BET) analysis, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), temperature programmed decomposition technic (TPDT) and elemental mercury adsorption testing were used to measure and evaluate various chars. The results indicated that only waste tire generated mercury chemisorption sites (sulfide) during pyrolysis process. Sulfide could oxidize Hg^0 into HgS on char T6 derived from tire waste whereas sulfate could not on char derived from Chinese medicinal residue. The evaporation of element Cl during pyrolysis process led to the low adsorption capacity of municipal waste

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derived char. The modification methods impeded T6 mercury removal performance, but they promoted other three chars without chemisorption sites. The results provide meaningful guidance that the nature of raw materials should be taken into account during the preparation of mercury sorbents, and the preparation method should also vary for different raw materials.

Keywords: inherent active constituent; modification; chars; elemental mercury removal

1. Introduction

Mercury pollution has been considered as a serious threat to public health and environment since it can cause brain damage and birth defects in humans and other species [1]. Fossil fuel combustion is a main anthropogenic source of mercury emission [2]. Coal-fire flue gas contains three forms of mercury: particle-bound mercury (Hg^{P}), oxidized mercury (Hg^{2+}) and elemental mercury (Hg^0). The Hg^{2+} and Hg^{P} can be easily cleaned because they can be captured by the flue gas desulfurization (FGD) system and dust control units, respectively [3, 4]. Nevertheless, the Hg^0 is relatively difficult to be removed using either of the above flue gas clean technologies because of its volatility and insolubility. Among the various technologies developed over the years for elemental mercury removal, activated carbon (AC) adsorption is one of the most mature technologies, and it is simple and effective for mercury removal. However, high cost restricts further application of AC adsorption technology.

Char is a promising substitute for activated carbon because its properties are very similar to AC yet it has far lower price. Therefore, many studies have tried to develop a highly effective adsorbent from various biomasses, such as mulberry twig [5], bamboo [6], coconut shells [7] and coke [8]. Moreover, various physical and chemical modification technologies were used to improve the adsorption capacity of these adsorbents. Shu et al. indicated that steam and high temperature activation could increase the surface area of char from $28.64 \text{ m}^2 \cdot \text{g}^{-1}$ to $414.94 \text{ m}^2 \cdot \text{g}^{-1}$, which enhanced its mercury adsorption capacity from $5.07 \mu\text{g} \cdot \text{g}^{-1}$ to $8.76 \mu\text{g} \cdot \text{g}^{-1}$ [5]. The studies of Tan et al. and Hsi et al. proved that the ZnCl_2 and sulfur modification could

add chemical adsorption sites to the surface of chars and improve the mercury adsorption capacity [6, 9]. Li's study suggested that nitric acid oxidation increased the lactone and carbonyl groups on the surface of sorbent, resulting in an increase of mercury adsorption capacity from 40 to 1520 $\mu\text{g}\cdot\text{g}^{-1}$ [10].

Though previous studies adequately researched the physical and chemical modification of chars, few studies focused on the effect of the inherent active constituents of the raw material and char on mercury removal. Waste tire and Chinese medicinal waste have high sulfur (S) content, and municipal solid waste has high chloride (Cl) content [11, 12]. The elements S and Cl elements have a strong affinity for metal mercury, which potentially allows them to transform into active adsorption sites of elemental mercury during pyrolysis process [13-15]. Cotton straw has high oxygen (O) content and low ash content, which is beneficial to the formation of oxygen-containing functional groups and pore structure. Relatively few studies have considered these factors. Furthermore, conventional physical and chemical modification methods likely remove or cover inherent sites. Therefore, the role of inherent active constituents in raw materials and char needs to be investigated in order to optimize modification methods for mercury removal.

In this study, four raw materials, waste tire (WT), cotton straw (CS), Chinese medicinal residue (MR) and municipal solid waste (MW) were pyrolyzed to produce chars. The Hg^0 adsorption capacity of various chars was measured using simulated adsorption testing. The active constituents and existing form of chars were tested by different characterization technique. Microwave/steam activation and NH_4Cl impregnation were used to modify various chars to investigate the effect of physical and chemical modification on the active constituents of char. NH_4Cl was selected as the impregnation reagent since it has been demonstrated to be the optimal modification reagent among NH_4Cl , HCl and ZnCl_2 in our previous study [16]. The purpose of this paper is to investigate the influence of inherent active constituents in raw materials and chars for the mercury removal and to further optimize the modification method of char.

