Interference Effect of Experimental Parameters on Mercury Removal Mechanism of Biomass Char under Oxy-fuel Atmosphere

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Characterization Data of Biomass Char

1. Industrial Analysis

It could be seen from Table S1 that the fixed carbon content of corn straw is 19.92%, which played an important role in the formation of biomass char. And the volatile content is the lowest, only 71.43%. Meantime, it could be seen that the ash content was 8.64% which was at a very low level and less volatilization during pyrolysis is helpful to complete and sufficient pyrolysis.

| Material | Water content | ash content | Volatile matter | Fixed carbon |
|----------|---------------|-------------|-----------------|--------------|
| CS       | 8.91%         | 8.64%       | 71.43%          | 19.92%       |

2. TGA Analysis

It could be seen from Figure S1 that the pyrolysis process can be divided into three processes: (1) the drying stage (<120°C) in which the biomass is dewatered; (2) the pyrolysis stage (160°C - 400°C) in which the biomass has obvious weight loss and a large number of gases are produced. The total weight loss in this stage reaches 73.46%; (3) the carbonization stage (>400°C). This process is the slow decomposition process of the residues in the biomass pyrolysis process and the char is finally generated.
**Figure S1.** TGA analysis of biomass char.

### 3. FTIR Analysis

Figure S2 showed that there are O-H stretching vibration absorption peaks near 3250 cm\(^{-1}\) for corn straw char, and absorption peaks also appeared near 1600 cm\(^{-1}\) for carbonyl C=O, which is the results of the action of lactone groups and carbonyl groups. In addition, there are also C-O stretching vibration peaks near 1100 cm\(^{-1}\) for corn straw char, which represented the presence of a phenolic hydroxyl functional group\(^1\). Meantime, it can be seen from the figure that there is an absorption peak of C-Cl functional group near 600 cm\(^{-1}\), which plays a key role in the adsorption process and oxidizes Hg\(^0\) to HgCl\(_2\) and other mercury chloride compounds. During the modification, NH\(_4\)Cl would react with carbon on the surface of biomass char to form chlorine containing functional group, which is easy to combine with Hg\(^0\), so as to promote the removal of Hg\(^0\). Previous studies\(^2-4\) also indicated that the existence of oxygen functional groups would do favor to Hg\(^0\) adsorption because they increased the neighboring site's activity for adsorption and the specific reaction formula is as S1-S4. Therefore, modification enriched the number and types of functional groups on the surface, which were beneficial to the adsorption of mercury by corn stalk char.

\[
\text{NH}_4\text{Cl} + \text{C}_x\text{H}_y\text{O}_z \rightarrow \text{NH}_3 + [\text{Cl}_2 + \text{C}_x\text{H}_y\text{O}_z]\quad (S1)
\]

\[
\text{Hg}^0 + [\text{Cl}]^+ \rightarrow [\text{HgCl}]^+ + 2e^{-} \quad (S2)
\]

\[
\text{Hg}^0 + 2[\text{Cl}]^{-} \rightarrow [\text{HgCl}_2] + 2e^{-} \quad (S3)
\]

\[
[\text{HgCl}_2] + 2[\text{Cl}]^{-} \rightarrow [\text{HgCl}_4]^{2-} \quad (S4)
\]
4. Pore Structure Analysis

Table S2 showed that after modification, the specific surface area increased from 59.9 m\(^2\)/g to 118.1 m\(^2\)/g, the average pore size increased from 1.398 nm to 1.570 nm, and the total pore volume increased from 0.031 cm\(^3\)/g to 0.061 cm\(^3\)/g, which indicated that modification resulted in more microporous structures and channels on the surface of corn stalk char. This is also consistent with the results of Liu et al.\(^5\) which showed that the increase of the number of micropore strongly improved the physical adsorption of adsorbents, and increased the adsorption sites, greatly enhancing the uptake of corn stalk char. According to Table S2, the specific surface area of micropores before modification is 51.7 m\(^2\)/g while that of micropores after modification is 96.7 m\(^2\)/g. Similarly, the volume of micropores rose from 0.026 cm\(^3\)/g to 0.050 cm\(^3\)/g. It can be seen that the specific surface area and volume of micropores after modification have been greatly improved, which also occupied for most proportion of all pores. Therefore, micropores and mesopores are the main adsorption pores in the adsorption process.

**Figure S2.** FTIR analysis of corn stalk char after 1%NH\(_4\)Cl modification.
Table S2. Pore Structure Analysis of Biomass Char.

| Biomass char | Specific surface area (m²/g) | Average aperture (nm) | Total pore volume (cm³/g) | Micropore area (m²/g) | Micropore volume (cm³/g) |
|--------------|------------------------------|------------------------|---------------------------|-----------------------|--------------------------|
| CS           | 59.9                         | 1.398                  | 0.031                     | 51.7                  | 0.026                    |
| CSM          | 118.1                        | 1.570                  | 0.061                     | 96.7                  | 0.050                    |

5. SEM Analysis

It could be seen from Figure S3 that before modification, there is no obvious pore structure on the surface of biomass char, and the surface is relatively smooth. After modification with 1% NH₄Cl solution, the surface of the adsorbent is rougher, showing a large number of sheet bulges, which makes the original closed pore into open and semi open structure, so it can be seen that more pore structures have been produced after modification. Combined with the data in Table S2, it can be seen that the increased pore structure increases the surface area and pore volume, this may because some of the solutes were attached to the surface of the corn stalk char and filled in the large pits, which provided a good adsorption sites for mercury⁶⁻⁷.

Figure S3. SEM Analysis of Biomass Char
Reference

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