Deep study on effects of activated carbon’s oxygen functional groups for elemental mercury adsorption using temperature programmed desorption method

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Highlights

- Ester group captures mercury prior to carbonyl group.
- Oxygen groups are more important than surface area above 130 °C.
- Ester group dominates mercury adsorption at 210 °C.
- Physisorption only occurs in the range from room temperature to 130 °C.

Abstract

Oxygen functional groups play an important role in elemental mercury adsorption by activated carbon (AC). However, the adsorption mechanism of oxygen functional groups is unclear. This study investigated the effects of oxygen functional groups on elemental mercury adsorption using temperature programmed desorption method. Nitric acid treatment, non-thermal plasma treatment, and heat treatment in nitrogen or carbon dioxide were used to modify AC’s oxygen functional groups and pore structures. Base–acid titration experiments were conducted to calculate the amount of oxygen functional groups of samples. Mercury removal efficiency tests and temperature programmed desorption experiments of AC were carried out in a bench-scale quartz reactor. The results suggested that the mercury removal performance of AC was determined by the comprehensive effects of surface area, carbonyl group and ester group, and each of them had different influences on mercury adsorption at different temperatures. Physisorption which related with surface area only occurred in the temperature range from 30 °C to 130 °C, and it was inhibited by increasing temperature; while carbonyl group and ester group could capture mercury in the temperature range from 30 °C to 210 °C. However, increasing temperature could inhibit the mercury adsorption by carbonyl group in the temperature range of 130–210 °C, and the ester group dominated mercury adsorption at 210 °C. In addition, carbonyl group and ester group had different priority levels for mercury adsorption, active sites related with ester group had the highest priority of capturing mercury, and active sites in correlation with carbonyl group was the second, while active sites corresponding with physisorption was the last one.

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1. Introduction

In recent years, mercury emissions have attracted wide attentions due to its potential risks to human health, particularly long term exposure to methyl mercury [1,2]. It is reported that coal fired power plants are one of the major anthropogenic mercury emission sources because of large amount of coal consumption [3]. The high-temperature boiler transforms most of the mercury compounds in the coal into elemental mercury (Hg0) in the flue gas. When the flue gas passes through the purification system, some of the elemental mercury is oxidized to oxidized mercury (Hg2+) by the DeNOx equipment, which is easily removed by the wet flue gas desulfurization (WFGD) because of its high solubility in water. Some of the elemental mercury is captured by fly ash and then removed by the dust removal device [4,5]. However, the remaining Hg0 in flue gas is very difficult to be removed by
existing tail gas treatment devices due to its high volatility and low solubility in water [6]. As a result, a number of studies focusing on the control of elemental mercury were conducted.

Activated carbon injection (ACI) technology is considered as one of the most effective way to remove Hg⁰ from flue gas [7–9]. Activated carbon (AC) has large specific surface, pore volume and pore diameter, which are beneficial to the mercury adsorption. Mercury removal efficiency via AC is determined by the combination effects of physisorption and chemisorption [10]. Physisorption is affected by the surface area of AC, while chemisorption has relationship with active sites of AC [11]. The working temperature of ACI technology is about 130 °C, at which temperature chemisorption plays a leading role [12]. So many efforts were made to increase the content of highly reactive active sites for mercury removal [13–16]. It has been proved that some kind of oxygen functional groups could increase AC’s mercury removal efficiency [17,18]. Analysis of different ACs on elemental mercury adsorption. In addition, the priority abilities with mercury than S and N groups. In our previous work [20], non-thermal plasma was used to increase the amount of carbonyl group and ester group of AC so as to improve AC’s mercury removal efficiency. However, it needs more work to deep study on effects of activated carbon’s oxygen functional groups for elemental mercury adsorption.

Temperature programmed desorption (TPD) method has been increasingly employed to identify mercury compounds in solids because of its low detection limit, good usability and high accuracy [21]. TPD method is based on that different mercury compounds desorbed at various temperatures, so the species of mercury compounds can be determined according to their desorption temperatures. Stefan and Thomas [22] employed it to determine mercury binding forms in contaminated soils. Lopez-Anton et al. [23,24] successfully used it to identify the mercury compounds in coal combustion products, and they found desorption temperature of main mercury species in sorbent or fly ash increased in the order of HgCl₂, HgS, HgO, HgSO₄. Wu et al. [25] revealed that HgO desorption temperature from the AC was higher than that from the HgO, because the HgO was stabilized by the AC surface. Hu et al. [26] reported the mercury removal mechanism by catalysts using TPD method. Tong et al. [27] adopted TPD method to study effects of multi-component flue gases on mercury removal over HNO₃ modified AC, and found that the Cl groups have the highest binding abilities with mercury than S and N groups. In our previous research [20,28], TPD method provided a helpful way to identify mercury compounds adsorbed by different active sites on the surface of AC. So far, there is no report about using TPD method to study the effect of activated carbon’s oxygen functional groups on elemental mercury adsorption. In this work, TPD method was used to reveal the influence of different oxygen functional groups of ACs on elemental mercury adsorption. In addition, the priority levels for mercury adsorption by oxygen functional groups were also investigated.