2. Materials and Methods

2.1. Sample preparation

Pyrolysis:

Four raw materials were used in this study: waste tire, cotton straw, Chinese medicinal residue and municipal solid waste. These raw materials underwent natural drying and then were subsequently dried for 2 h at 90 °C. The materials were crushed to the size of 8.0 to 10.0 mm. The crushed raw materials were placed in a quartz reactor (160 mm in diameter and 400 mm in depth). Initially, the reactor was purged of oxygen, and then was maintained with oxygen-free environment with a N₂ flow of 100 mL·min⁻¹ during whole pyrolysis process. The quartz reactor was heated at 20 °C·min⁻¹ from room temperature to 600 °C and then remained at 600 °C for 60 min. Under the N₂ atmosphere, the pyrolysis reactor was cooled to room temperature. The pyrolysis chars from WT, CS, MR and MW were denoted as T6, C6, M6 and W6, respectively.

Physical activation:

The microwave activation process occurred in a quartz bottle activation reactor (50 cm³) under a constant N₂ flow (40 mL·min⁻¹). The 2 g of pyrolysis chars were activated for 4 h in the activation reactor. Steam was generated in the activation reactor by injecting deionized water into the reactor using a peristaltic pump with a flow rate of 4 mL·h⁻¹. The activation reactor was placed in a 950 W power microwave oven. The derived chars from T6, C6, M6 and W6 were denoted as T6W, C6W, M6W and W6W, respectively.

Chemical modification:

The four pyrolysis chars were impregnated with 1 wt.% NH₄Cl solution. The ratio of char to NH₄Cl solution is 1:5 g·mL⁻¹. The solid-liquid mixtures were stirred for 12 h and dried for 4 h in a water bath at 80 °C. The mixtures were dried in an oven for 12 h at 105 °C. The modified chars from T6, C6, M6 and W6 were denoted as T6N5, C6N5, M6N5 and W6N5, respectively.

All chars were sieved through an 80-100 mesh prior to the adsorption testing.

2.2. Characterization techniques

The proximate analysis of the four raw materials was measured according to the

Chinese National standards (GB/T 212-2008) and the ultimate analysis was determined using the Elementar EA3000 (LEEMAN, China). Specific surface area (S_{BET}), pore volume (V), and micropore volume (V_{micro}) were measured by N_2 adsorption at $-196\text{ }^\circ\text{C}$ on an ASAP 2020 automated gas adsorption system (Micromeritics, USA). FTIR were measured on Thermo Nicolet NEXUS infrared spectrometer (U.S. Thermo Fisher Co.) at a range of $3200\text{--}400\text{ cm}^{-1}$. The elemental (Cl, S and Hg) valence state was analyzed using X-ray photoelectron spectroscopy (XPS) with Mg X-ray source by Axis Ultra DLD (Kratos Analytical Ltd, Britain). All binding energies were calibrated with the C 1s peak at 284.6 eV . The temperature programmed decomposition technic (TPDT) was used to identify the mercury species on the chars. The reference samples including mercury compounds (HgCl_2 , HgS , HgO and HgSO_4) were heated to obtain TPDT reference profiles. The schematic of TPDT system (Fig. S1) and testing procedure were provided in the Supplementary material.

2.3. Mercury adsorption testing

The schematic of the mercury adsorption testing used to evaluate the property of various sorbents for mercury adsorption is 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. The simulated flow of flue gas was $850\text{ mL}\cdot\text{min}^{-1}$, including 6 vol.% O_2 and N_2 . N_2 flow, serving as the carrier gas, passed through the permeation tube to generate the Hg^0 vapor. The permeation tube within a U-type glass tube was placed in a temperature-controlled thermostat water bath to maintain the Hg^0 concentration at $29.0 \pm 1\text{ }\mu\text{g}/\text{m}^3$. The reactor (10 mm in inner diameter and 400 mm in a length) was placed in a temperature-controlled electric furnace. The sorbent (0.1) g was placed in the adsorption zone of the reactor. The space velocity is 260000 h^{-1} . The whole gas line was kept at $80\text{ }^\circ\text{C}$ to avoid the 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 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 the Hg^0 removal efficiency, C_{in} and C_{out} ($\mu\text{g}\cdot(\text{Nm}^3)^{-1}$) are the 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.

