Supporting Information

Study on the Effect of Adsorption Temperature on Elemental Mercury Removal Performance of Iron-Based Modified Biochar

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(College of Electrical and Power Engineering, Taiyuan University of Technology, Taiyuan, 030024, P. R. China)**1. Pyrolysis Characteristics.**

As shown in Fig. SI1, the pyrolysis curves of modified and unmodified WS are similar.^{SI1} The pyrolysis process can be divided into three stages: the dehydration and preheating stage (room temperature- T_1), the main pyrolysis stage (T_1 - T_3), and the slow carbonization stage (T_3 -final temperature). The relevant pyrolysis parameters are shown in Table SI1. A comprehensive index of pyrolysis characteristics (D) was proposed to characterize the degree of difficulty for volatile devolatilization from biomass, which was solved by Eq SI1. The larger the D value was, the more likely the pyrolysis occurred. As shown, Fe-Cu/BC was more easily to pyrolysis.

$$D = \frac{(dw/dt)_{1max} \cdot (dw/dt)_{mean} \cdot V}{T_1 \cdot T_2 \cdot \Delta T_{1/2}}$$
(SI1)

Where, T_1 is the temperature corresponding to about 10% weight loss rate (°C), T₂ corresponds to the maximum rate of volatile in the second stage (°C), (dw/dt)_{1max} is the maximum weight loss rate corresponding to the second pyrolysis stages (%/min), $\Delta T_{(1/2)}$ is the temperature corresponding to (dw/dt)/(dw/dt)_{1max}=1/2 (°C), (dw/dt)_{mean} is the average weight loss rate of the second and third stages (%/min), and V is the total weight loss ratio of the second and third stages (%).

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Compared with unmodified WS, the T₁ of modified WS was lower, while the $(dw/dt)_{1max}$ was higher, and the pyrolysis solid residue reduced. The temperature region of weight loss peak at DTG curves became narrow, and the TG curves moved to the high temperature zone as a whole. This was because, on the one hand, oxidation etching and deep washing effect on WS by HCl promoted the development of porous structure during the modification, which facilitated the rapid diffusion and precipitation of volatiles.^{SI2} Moreover, the crystallinity of cellulose weakened due to the destruction of HCl, making WS more susceptible to thermal cracking.^{S13} On the other, the loaded Fe, Cu and Mn ions on WS strengthened the cracking of internal straight and side chains as well as the dehydrogenation of aromatic structure (such as C-H cracking).^{SI4,SI5} Meanwhile, these active metals contributed to the catalytic pyrolysis of WS, reducing the apparent activation energy of pyrolysis as well as the energy barrier of macromolecular groups cracking and reconstruction.^{SI6} Furthermore, the initial pyrolysis temperature of WS lowered, and their catalytic cracking accelerated. And the loaded ions strengthened the heat transfer process, leading the TG curves to move toward the high temperature region. The corresponding (dw/dt)_{1max} of Fe/BC was nearly 10% higher than that of BC, which was caused by the decomposition of Fe(OH)₃ supported on the WS at about 330°C, as shown in Eq SI2. Compared with BC and Fe/BC, another two obvious weight loss peaks appeared at 650°C or 850°C in the third stage of FeMn/BC or FeCu/BC, respectively, and the corresponding weight loss rate was faster. It referred that KMnO₄ and CuSO₄ started to decompose at high temperature. The relative equations as follows:

$$2Fe(OH)_3 \xrightarrow{330^\circ C} Fe_2O_3 + 3H_2O \tag{SI2}$$

$$2CuSO_4 \xrightarrow{600^{\circ}C} 2CuO + 2SO_2 + O_2 \tag{SI3}$$

$$4KMnO_4 \xrightarrow{290^{\circ}C} K_2MnO_4 + K_2O \cdot 3MnO_2 + \frac{5}{2}O_2$$
(SI4)

$$3K_2MnO_4 \xrightarrow{650-700^{\circ}C} 2K_3MnO_4 + MnO_2 + O_2$$
 (SI5)

2. Surface Functional Groups.

The Fourier transform infrared spectra of sorbents are shown in Fig. SI2, which can be mainly divided into five regions: the hydroxyl -OH stretching vibration zone (3600-3000cm⁻¹), the aliphatic chain CH_x asymmetric stretching vibration zone (3000-2700cm⁻¹), the oxygen-containing functional group stretching and bending vibration zone (1800-1000cm⁻¹), the metal hydroxyl M-OH vibration zone (1000-900cm⁻¹), and the aromatic C-H bending vibration zone (900-700cm⁻¹). Among them, the absorption peak near to 1700cm⁻¹ was mainly attributed to the stretching vibration of C=O bonds from C=O and COOH functional groups. The peaks around 1600cm⁻¹ and 1200-1350cm⁻¹ belonged to C=C and C-O groups, respectively. And the vibration peak from 1000 to 1200cm⁻¹ mainly corresponded Si-O functional groups.^{SI7,SI8}

