Adsorption of Mercury on Activated Carbon in Simulated Flue Gas with Continuous Components Change

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(Received: 26 March 2013; Accepted: 29 August 2013) AJC-14044

This paper focused on the influence of flue gas component change on elemental mercury (Hg⁰) adsorption by powder activated carbon from apricot’s shell and discussed the Hg⁰ adsorption characteristics and mechanism of activated carbon. Experimental results showed that activated carbon from apricot’s shell had no Hg⁰ adsorption ability in the non-oxidizing atmosphere, such as N₂, N₂ + CO₂ etc. Though the influence on homogeneous oxidation reaction of Hg⁰ was limited, NO₂ was the key factor on heterogeneous catalytic oxidation reaction of Hg⁰ on the surface of activated carbon. It was easy to form NO₃ by reaction between the NO and O₂. It could also enhance the Hg⁰ adsorption ability of activated carbon through preloading NOₓ on the surface. Based on these experimental results, it finely proved that Hg⁰ adsorption by activated carbon was a heterogeneous catalytic oxidation reaction.

Key Words: Apricot shell, Activated carbon, Elemental mercury, Oxidization, Chemical adsorption.

INTRODUCTION

Mercury emission from coal fired is one of the main anthropogenic mercury pollution sources. There are three types of mercury speciation existing in the flue gas, zero-valent mercury (Hg⁰), bivalent mercury (Hg²⁺) and particle mercury (Hg⁰). The ratio of mercury speciation will transform with the change of flue gas components, temperature and time, etc.¹. Mercury speciation is the key influence factor on choosing the flue gas mercury control technology. Hg⁰ is the main source to induce global mercury pollution, because it is difficult to be controlled for its insolubility in water and stabilization within 1-2 years in the atmosphere. Adsorbent injection mercury control technology has widely applicable and can satisfy the higher mercury emissions control standard, which can be used alone or in combination of other technologies and is one of the effective flue gas mercury control technologies.

The Hg⁰ adsorption mechanism by activated carbon in different flue gas is very important for developing new low-cost carbon based adsorbents. Many papers²³ reported the researches on mercury adsorption mechanism of carbon based adsorbents. It found that some flue gas components could always promote adsorption of mercury by activated carbon in different conditions⁴⁵⁶. The latest research¹ showed that in the non-oxidizing atmosphere and without oxidizing elements on the surface, activated carbon had no Hg⁰ adsorption ability and physical adsorption process did not exist between the activated carbon and Hg⁰. Further research found activated carbon had efficient Hg⁰ adsorption ability in simulated flue gas and Hg²⁺ was almost the only speciation at the outlet of fixed bed when Hg⁰ adsorption on activated carbon was saturated³. It showed that the chemical oxidization adsorption existed in the process of activated carbon adsorption of Hg⁰.

This paper mainly discussed the Hg⁰ adsorption characteristics of powder activated carbon from apricot’s shell (AS-AC) in simulated flue gas with continuous change of components. It focused on the influence of flue gas component change on mercury adsorption by AS-AC and the mercury adsorption mechanism of activated carbon, which would be helpful to develop effective low-cost carbon-based adsorbents.

EXPERIMENTAL

Experimental setup of adsorption: The bench-scale Hg adsorption experimental setup is shown in Fig. 1 including simulated flue gas, fixed adsorption bed, flue gas Hg continuous emission monitor (CEM), conventional flue gas pollution, adsorption temperature control system and tail gas treatment, etc. The experimental setup is stable and reliable⁴⁵. The simulated flue gas consisted of three parts: conventional flue gas components, H₂O and Hg⁰ source. The simulated
conventional flue gas components, such as N₂, CO₂, O₂, SO₂, NO, NO₂, and HCl, were adjusted by mass flowmeters of the standard gas sources. H₂O was added to the simulated flue gas using a peristaltic pump which transferred water into the glass tube wrapped with heating line. Hg⁰ was generated by a mercury permeation tube. The Hg⁰ concentration was changed by altering the temperature of permeation tube or the flow rate of carrier gas.

The fixed adsorption bed was made by silicate glass and quartz filter, whose height was 80 mm and inner diameter was 10 mm. The pore diameter of quartz filter was less than 0.05 mm and the filter could hold the activated carbon. In this study, the AS-AC made by steam activated method was used. Steam activation is a common activation technique for AC production and is effective for creating more surface area physically by opening up more micropores. The surfaces of AS-AC had no specific active element besides some possible hydrogen and oxygen elements according to their steam activation method. The surface physical characteristics of AS-AC are given in Table-1.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Specific surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Micropore volume (&lt; 20 Å) (cm³/g)</th>
<th>Particle size (mm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS-AC</td>
<td>1070</td>
<td>0.81</td>
<td>0.48</td>
<td>0.08</td>
<td>57</td>
</tr>
</tbody>
</table>