For the experimental error is inevitable, the Hg^0 removal efficiency is the average of two parallel experimental data and the relative error of all parallel experimental data is less than 8 %.

3. Results and Discussion

3.1 Sample characteristic analysis

3.1.1 Proximate and ultimate analysis

The proximate and ultimate analysis of the four raw materials is shown in Table 1. The texture property of the four raw materials has an obvious difference in both proximate and ultimate analyses. As shown in Table 1, the waste tire and cotton straw both has low ash content (7.1 wt.% and 8.3 wt.%) and high volatile content (62.2 wt.% and 63.0 wt.%). In contrast, the ash content of the Chinese medicinal residue and municipal solid waste is relatively high (32.9 wt.% and 45.8 wt.%, respectively). The volatile content of the Chinese medicinal residue and municipal solid waste is relatively low with only 39.0 wt.% and 17.1 wt.%, respectively. The ash and volatile content have an important effect on the formation of the pore structure during the pyrolysis process. The overmuch ash can block the pore structure and inhibit pore formation. The moisture content of the four raw materials is low mainly because the pretreatment reduced the moisture content. The fixed carbon (FC) content of four raw

materials is in the range of 25.7 to 35.1 wt.%.

According to the ultimate analysis, C is the main element for all four raw materials and the C content falls in the range of 43.6 to 88.1 wt.%. The O content of cotton straw and Chinese medicinal waste is 49.8 wt.% and 41.2 wt.%, respectively. The high O content was potentially beneficial to the development of oxygen-containing functional groups which could serve as adsorption sites for elemental mercury [10]. The municipal solid waste and waste tire have relatively low O content, especially the waste tire, its O content is only 1.8 wt.%. However, it is noteworthy that the waste tire, Chinese medicinal waste and municipal solid waste contain S element. On the basis of previous study, the sulfide and element sulfur modification could promote the mercury adsorption [17, 18]. Municipal solid waste contains 2.4 wt.% Cl. This halide element also can serve as chelating agent and has affinity for elemental mercury [15, 19]. Therefore, high Cl content in a raw material can improve the mercury adsorption capacity of derived chars. In summary, the specific properties of four raw materials are potential factors in facilitating mercury removal.

3.1.2 Pore analysis

Pore structure parameters of various chars, including BET surface area (S_{BET}), micropore volume (V_{micro}), total pore volume (V) and the ratio of micropore to total pore volume (V_{micro}/V), are listed in Table 2. Pore properties vary among the chars derived from the four raw materials. According to Table 2, chars T6 derived from waste tire and C6 derived from cotton straw show good pore structure. In contrast, M6 derived from Chinese medicinal waste and W6 derived from municipal solid waste have poor pore structure. This result is consistent with the texture characteristics in Table 1. The high volatile content is conducive to the development of pore structure during pyrolysis process, and vice versa.

For all chars, the microwave activation improved BET surface area, micropore pore volume and total volume. The BET surface area of M6W and W6W rise from 2.4 and 4.0 $\text{m}^2\cdot\text{g}^{-1}$ to 67.9 and 48.1 $\text{m}^2\cdot\text{g}^{-1}$, respectively. Moreover, the growth of V_{micro}/V indicates that microwave activation had a positive role on the micropore region. This

growth in V_{micro}/V is possibly beneficial to mercury physisorption because micropores usually serve as the physisorption sites for elemental mercury.