As shown, the position of absorption peaks of each sorbent was basically identical, while the intensity of them changed. The Si-O vibration peaks of modified sorbents after removal of ash by acid washing were weakened.^{SI9,SI10} The vibration peaks of -OH were also significantly weakened, which was due to the cross-linking reaction between active metals and biochar as well as the formation of furans during pyrolysis, strengthening the cracking and reforming of internal structure as well as the dehydration reaction.^{SI11} In addition, the absorption peaks of aliphatic and aromatic C-H groups were also weakened to varying degrees. This was because the catalytic action of active metals exacerbated the secondary cracking and dehydrogenation of methyl, methylene groups, and other volatiles, leading to an increase in the amount of

H₂ precipitation.^{SI12} Meanwhile, the catalytic cracking and reforming of semi-volatile organic compounds containing C=O and COOH was promoted after metal modification, causing a decrease in their content. However, Fe, Cu, and Mn ions enhanced partial oxidation of inherent C-O, C=C bonds, and newly oxidized C-O intermediates on the biochar surface to generate a large amount of functional groups containing C=O bonds. Therefore, the absorption peaks intensity of C=O in Fe/BC and FeCu/BC were significantly improved, especially for FeCu/BC. While the peak intensity of C=O in FeMn/BC was substantially retained, which was attributed to the strong oxidation of KMnO₄.^{SI13} Numerous studies showed that volatile Hg⁰ could be oxidized into low-volatile Hg²⁺ by C=O and COOH in the flue gas, and adsorbed on the surface of sorbents stably in the form of Hg-OM complex.^{SI14} And their adsorption capacity could be greatly facilitated by raising temperature appropriately. Additionally, the relative content of aromatic skeleton C=C and aromatic -CH of modified biochar reduced, which were the main components of aromatic rings. It could be concluded that the aromaticity and graphitization degree of modified biochar decreased in comparison with BC, so as to the reactivity was improved, which was consistent with the above XRD results.





Fig. SI1 Pyrolysis curves of modified and unmodified WS: (a) TG curves; (b) DTG curves



Fig. SI2 Fourier transform infrared spectra of sorbents



Fig. SI3 The penetration coefficient for Hg⁰ of the modified biochar: (a) BC; (b) Fe/BC; (c) FeCu/BC; (d) FeMn/BC

Tables

 T_1 T_2 T_3 T_4 $(dw/dt)_{1max}$ (dw/dt)_{2max} V (dw/dt)_{mean} $\Delta T_{(1/2)}$ Sorbents D °C °C °C °C °C %/min %/min % %/min 1.12×10⁻⁵ BC 242 353 532 -5.91 69.08 -0.87 372 / / / Fe/BC 240 360 541 / -6.31 75.51 -0.91 281 1.79×10-5 FeCu/BC 166 370 544 851 -6.43 -1.05 79.26 -0.94 280 2.79×10-5 FeMn/BC 365 -6.52 -2.63 79.54 2.29×10-5 217 697 -1.00 286 566

Table SI1. Pyrolysis Parameters of Modified and Unmodified WS

Where, (dw/dt)_{2max} is the maximum weight loss rate corresponding to the third pyrolysis stages (%/min), and

 T_4 is the temperature corresponding to $(dw/dt)_{2max}$ (°C).

Table SI2 Fitting Results of Adsorption Kinetic Models

Sorbents	Pseudo-first-order model		Pseudo-second-order model	
	R ²	$q_e (\mu g/g)$	R ²	$q_e \left(\mu g/g\right)$
BC	0.9908	1.20	0.9936	1.73
Fe/BC	0.9992	119.76	0.9999	237.20
FeCu/BC	0.9999	301.50	0.9999	605.30
FeMn/BC	0.9988	150.86	0.9999	300.52
CSAC	0.9999	123.2	0.9998	245.04