2. Experimental procedures

2.1. Sample treatment and characterization

The activated carbon sample (purchased form Changzhou light activated carbon Co. Ltd) was coconut shell based activated carbon. The ultimate and proximate analysis of original AC was given in Table 1. The activated carbon samples (0.2–0.3 mm diameter) were dried at 105 °C for 24 h after being washed with deionized water. After that, AC samples were treated by different ways to modify the oxygen functional groups prior to mercury adsorption experiments. Samples designated as ‘AC–HNO₃’ undergoes the following treatment process, first being immersed in 5 N HNO₃ solution for 10 h at 30 °C, then being washed using deionized water, finally, being dried at 105 °C for 8 h in an oven. It has been proved that the HNO₃ solution treatment could increase oxygen functional groups of AC [15]. AC samples designated as ‘AC–Plasma’ were obtained by using non-thermal plasma treatment to add oxygen functional groups to AC, and the treatment equipment was similar to that in our previous researches [19]. In each non-thermal plasma treatment process, 2 g of activated carbon was laid flat on the reactor, and then treated in air environment by non-thermal plasma for 30 mins with 45 kW working energy. AC was treated by thermal treatment at 900 °C for 1 h in high purity nitrogen to remove the oxygen functional groups for comparison [29] (AC-900N₂). The AC sample with highest surface area was produced by activating AC at 800 °C for 2 h under high purity CO₂ (AC-800CO₂). Then, the Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size of treated ACs were tested by a Micromeritics ASAP 2020 nitrogen adsorption instrument after degassing at 453 K for 24 h. The amount of oxygen functional groups on the AC surface was calculated by base–acid titration with (a)NaHCO₃, (b)Na₂CO₃, (c) NaOH and (d)Na₂CO₃·H₂O (0.1 N) using Boehm’s method [30]. The filtrate was back-titrated with HCl (0.05 N) after 24 h of storage and shaking in NaHCO₃, Na₂CO₃, NaOH and Na₂CO₃·H₂O. The carbonyl groups (C=O) only react with NaHCO₃, the phenolic hydroxyl groups (C-OH) can be neutralized by Na₂CO₃ and NaHCO₃, the ester/lactone groups (C(O)-O-C) can be neutralized by Na₂CO₃, NaHCO₃ and NaOH, the carboxyl groups (COOH) react with Na₂CO₃, NaHCO₃, NaOH and NaOC₂H₅. Therefore, the amount of the corresponding functional groups can be calculated from the difference in the acid consumption.

2.2. Mercury adsorption experiment

A fixed-bed adsorption system containing a bench-scale quartz reactor was employed to test mercury removal efficiency of sorbents, similar to our previous work [19]. Approximately 0.5 g of each sorbent adsorbed mercury for 1 h at different temperatures. A total flow rate of 1.0 L/min containing 90 μg/m³ Hg⁰ vapor was provided to the reactor. A continuous mercury analyzer (VM3000, Mercury Instruments GmbH, Germany) was used to measure the mercury concentration before and after adsorption. The instantaneous mercury removal efficiency η of sorbent was calculated by Formula (1).

$$\eta = \frac{C_{\text{inlet}} - C_{\text{outlet}}}{C_{\text{inlet}}} \times 100\%$$

(1)

C_{\text{inlet}} and C_{\text{outlet}} represent the instantaneous mercury concentration (μg/m³) at the reactor inlet and reactor outlet, respectively. The average mercury removal efficiency (ηₐ) was calculated using Formula (2):

$$\eta_a = \frac{\sum C_{\text{inlet}} - \sum C_{\text{outlet}}}{\sum C_{\text{inlet}}} \times 100\%$$

(2)

\(\sum C_{\text{inlet}}\) and \(\sum C_{\text{outlet}}\) are the accumulation mercury concentration in 5 min at the inlet and outlet of reactor, respectively.

2.3. Temperature programmed desorption experiment

Our previous study proved that TPD was an effective way to identify the mercury occurrence in coal [31]. Therefore, this study performed TPD experiments to investigate the desorption kinetics and the surface characteristics of sorbents after adsorbing mercury.