The NH_4Cl impregnation inhibited the development of pore structure. The S_{BET} of T6N5 and C6N5 decrease from 85.4 and 165.1 $\text{m}^2\cdot\text{g}^{-1}$ to 45.5 and 78.5 $\text{m}^2\cdot\text{g}^{-1}$, respectively. Similarly, the pore volume declines from 0.311 $\text{cm}^3\cdot\text{g}^{-1}$ to 0.152 $\text{cm}^3\cdot\text{g}^{-1}$ for T6N5 and from 0.119 $\text{cm}^3\cdot\text{g}^{-1}$ to 0.087 $\text{cm}^3\cdot\text{g}^{-1}$ for C6N5. In addition, decreases of the ratio of V_{micro} to V imply that the NH_4Cl reagent may have absorbed onto the micropore region.

3.1.3 FTIR analysis

Fig. 1 presents the FTIR analyses of the four original chars (T6, C6, M6 and W6). These four chars all contains some hydrocarbon skeletal structure. The aromatic skeletal stretching bands were at 1442 cm^{-1} and 1597 cm^{-1} [20, 21]. Various C-H bending/wags characteristic peaks appear at 817 cm^{-1} , 872 cm^{-1} and 2924 cm^{-1} [20, 21]. As shown in Fig. 1, the spectrum of char T6 contains several S-containing groups characteristic peaks, which includes C-S stretching (663 cm^{-1}), S=O stretching vibrations (1395 cm^{-1}), sulfide groups (1105 cm^{-1}) and free sulfur group vibrations (480 cm^{-1}) [22-24]. This result indicates that the organic sulfur in waste tire is transformed into sulfur-containing groups during the pyrolysis process. For C6, the C=O group and carboxylate group appear at 1697 and 1400 cm^{-1} , respectively [25]. The broad peak in range of 1150-1260 cm^{-1} represents formic ester, propionic acid and acetate groups. According to Table 1, high O content in cotton straw can promote the formation of oxygen-containing functional groups. On the spectrum of M6, the sulfate characteristic peak is near 1042 cm^{-1} and the Si-O group appears at 464 cm^{-1} [26, 27]. For W6, the sulfate and Si-O peaks also appear on the spectrum. The peak near 2846 cm^{-1} is assigned to CH_3 stretching for the methoxyl group. Although municipal solid waste has a high Cl content on the basis of ultimate analysis, derived char W6 does not include Cl-containing functional group at the characteristic peak of 733 cm^{-1} [23].

3.2 Mercury adsorption testing

3.2.1 Mercury removal performance of original chars

In order to evaluate the mercury adsorption performance of the various chars, mercury adsorption test was carried out in the simulated flue gas. As shown in Fig. 2, the chars have a huge difference in mercury adsorption performance. It is noteworthy that the original char T6 has a much better mercury removal performance than other original chars. The initial removal efficiency of T6 reached 88.3% and retained more than 66.3% at $t=300$ min. According to Table 2, T6 has a worse pore structure than C6, but its mercury adsorption performance is far superior to C6. This result indicates that physisorption depending on pore structure is not a key factor in the adsorption performance of T6. There are two possible mechanisms for adsorbing elemental mercury: physical adsorption due to porous structure and chemical adsorption due to the reactions between the functional groups and mercury. Therefore, it is a reasonable inference that some chemisorption sites possibly formed on the surface of T6 and improved its mercury removal efficiency. According to Table 1 and FTIR analysis, chemisorption sites are likely the sulfur-containing compounds on the surface of T6.

The chars C6, M6 and W6 showed similar mercury removal efficiency and their order followed: $C6 > M6 > W6$. The initial removal efficiencies of C6, M6 and W6 are 35.1%, 22.2% and 12.8%, respectively. The ultimate and FTIR analyses show that char C6 has a good pore structure and many oxygen-containing functional groups. The micropore and oxygen-containing functional group are usually considered as physisorption and chemisorption sites for mercury. Therefore, char C6 showed relatively good mercury removal performance. Although Chinese medicinal waste also has a high S content, derived char M6 performed low mercury removal efficiency, indicating that its S did not form effective adsorption sites for mercury during pyrolysis process. According to the FTIR analysis, T6 contains various sulfur-containing functional groups while M6 only shows sulfate groups. These results imply that different sulfur-containing compounds formed via pyrolysis process possibly lead to different mercury adsorption performance. In addition, the poor mercury removal performance of W6 implies that high Cl content does not transform into available adsorption sites during the pyrolysis process of municipal solid waste.