A continuous emission monitor of DM/6A/MS/1A was used to measure mercury in experiments. The continuous emission monitor has the additional capability of determining mercury speciation in the sample gas stream. Firstly, the sample gas was washed by a potassium chloride solution to capture the divalent mercury. Secondly, the washed sample gas passes through a gas-liquid separator and a potassium hydroxide scrubber to remove interferential gases such as SO₂. Thirdly, the remaining sample gas passes through a chiller to remove moisture and the CVAAS (cold vapour generation atomic absorption spectrometry) detector to make a measurement of gaseous Hg⁰. On the other hand, the KCl solution containing the Hg²⁺ reacts with a tin chloride solution to reduce the Hg²⁺ to the gaseous Hg⁰. The gaseous Hg⁰ is transported by the carrier gas passing through a gas-liquid separator and a KOH scrubber to remove interferential gases. After dehumidification, the carrier gas with Hg⁰ passes through another CVAAS detector to make a measurement of Hg²⁺ in the flue gas stream. The CEM with automatic zero adjustment has a nominal range of 0.1-1000 µg/m³ and it is calibrated by an internal permeation device with the response time of less than 1 min and with the sensitivity of 0.1 µg/m³.

These conventional gases, CO₂, O₂, SO₂, NO and NO₂, were continuously measured by NGA 2000 MLT Series. The concentrations of HCl and H₂O were determined according to concentration and flow rate of corresponding standard gases. In the experimental system, all gas pipelines and fixed bed were heated to desired temperature. The tail gas was treated before emitting into the atmosphere.

**Experimental process:** The temperature of adsorption bed and gas pipelines was set at 130 °C. The 0.0505 g AS-AC was used as the sorbent. The total flow was controlled at 1.3 L/min including 300 mL/min N₂ gas for carrying Hg⁰. The continuous change process of flue gas components was divided into 17 phases (Table-2). It shows the adsorption condition, components of simulated flue gas and the corresponding experimental time.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Through FAD</th>
<th>Components of simulated flue gas</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No</td>
<td>N₂+Hg²⁺+H₂O</td>
<td>0-13</td>
</tr>
<tr>
<td>2</td>
<td>Yes</td>
<td>N₂+Hg²⁺+H₂O</td>
<td>14-33</td>
</tr>
<tr>
<td>3</td>
<td>Yes</td>
<td>CO₂+Hg²⁺+H₂O</td>
<td>34-60</td>
</tr>
<tr>
<td>4</td>
<td>Yes</td>
<td>O₂+CO₂+Hg²⁺+H₂O</td>
<td>61-88</td>
</tr>
<tr>
<td>5</td>
<td>Yes</td>
<td>SO₂+O₂+CO₂+Hg²⁺+H₂O</td>
<td>89-120</td>
</tr>
<tr>
<td>6</td>
<td>Yes</td>
<td>NO₂ SO₂+O₂+CO₂+H₂O</td>
<td>121-173</td>
</tr>
<tr>
<td>7</td>
<td>Yes</td>
<td>NO₂ SO₂+O₂+Hg²⁺+H₂O</td>
<td>174-181</td>
</tr>
<tr>
<td>8</td>
<td>Yes</td>
<td>HCl+NO₂+SO₂+O₂+H₂O</td>
<td>182-194</td>
</tr>
<tr>
<td>9</td>
<td>No</td>
<td>HCl+NO₂+SO₂+O₂+H₂O</td>
<td>195-199</td>
</tr>
<tr>
<td>10</td>
<td>Yes</td>
<td>HCl+NO₂+SO₂+O₂+H₂O</td>
<td>200-208</td>
</tr>
<tr>
<td>11</td>
<td>Yes</td>
<td>HCl+NO₂+SO₂+O₂+H₂O</td>
<td>209-227</td>
</tr>
<tr>
<td>12</td>
<td>Yes</td>
<td>HCl+NO₂+SO₂+Hg²⁺+H₂O</td>
<td>228-238</td>
</tr>
<tr>
<td>13</td>
<td>Yes</td>
<td>HCl+SO₂+CO₂+Hg²⁺+H₂O</td>
<td>239-292</td>
</tr>
<tr>
<td>14</td>
<td>Yes</td>
<td>HCl+CO₂+Hg²⁺+H₂O</td>
<td>293-312</td>
</tr>
<tr>
<td>15</td>
<td>Yes</td>
<td>HCl+CO₂+Hg²⁺+H₂O</td>
<td>313-323</td>
</tr>
<tr>
<td>16</td>
<td>Yes</td>
<td>N₂+Hg²⁺+H₂O</td>
<td>324-395</td>
</tr>
<tr>
<td>17</td>
<td>No</td>
<td>N₂+Hg²⁺+H₂O</td>
<td>396-400</td>
</tr>
</tbody>
</table>

FAD: fixed adsorption bed.