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for 1 h. During the TPD experiments, the used sorbents was heated from 20 °C to 600 °C at a constant heating rate of 10 °C/min. A continuous mercury analyzer was used to measure the mercury releasing concentration under different temperatures in real time. The mercury mass balance between the adsorption and TPD was calculated using the following equation:

\[
\text{mass balance} = \frac{(\eta \times C_{\text{inlet}} \times L_{\text{ads}})}{C_{\text{TPD}} \times L_{\text{TPD}}} \times 100\%
\]

where \(C_{\text{inlet}}\) is the mercury concentration (\(\mu\text{g/m}^3\)) during TPD experiments, \(L_{\text{ads}}\) and \(L_{\text{TPD}}\) represent the gas flow in adsorption experiment and TPD experiment, respectively.

### 3. Results and discussion

#### 3.1. Textural Properties of sorbents

Different oxygen functional groups calculated according to the base–acid titration and the results are given in Table 2. It can be seen that AC-HNO₃ has more carboxyl, ester, carbonyl oxygen functional groups than the raw AC sample. AC-Plasma also has more ester group and carbonyl group than AC. However, only very little oxygen functional groups are contained in AC-900N₂ and AC-800CO₂. It confirms that the thermal treatment under N₂ or CO₂ at elevated temperatures can wipe off most of oxygen functional groups [29].

Table 3 lists the BET results of each sample. As shown in Table 3, the BET surface area of sorbents decreases in the order of AC-800CO₂, AC-900N₂, AC, AC-HNO₃ and AC-Plasma. And the pore volume and average pore size of AC-900N₂ has a significant increase. In the process of thermal treatment at 30°C, as shown in Fig. 2. At 30 °C, raw AC only has a mercury removal efficiency of 57.3%. However, after the oxidation treatment with nitric acid and non-thermal plasma, AC-HNO₃ and AC-Plasma, all show a big increase (around 80%) in mercury removal efficiency. As shown in Table 2, AC-HNO₃ and AC-Plasma have smaller surface area and higher content of ester group and carbonyl group. It indicates that carbonyl group and ester group play an important role in the reaction between Hg⁰ and sorbents, which is perfectly matched with previous study [19,35]. Meanwhile, despite a large surface area, AC-900N₂ is inferior to AC at 30 °C in mercury removal efficiency due to that most oxygen functional groups were removed by thermal treatment. However, the AC-800CO₂ has the highest mercury removal efficiency (nearly 100%). This possibly results from the physisorption which is caused by very large surface area. In conclusion, the above analysis suggests that surface area and oxygen functional groups both influence the mercury adsorption by activated carbon at 30 °C.

From Fig. 2, it also can be seen that each sample shows different mercury removal performance at various temperature. For raw AC, mercury removal efficiency decreases with increasing temperature.

### 3.2. The mercury adsorption performance of sorbents

The instantaneous mercury removal efficiency curves of each sample were shown in Fig. 1. It could be found from Fig. 1 that the downtrends of all instantaneous mercury removal efficiency curves become sharper with increasing temperature. And the removal efficiency curves of each samples within the first 5 minutes have different tendencies with increasing temperature. For example, AC-Plasma has higher mercury removal efficiency at 90 °C and 130 °C than that at 30 °C within the first 5 minutes. In general, sorbents only have very short residence time (5–20 s) in flue gas, so their mercury removal efficiency in start stage can represent their performance in flue gas. As a result, the average mercury removal efficiency in beginning 5 min was used to represent mercury removal performance of sorbents. Mercury removal efficiency of each sample were calculated at different temperatures (30–210 °C), as shown in Fig. 2. A t30°C, raw AC only has a mercury removal efficiency of 57.3%. However, after the oxidation treatment with nitric acid and non-thermal plasma, AC-HNO₃ and AC-Plasma, all show a big increase (around 80%) in mercury removal efficiency. As shown in Table 2, AC-HNO₃ and AC-Plasma have smaller surface area and higher content of ester group and carbonyl group. It indicates that carbonyl group and ester group play an important role in the reaction between Hg⁰ and sorbents, which is perfectly matched with previous study [19,35]. Meanwhile, despite a large surface area, AC-900N₂ is inferior to AC at 30 °C in mercury removal efficiency due to that most oxygen functional groups were removed by thermal treatment. However, the AC-800CO₂ has the highest mercury removal efficiency (nearly 100%). This possibly results from the physisorption which is caused by very large surface area. In conclusion, the above analysis suggests that surface area and oxygen functional groups both influence the mercury adsorption by activated carbon at 30 °C.