This result corresponds to the FTIR analysis result that no Cl-containing functional group appears in W6.

3.2.2 The effect of microwave activation on mercury removal

The influence of microwave activation on the mercury removal efficiency is shown in Fig. 3. It is evident that the microwave activation exerted a positive influence on the mercury removal performance of C6W, M6W and W6W. Their initial removal efficiency increased from 35.1%, 22.2% and 12.8% (original chars) to 50.2%, 35.1% and 22.9%, respectively. The adsorption time was also extended to 200, 150 and 130 min for C6, M6 and W6, respectively. Based on Table 2, the increase of mercury removal performance is ascribed to the improvement of pore structure. The microwave activation increased the development of the surface area, micropore volume and total pore volume. The macropore serves as a gate of mercury; the mesopore serves as a mercury transmission channel from the surface to adsorption sites; and the micropore serves as physisorption sites for elemental mercury. Therefore, the pore structure development increases the adsorption capacity of elemental mercury.

Results of T6W were opposite to the above chars. Though pore property of T6W was improved by microwave activation, the initial mercury removal efficiency decreased from 88.3% to 58.4% after activation. This once again suggests that physisorption is not the crucial factor affecting mercury adsorption capacity for tire derived char. Other adsorption sites possibly exist on T6 and dictate the mercury removal capacity. The microwave activation may have removed part of the chemisorption sites, resulting in the decrease of mercury removal capacity.

3.2.3 Effect of NH_4Cl impregnation on mercury removal

The effect of NH_4Cl impregnation on mercury removal is shown in Fig. 4. The NH_4Cl modification increased the mercury adsorption performance of C6, M6 and W6. The highest mercury removal efficiency of C6, M6 and W6 reached 75.9%, 67.5% and 44.1%, respectively. The NH_4Cl impregnation potentially formed a large number

of chemisorption sites on the surface of chars. According to Table 2, the micropores are the main adsorption sites of the chemical modification reagent. Therefore, the better pore structure of C6 formed more chemisorption sites and resulted in higher mercury removal capacity.

However, the NH_4Cl impregnation had a weakly negative influence on the mercury removal performance of T6. The initial removal efficiency decreased from 88.3% for T6 to 83.1% for T6N5, indicating that the NH_4Cl impregnation inhibited the mercury removal efficiency. This efficiency drop is possibly explained by changes of adsorption sites. Though NH_4Cl impregnation can form some adsorption sites, it also possibly covers up the original adsorption sites. For C6, M6 and W6, the original chemisorption sites are limited or even none, so the adsorption sites obtained from NH_4Cl impregnation can obviously increase their removal efficiency. In contrast, original char T6 possibly have had so many chemical adsorption sites on the surface that the NH_4Cl impregnation could not form more adsorption sites and even decreased the number of original adsorption sites because of impregnation covering. The impregnation covering thereby cut off original adsorption site exposure to elemental mercury, resulting in the invalidation of the original adsorption sites. Hence, the NH_4Cl impregnation did not improve the mercury removal efficiency of T6, but decreased its mercury removal performance instead.

3.2.4 Comparison of Hg^0 removal efficiencies of chars

Fig. 5 compares the Hg^0 removal efficiencies of different chars. For C6, M6 and W6, both microwave activation and chemical impregnation have a positive impact on the mercury removal performance. Initial mercury removal efficiency was enhanced via microwave activation by 15.1%, 12.9% and 10.1% for C6, M6 and W6, respectively. Then the NH_4Cl impregnation improves the mercury removal efficiency of C6, M6 and W6 by 40.8%, 45.4% and 31.3%, respectively. This result indicates that chemical modification possibly formed more mercury adsorption sites than physical modification. Furthermore, these results suggest that chemical modification is more important than physical activation for mercury removal of various chars.

According to Fig. 5, both microwave activation and chemical impregnation

inhibited mercury removal performance of T6. This is ascribed to the negative influence of physical and chemical modification on the original adsorption sites of T6. It means that both physical and chemical modification played negative influence on the original adsorption site of T6. The pyrolysis of waste tire can generate some effective adsorption sites (sulfide) on the char T6. However, the subsequent physical and chemical modifications remove or cover up these adsorptions sites.