**RESULTS AND DISCUSSION**

The experimental study of Hg⁰ adsorption characteristics of AS-AC in simulated flue gas with continuous change of components could be divided into three processes. The first was to add components into simulated flue gas, respectively from phase 1-10. The second was simulated flue gas passing in bypass, i.e., phase 9. The third was to remove components from simulated flue gas, respectively from phase 10-16.

In the experimental process, the concentrations of five flue gas components were recorded (Fig. 2). The horizontal
In the same time, Hg\textsubscript{0} meant that SO\textsubscript{2} process could be understood as reaction (1), which meant that by one:

\[
\text{SO}_2 + O_2 + Hg \rightarrow HgSO_4
\]  

(1)

The concentrations of Hg\textsuperscript{0} and Hg\textsuperscript{2+} during the whole experimental process were shown as Fig. 3. The Hg\textsuperscript{2+} concentration almost did not change, which meant that no Hg\textsuperscript{2+} passed through the adsorption fixed bed.

![Fig. 3. Concentrations of Hg\textsuperscript{0} and Hg\textsuperscript{2+} during the whole experimental process](image)

Ordinate denotes the experimental time (min). There are three vertical coordinates of A, B and C axis. A shows the concentrations (%) of CO\textsubscript{2} and O\textsubscript{2}; B shows the concentrations (ppm) of NO and NO\textsubscript{2}; and C shows the concentration (ppm) of SO\textsubscript{2}. According to the Table-2, Fig. 2 shows the outlet concentrations of fixed adsorption bed at different phases. At the 9\textsuperscript{th} phase, the flue gas did not through the adsorption bed. The concentrations of HCl and H\textsubscript{2}O were not monitored and their original concentrations were 50 ppm and 10 %, respectively.

At the 6\textsuperscript{th} phase, the Hg\textsuperscript{0} concentration was almost still hold at ca. 14.1 \mu g/Nm\textsuperscript{3}. On the other hand, the increasing of NO would suppress the reaction eqn. 2.

\[
Hg + NO_2 \rightarrow \text{HgO} + NO
\]  

(2)

NO was added at the 7\textsuperscript{th} phase. As a result, NO\textsubscript{2} concentration rose from 0.1 to 14.0 ppm with the common function of O\textsubscript{2} through eqn. 3. The conversion efficiencies of Hg\textsuperscript{2+} to Hg\textsuperscript{0} at the 6\textsuperscript{th} phase and the 7\textsuperscript{th} phase were almost same as 78 %. The increment of NO\textsubscript{2} did not further promote the Hg\textsuperscript{2+} adsorption, which was mainly because that the existing NO\textsubscript{2} concentration (original was 22.2 ppm) was much higher than Hg\textsuperscript{2+} concentration (ca. 14.1 \mu g/Nm\textsuperscript{3}).

\[
2NO + O_2 \rightarrow 2NO_2
\]  

(3)

At the 8\textsuperscript{th} phase, HCl did not further promote AS-AC to adsorb Hg\textsuperscript{0}, because it was very difficult to form active Cl by HCl in the range of experimental temperature.

**Hg\textsuperscript{0} speciation in bypass (the 9\textsuperscript{th} phase):** When the simulated flue gas was switched back to the bypass at the 9\textsuperscript{th} phase, the Hg\textsuperscript{0} concentration almost went back to the original Hg\textsuperscript{0} concentration level (Fig. 3). It indicated that the influence of simulated flue gas on Hg\textsuperscript{0} speciation was limited at the experimental temperature and Hg\textsuperscript{0} was the dominant speciation in the simulated flue gas without the catalytic action of carbon on the surface of AS-AC. These results matched that of reference\textsuperscript{11}. Comparing the concentrations of simulated flue gas components through the bypass and the adsorption bed, as shown in Fig. 2 and Table-3, various simulated flue gas components would always be adsorbed or changed in speciation in different degree when they passed through the AS-AC adsorption bed.