From Fig. 2, it also can be seen that each sample shows different mercury removal performance at various temperature. For raw AC, mercury removal efficiency decreases with increasing temperature.
In the temperature range from 30°C to 130°C, the mercury removal efficiency decreases slowly, but the descending rate shows an accelerating tendency after 130°C. The efficiency of AC-HNO₃ and AC-Plasma slightly increases before 130°C and decreases after 130°C, but it is still at a high level at 210°C. It should be noted that the efficiency of AC-800CO₂ and AC-900N₂ decreases with increasing temperature from 30°C to 210°C. As shown in Fig. 2, AC-800CO₂ and AC-900N₂ almost cannot adsorb mercury at temperature higher than 170°C. Considering high surface area over AC-800CO₂ and AC-900N₂ and rich ester group and carbonyl groups over AC-HNO₃ and AC-Plasma, it can be concluded that more ester group and carbonyl group contributes to better mercury removal performance by chemisorption at temperature higher than 130°C. Moreover, the sample of AC-800CO₂, which only has large surface area without oxygen functional groups, has poor mercury removal efficiency at temperature above 130°C. This temperature is quite close to that of sorbents injection into the flue gas. It suggests that increasing the active sites of sor-
bents is more effective than enlarging surface area for mercury adsorption in the practical application of the adsorbent injection.

3.3. Mercury temperature programmed desorption

Each sample after adsorbing mercury for 1 h at 30 °C was used for TPD experiments. The mercury mass balances between the adsorption experiment and TPD experiment were calculated. In this study, the calculated mass balances varied from 92% to 105% (shown in Table 4), which is in the allowed error range. In addition, carbonyl groups and ester groups were stable at 600 °C and decomposed at 700 °C [36], so the decomposition of the carbonyl group and ester group did not influence the mercury desorption.

Fig. 3 shows the TPD curves of each sample. From Fig. 2, it can be seen that desorption peaks of different sorbents are different, which indicates that different samples adsorbed mercury via different active sites. Two mercury desorption peaks of AC can be seen at the temperature around 110 °C and 230 °C. AC-HNO3 and AC-Plasma have two large mercury desorption peaks at the temperature of about 230 °C and 320 °C. However, AC-800CO2 and AC-900N2 only have one mercury desorption peak at temperature 110 °C. The mercury desorption peak at 110 °C should correspond to mercury desorption by means of physisorption because thermal treatment almost wiped off all carbonyl and ester groups over AC-800CO2 and AC-900N2. Similarly, the peaks at 230 °C and 320 °C should have correlation with ester group and carbonyl group. Liu et al. [35] has reported that carbonyl group and ester group could increase the neighboring carbon site’s activity for mercury adsorption, and mercury adsorption energy for the carbonyl group and ester group were 130 kJ/mol and 164 kJ/mol, respectively. It means that the mercury bonding with ester group was more stable than that with carbonyl group, which results in a higher desorption temperature. It can be deduced that the mercury desorption peaks at 230 °C and 320 °C should be contributed by mercury desorption from carbonyl groups and ester group respectively, this deduction was consistent with the previous research [37].

To better analyze the influence of adsorption temperature on mercury removal by carbonyl group and ester group, the mercury TPD curves of the used AC-Plasma sorbents absorbing mercury at different adsorption temperature (30 °C, 130 °C, 170 °C and 210 °C) are presented in Fig. 4. From Fig. 4, it can be seen that the desorption peak of the carbonyl group at 230 °C decreases with the adsorption temperature increasing from 130 °C. It can be deduced that increasing temperature at the range of 130–210 °C will inhibit mercury adsorption by carbonyl group, and the ester group dominates mercury adsorption at 210 °C. It also can explain why mercury removal efficiency of AC sample containing little carbonyl group has sharper decrease tendency after 130 °C.