3.3 Adsorption mechanism exploration via XPS analysis

X-ray photoelectron spectroscopy (XPS) is an effective technology to analyze the elemental valence state on the surface of the chars. In this study, the mercury adsorption mechanism was investigated via XPS analysis.

3.3.1 NH_4Cl modification analysis

Fig. 6A and 6B presents the valence state of Hg and Cl on the surface of M6N5 before and after mercury adsorption testing. As shown in Fig. 6A, only one spectral peak appears on the fresh M6N5. The peak at 102.3 eV represents Si, indicating the absence of mercury on the fresh char [28, 29]. However, after the mercury adsorption testing, a new peak appears at 104.3 eV representing oxidized mercury (Hg^{2+}) [30, 31]. This result indicates that the adsorbed mercury exists in the form of oxidation state.

According to Fig. 6B, two characteristic peaks at 198.4 and 200.0 eV show at the Cl 2p spectrum of both the fresh and used M6N5. The low binding energy peak corresponds to Cl^- and the high binding energy peak belongs to C-Cl group [32]. The peak area ratio of C-Cl with Cl^- was 8.45 prior to mercury adsorption whereas it decreased to 0.9 after mercury adsorption testing. This implies that some C-Cl groups possibly transformed into Cl^- . Connecting with the existing form of mercury, the mercury likely adsorbed on the char in the form of HgCl_2 . The C-Cl group, serving as chemisorption site, oxidized the Hg^0 into HgCl_2 during the adsorption process. Therefore, the C-Cl group ratio decreased and the Cl^- ratio rose after mercury adsorption testing. According to above analysis, the mechanism of halide modified chars could be described as follows: (1) the chloride ions reacted with carbon atom to form C-Cl groups; (2) the elemental mercury transferred from gas phase to the surface

of chars; (3) the C-Cl groups oxidized elemental mercury into mercury halides. Combining with previous studies, the specific adsorption mechanism can be ascribed using the following reactions [33-37]:

3.3.2 T6 adsorption mechanism analysis

Based on FTIR analysis and adsorption test, sulfur-containing compounds are the possible mercury adsorption sites. In order to further verify specific the adsorption sites, the valence state change of Hg and S in T6 were analyzed using XPS in Fig. 6C and 6D, respectively. According to Fig. 6C, the spectrum of fresh T6 has only one peak for Si at 103.1 eV [28, 29]. After mercury adsorption test, two new peaks appear at 101.1 and 104.7 eV, which represents Hg^{2+} [30, 31]. It proved that the elemental mercury was oxidized into Hg^{2+} and adsorbed on the surface of T6.

As shown in Fig. 6D, two peaks at 161.9 eV and 163.7 eV appear on the spectrum of S 2p. The low peak corresponds to the sulfide groups and the high peak corresponds to the organic sulfur or elemental sulfur. On the basis of our previous study, sulfide groups were proved to be crucial chemisorption sites for tire derived char via contrasting and exploring the effect of sulfide, organic sulfur, sulfate and oxygen-containing functional groups on mercury removal [38]. According to Fig. 6D, the peak area ratio of organic/elemental sulfur to sulfide is 0.41 for fresh T6 and 0.83 for used T6. The ratio increase is attributed to the oxidation of sulfide to elemental sulfur. The elemental sulfur served as the chemisorption sites oxidizing Hg^0 into HgS . Then HgS further adsorbed on the surface of T6. Therefore, the elemental mercury adsorption mechanism followed three steps: (1) elemental mercury adsorbed on the char; (2) the sulfide (ZnS) was oxidized into elemental sulfur; (3) the elemental sulfur reacted with adsorbed mercury to form HgS . The adsorption mechanism can be ascribed as follows [38]:

386 3.3.3 Adsorption mechanism analysis of original chars

387 According to the above analysis, Cl and S were likely the reason for good mercury
 388 removal performance. Chinese medicinal waste and municipal solid waste also
 389 contain high S and Cl content (Table 1), but the derived chars M6 and W6 exhibited
 390 low mercury removal efficiency. The reason is investigated in the following
 391 paragraph.