**Hg\textsuperscript{0} adsorption when flue gas components added one by one:** As shown in Fig. 3, the AS-AC had no Hg\textsuperscript{0} adsorption ability in the simulated flue gas atmosphere of N\textsubscript{2}, N\textsubscript{2} + CO\textsubscript{2}, or N\textsubscript{2} + CO\textsubscript{2} + O\textsubscript{2} from the 2\textsuperscript{nd} to 4\textsuperscript{th} phase, which was very similar with the reported papers\textsuperscript{4,12}. When SO\textsubscript{2} was added at the 5\textsuperscript{th} phase, the concentration of Hg\textsuperscript{0} decreased a little, which meant that SO\textsubscript{2} could promote the Hg\textsuperscript{0} adsorption by AS-AC. In the same time, Hg\textsuperscript{2+} appeared. The key point of adsorption process could be understood as reaction (1), which meant that SO\textsubscript{2} could oxidize the Hg\textsuperscript{0} to Hg\textsuperscript{2+} with the action of O\textsubscript{2} on the surface of AS-AC.

\[
SO_2 + O_2 + Hg \rightarrow HgSO_4
\]  

At the 6\textsuperscript{th} phase, the Hg\textsuperscript{0} adsorption ability of AS-AC increased substantially when NO\textsubscript{2} was added. According to the concentration change of flue gas components (Fig. 2 and Table-3), the NO\textsubscript{2} concentration at the outlet of adsorption bed was only 0.1 ppm far less than the original NO\textsubscript{2} concentration of 22.2 ppm in the 9\textsuperscript{th} phase. At the same time, the NO concentration at the outlet of adsorption bed was 8.7 ppm though NO was not added in the simulated flue gas at this phase.

Many researchers\textsuperscript{14-18} believed that O\textsubscript{3}, NO\textsubscript{2} and NO had less effect on the gaseous homogeneous oxidizing reaction of Hg\textsuperscript{0} because there were some restrictions of reaction kinetics among them. However, they played a key role in the heterogeneous oxidizing reaction of Hg\textsuperscript{0}\textsuperscript{19,20}. Regarding the concentration change of Hg\textsuperscript{0}, NO\textsubscript{2} and NO, it could be considered that NO\textsubscript{2} oxidized Hg\textsuperscript{0} on the surface of AS-AC and generated NO simultaneously. The reaction process was as the following eqn. 2.
As O$_2$ was removed at the 12th phase, the reaction (2) stopped. Correspondingly, NO concentration had a significant rise stage and NO$_2$ concentration had a rapid decline to ca. 0.3 ppm. At the same time, as shown in Fig. 3, Hg$^0$ concentration at the outlet of adsorption bed rised. The Hg$^0$ oxidation ability by gaseous NO$_2$ disappeared gradually.

At the 13th phase, NO was removed. The Hg$^0$ adsorption ability of AS-AC further dropped and Hg$^0$ concentration continuously rised. However, the curve of Hg$^0$ concentration was in a parabolic form because the elements of NO, NO$_2$ and O$_2$ which were already adsorbed on the surface of AS-AC through previous phases, still worked on Hg$^0$ adsorption by AS-AC. The situation was quite different with Hg$^0$. It was fulfilled by NO, NO$_2$ and HCl in a parabolic form because the elements of NO, NO$_2$ and O$_2$ from NO, NO$_2$ adsorption by AS-AC in the process when flue gas components were added, respectively. In 14th and 15th phases, SO$_2$ and HCl were removed sequentially, which made Hg$^0$ concentration curve appear certain wave; the Hg$^0$ concentration increase slightly, which meant that they both had worked on promoting of Hg$^0$ adsorption.

Though all simulated components were removed after the 16th phase, the AS-AC still had the Hg$^0$ adsorption ability in N$_2$ gas. The Hg$^0$ concentration curve continuously increased in a parabolic form. It was because that the Hg$^0$ adsorption was fulfilled by the components of NO, NO$_2$ and O$_2$, etc., while all the components had already been adsorbed on the surface of AS-AC after nearly 3 h flue gas adsorption. It was the reason that it took ca. 187 min for the third process of Hg$^0$ adsorption by AS-AC to reach the original concentration and the duration was ca. 53 min longer than that of the first phase. As shown in Fig. 3, Hg$^0$ concentration curve was symmetrically distributed around the second phase.

**Conclusion**

According to the experimental results and discussion, it showed that the AS-AC had no Hg$^0$ adsorption ability in the non-oxidizing atmosphere, such as N$_2$ and N$_2$ + CO$_2$, etc. However, the AS-AC showed strong Hg$^0$ adsorption ability in the oxidizing atmosphere with NO$_2$ and NO, etc. Though the influence on homogeneous oxidation reaction of Hg$^0$ was limited, NO$_2$ was the key factor on heterogeneous catalytic oxidation reaction of Hg$^0$ on the surface of AC. It was easy to form NO$_3$ by reaction between the NO and O$_2$, which was an effective way for Hg$^0$ oxidation. It also could enhance the Hg$^0$ adsorption ability of AC through preloading NO$_2$ on the surface. Hg$^0$ adsorption by AS-AC, produced by physical method, was a complicated chemical adsorption process with the function of oxidising components of simulated flue gas and surface of AC. Based on these experimental results, it finely proved that the Hg$^0$ adsorption by AC was a heterogeneous catalytic oxidation reaction.