To investigate the mercury adsorption priority of carbonyl group, ester group and physisorption, mercury TPD curves of

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peak 110 °C</th>
<th>Peak 230 °C</th>
<th>Peak 320 °C</th>
<th>Hg amount (ng)</th>
<th>Mass balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Area(ng)</td>
<td>Ratio(%)</td>
<td>Area(ng)</td>
<td>Ratio(%)</td>
<td>Adsorption</td>
</tr>
<tr>
<td>AC (1 h 30 °C)</td>
<td>281.9</td>
<td>14.0</td>
<td>1190.0</td>
<td>59.1</td>
<td>541.7</td>
</tr>
<tr>
<td>AC-HNO3 (1 h 30 °C)</td>
<td>–</td>
<td>–</td>
<td>1602.5</td>
<td>35.6</td>
<td>2894.7</td>
</tr>
<tr>
<td>AC-Plasma (1 h 30 °C)</td>
<td>–</td>
<td>–</td>
<td>1853.7</td>
<td>44.7</td>
<td>2293.2</td>
</tr>
<tr>
<td>AC-900N2 (1 h 30 °C)</td>
<td>1213.1</td>
<td>100</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>AC-800CO2 (1 h 30 °C)</td>
<td>3256.8</td>
<td>100</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>AC-Plasma (1 h 130 °C)</td>
<td>–</td>
<td>–</td>
<td>1745.2</td>
<td>42.6</td>
<td>2351.6</td>
</tr>
<tr>
<td>AC-Plasma (1 h 170 °C)</td>
<td>–</td>
<td>–</td>
<td>271.0</td>
<td>12.5</td>
<td>1897.1</td>
</tr>
<tr>
<td>AC-Plasma (1 h 210 °C)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>634.2</td>
</tr>
<tr>
<td>AC-Plasma (5 min 30 °C)</td>
<td>–</td>
<td>–</td>
<td>99.3</td>
<td>25.7</td>
<td>286.9</td>
</tr>
<tr>
<td>AC-Plasma (2 h 30 °C)</td>
<td>–</td>
<td>–</td>
<td>3743.6</td>
<td>54.3</td>
<td>3150.6</td>
</tr>
<tr>
<td>AC-Plasma (4 h 30 °C)</td>
<td>1206.8</td>
<td>12.1</td>
<td>4717.6</td>
<td>0.473</td>
<td>4149.0</td>
</tr>
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</table>
AC-Plasma within different adsorption time (5 min, 1 h, 2 h, and 4 h) were obtained and shown in Fig. 5. The vertical axis shows the ratio of real-time concentration to maximum concentration. The mercury desorption peaks of the carbonyl group and ester group can be found in all TPD curves. For samples adsorbing mercury for only 5 min, the peak of ester group appears to be dominated. The above analyses suggest that ester group have a higher priority level of mercury adsorption than carbonyl group, and ester group dominates mercury removal efficiency in the beginning phase of mercury removal. However, with the increasing adsorption time, the peak area of ester group decreases while the peak area of carbonyl group increase. In addition, the physisorption of mercury only can be found on the used AC-Plasma sorbents after mercury adsorption for 4 h. It implies that mercury is likely to be firstly adsorbed by active sites which are relevant with functional group, and physisorption of mercury does not occur until active sites being almost exhausted. In conclusion, the mercury adsorption priority is as follows: ester group, carbonyl group, physisorption.

In addition to quantify the amount of mercury adsorbed by different active sites, a quantitative analysis of TPD curves was carried out. The optimum fitting was achieved by deconvolution and Gaussian curve fitting of three peaks for each TPD curves. The TPD peaks of AC and AC-Plasma was fitted into three peaks and two peaks, respectively. As shown in Fig. 6, it can be see the fitting curves were close to the TPD curves. Table 4 showed the peak area and ratio of all samples. These results agree well with above mercury adsorption and TPD results and it validated our deduction indirectly.

4. Conclusions

In this study, temperature programmed desorption method was employed to perform an in-depth study on the effects of oxygen functional groups for elemental mercury removal. Among oxygen functional groups, the carbonyl group and ester group had direct influence on mercury removal efficiency, and they are beneficial for mercury capture. The mercury removal performance of AC was determined by the comprehensive effects of surface area, carbonyl group and ester group, but they had different influence on the mercury adsorption performance at different temperatures. Physisorption which related with surface area occurred in the temperature range from 30 °C to 130 °C. At 30 °C, surface area and oxygen functional groups both influence the mercury adsorption by activated carbon. However, the sample which only has high surface area without rich oxygen functional groups had poor mercury removal performance at temperature higher than 130 °C. Therefore, increasing sorbents’ carbonyl group and ester group was more effective than enlarging surface area for mercury adsorption at the temperature above 130 °C. Moreover, with the temperature increasing from 130 °C to 210 °C, the adsorption abilities of ester group increased with the increasing temperature, whereas the carbonyl group behaved oppositely. It could be deduced that the mercury desorption peaks of physisorption, carbonyl group and ester group occurred at the temperature of 110 °C, 230 °C and 320 °C, respectively. Moreover, mercury was firstly captured by ester group, and secondly by carbonyl group; physisorption of mercury did not occur until active sites were almost exhausted.

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