392 Fig. 6E shows the comparison of the XPS analysis of Cl 2p for fresh M6N5 and
 393 W6. The Cl 2p spectrum of fresh M6N5 has two characteristic peaks for C-Cl and Cl⁻
 394 groups. The C-Cl groups can serve as chemical adsorption sites for elemental mercury.
 395 However, fresh W6 does not show any characteristic peak on the Cl 2p spectrum,
 396 indicating that fresh W6 does not contain Cl element. It is consistent with the result of
 397 FTIR analysis. The chlorine-containing compounds in the raw municipal solid waste
 398 were possibly released in gaseous form during pyrolysis process. Therefore, the
 399 derived char W6 did not form effective mercury adsorption sites. As a result, though
 400 municipal solid waste has a high Cl content, the char W6 performed low mercury
 401 removal efficiency.

402 The XPS analysis of T6 and M6 was used to explore the reason for the difference in
 403 their mercury removal performance (Fig. 6F). For T6, the characteristic peaks of both
 404 sulfide and organic sulfur appear in Fig. 6F. But for M6, only one characteristic peak
 405 at 168.9 eV belongs to the sulfate groups. These results are also consistent with the
 406 FTIR analysis. It could infer that the sulfur element in Chinese medicinal waste was
 407 predominantly transformed into sulfate groups but no sulfide group formed during
 408 pyrolysis process. The sulfate groups cannot serve as chemisorption sites. Thereby,
 409 the M6 had a low mercury removal performance because of its lack of adsorption
 410 sites.

411 3.4 TPDT analysis

412 In order to further investigate the adsorption mechanism of elemental mercury on

various chars, the temperature programmed decomposition technic (TPDT) was used to identify the mercury species on the chars. The reference samples including mercury compound (HgCl_2 , HgS , HgO and HgSO_4) were heated to obtain TPDT reference profiles. The reference profiles are shown in Fig. 7A. The temperature appearance of the various pure mercury species is arranged in an increasing order as $\text{HgCl}_2 < \text{HgS} < \text{HgO} < \text{HgSO}_4$. The characteristic peak temperatures of the reference profiles are compared with other studies in Table 3. The characteristic peak temperature of same mercury compound is basically similar in different studies. The noted difference is ascribed to testing condition variation, such as carriers, heating rate and apparatus structure.

As shown in Fig. 7, the TPDT decomposition profiles of the used W6N5 and T6 cover a wide temperature range, indicating that mercury adsorbed on chars involves different adsorption sites. These profiles were separated and fitted using the PeakFit program with a Gauss distribution. The mercury species on the NH_4Cl impregnated char (W6N5) after mercury adsorption testing are identified and presented in Fig. 7B. Three thermal decomposition peaks of used W6N5 represent three adsorbed states at least. The lowest peak at 198°C is related to physically or weakly chemically adsorbed mercury. The highest temperature at 315°C is related to the compound HgO . The middle peak at 260°C refers to HgCl_2 (Table 3). The peak area percent of HgCl_2 compound is 88.5%, indicating the Cl-containing groups are the main mercury adsorption sites for W6N5. This result is consistent with the above adsorption mechanism of elemental mercury via C-Cl groups.

As shown in Fig. 7C, two characteristic peaks appear on the decomposition profile of used T6. The first peak at 208°C is considered to be weakly adsorbed mercury. Compared with used W6N5, used T6 has better removal performance in this type mercury adsorption. This is potentially ascribed to the good pore property of T6. Therefore, the weakly adsorbed mercury is inferred to be physically adsorbed mercury. The second peak at 346°C belongs to the HgS compound which accounts for 90.8% of total adsorbed mercury. This result proves that the S-containing groups are the

main adsorption sites for elemental mercury and the form of adsorbed mercury is HgS on T6. This conclusion conforms to the mercury adsorption mechanism in reaction (6-7). There is no obvious HgO peak on the decomposition profile of used T6. This result agrees with our previous research conclusion that the O-containing group was not key factor on the mercury removal for T6 [38]. Therefore, original T6 could be a good and low-cost sorbent for mercury capture because waste tire could directly generate many chemical adsorption sites via pyrolysis without any modification.

The thermal decomposition profiles (Fig. S3) of used M6, W6 and C6 as well as the analysis results are provided in the Supplementary material. In the decomposition profile, the M6 and W6 does not contain characteristic peak of HgSO₄ compound, indicating that the adsorbed mercury does not exist in form of HgSO₄. It proves that the sulfate is not an effective adsorption site for elemental mercury, confirming the reason for poor mercury adsorption performance of M6. Similarly, the decomposition profile of used W6 does not include the peak of HgCl₂, which proves the lack of Cl-containing groups. This is consistent with the results of the FTIR and XPS analyses.

4. Conclusion

In this study, the action of inherent active constituents of four raw materials was analyzed and investigated to identify their role in the mercury removal. The results indicate that potentially activated constituent in raw materials do not all formed effective adsorption sites during pyrolysis process. Both volatile and inactive form possibly disabled inherent active constituents. The conventional modification methods (physical activation and chemical impregnation) promoted the mercury capture performance of chars derived from CS, MR and MW since the modification added the adsorption sites. However, both physical activation and chemical impregnation inhabited the mercury capture of char derived from WT because the inherent active sites were removed or covered during modification process. This discovery provides guidance for the preparation method of mercury-removal sorbents. The inherent active constituent is a key factor to char properties. Blind and unselective activation or modification to chars possibly not only cause a high cost, but also harm the inherent

active constituents, resulting in a decrease of adsorption capacity. Therefore, careful attention should be paid to the inherent active constituent of raw material during the preparation process of mercury sorbents.

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Fig. 1 FTIR analysis of four original chars

Fig. 2 Hg^0 removal efficiency of original chars

Fig. 3 Hg^0 removal efficiency of microwave activated chars

Fig. 4 Hg^0 removal efficiency of chloride modified chars

Fig. 5 Comparison for initial Hg^0 removal efficiencies of various chars

Fig. 6 XPS analysis result: (A) Hg 4f and (B) Cl 2p for the fresh and used M6N5; (C) Hg 4f and (D) S 2p for the fresh and the used T6; (E) Cl 2p for fresh M6N5 and W6; (F) S 2p for fresh T6 and M6

Fig. 7 Thermal decomposition profile of (A) pure mercury species, (B) used W6N5 and (C) used T6

600 Table 1 Proximate and ultimate analysis of four raw materials

Sample	Proximate analysis (wt.%)				Ultimate analysis (wt.%)						
	Moisture	Volatile	Ash	FC	C	H	O	N	S	Cl	Zn
WT	1.3	62.2	7.1	29.4	88.1	7.1	1.8	0.4	1.4	0	1.2
CS	0.2	63.0	8.3	28.5	43.6	5.8	49.8	0.8	0	0	0
MR	2.4	39.0	32.9	25.7	49.2	5.0	41.2	3.5	1.1	0	0
MW	2.0	17.1	45.8	35.1	59.0	6.3	28.7	3.3	0.3	2.4	0

601

602 Table 2 BET analysis of samples

Sample	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \cdot \text{g}^{-1}$)	V ($\text{cm}^3 \cdot \text{g}^{-1}$)	V_{micro}/V (%)
T6	85.4	0.007	0.311	2.2
C6	165.1	0.026	0.119	21.8
M6	2.4	0.002	0.014	14.3
W6	4.0	0.002	0.029	6.9
T6W	225.4	0.058	0.447	13.0
C6W	404.0	0.105	0.247	42.5
M6W	67.9	0.012	0.059	20.3
W6W	48.1	0.010	0.072	13.9
T6N5	45.5	0.000	0.152	0.0
C6N5	78.5	0.010	0.087	11.5

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604 Table 3 Comparison of characteristic peak temperatures of various mercury compounds

Mercury compound	Characteristic peak in this study	Characteristic peak in other studies
HgCl ₂	250 ± 10 °C	240 °C [34], 210 °C [35]
HgO	330 ± 15 °C	340 °C [34], 415-445 °C [36]
HgS-red	350 ± 6 °C	350 °C [34]
HgSO ₄	540 ± 3 °C	550-590 °C [36]

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XPS analysis