Table SI3 Fitting Results of Adsorption Kinetic Models

Sorbents	Pseudo-first-order model		Pseudo-second-order model	
	R ²	$q_e (\mu g/g)$	R ²	$q_e (\mu g/g)$
AC	0.9999	124.2	0.9998	223.0
PS-KBr	0.9972	38.11	0.9974	67.27
CaCO ₃ /BA	0.9997	5.50	0.9997	9.97

EC/NH ₄ Cl	0.9930	20.58	0.9970	11.14
Fe/BC	0.9992	119.76	0.9999	237.20
FeCu/BC	0.9999	301.50	0.9999	605.30
FeMn/BC	0.9988	150.86	0.9999	300.52

References

(SI1) Fiore, S.; Berruti, F.; Briens, C. Investigation of Innovative and Conventional Pyrolysis of Ligneous and Herbaceous Biomasses for Biochar Production. *Biomass*

Bioenerg. 2018, 119, 381-391. DOI: 10.1016/j.biombioe.2018.10.010

(SI2) Wu, L. Experimental Study on Pyrolysis Characteristics of Walnut Shell. T.

M.S. Thesis, Northwestern University, Xian, Shanxi, China, 2017.

(SI3) Gong, X. Z.; Guo, Z. C.; Wang, Z. Effects of Fe₂O₃ on Pyrolysis Reactivity of Demineralized Higher Rank Coal and Its Char Structure. *J. Chem. Ind. Eng.* 2009, *60*(9), 2321-2326.

(SI4) Pang, Y. J.; Li, T. F.; Chen, Y. S.; etc. Effects of Mineral Additives on Catalytic Pyrolysis Characteristics of Corn Stalk Powder. *Trans. Chin. Soc. Agric. Eng.* 2018, 34 (14), 221-226.

(SI5) Cui, K. Study on Preparation of Bagasse and Eucalyptus Bio-char by Fast Pyrolysis and Its Reactivity. T. M.S. Thesis, Guangxi University, Nanning, Guangxi, China, 2018.

(SI6) Zhou, Z. Y.; Chen, X. M.; Ma, H.; etc. Real-time Monitoring Biomass Pyrolysis via On-line Photoionization Ultrahigh-Resolution Mass Spectrometry. *Fuel* 2019, 235, 962-971. DOI: 10.1016/j.fuel.2018.08.098

(SI7) Dang, Hao.; Liao, Y.; Ng, T. W.; etc. The Simultaneous Centralized Control of Elemental Mercury Emission and Deep Desulfurization from the Flue Gas Using Magnetic Mn–Fe Spinel as a Co-benefit of the Wet Electrostatic Precipitator. *Fuel Process. Technol.* **2016**, *142*, 345-351. DOI: 10.1016/j.fuproc.2015.10.036

(SI8) Fu, P.; Hu, S.; Xiang, J.; etc. Mechanism Study of Rice Straw Pyrolysis by
Fourier Transform Infrared Technique. *Chin. J. Chem.* 2009, *17* (3), 522-529. DOI:
10.1016/S1004-9541(08)60240-2

(SI9) Zhu, H. M.; Yan, J. H.; Jiang, X. G.; etc. Study on Pyrolysis of Typical Medical Waste Materials by Using TG-FTIR Analysis. *J. Hazard. Mater.* 2008, *153* (1-2), 670-676. DOI: 10.1016/j.jhazmat.2007.09.011

(SI10) Park, Y. H.; Kim, J.; Kim, S. S.; etc. Pyrolysis Characteristics and Kinetics of Oak Trees Using Thermogravimetric Analyzer and Micro-tubing Reactor. *Bioresour*. *Technol.* **2009**, *100* (1), 400-405. DOI: 10.1016/j.biortech.2008.06.040

(SI11) Liu, H. H.; Zou, J.; Deng, Y.; etc. Influence of Modified Biomass Char on Releases Characteristics of Volatiles During Pyrolysis of Cotton Stalk. *Trans. Chin. Soc. Agric. Eng.* **2016**, *32* (22), 239-243. DOI: 10.11975/j.issn.1002-

6819.2016.22.033

(SI12) Li, Y. H.; Lee, C. W.; Gullett, B. K. Importance of Activated Carbon's Oxygen Surface Functional Groups on Elemental Mercury Adsorption. *Fuel* **2003**, *82* (4), 451-457. DOI: 10.1016/S0016-2361(02)00307-1

(SI13) Tan, Z. Q. Experimental and Mechanism Study of Elemental Mercury Removal in Flue Gas by Modified Bamboo-Based Sorbents. Ph.D. Thesis, Huazhong University of Science and Technology, Wuhan, Hubei, China, 2012.

(SI14) Zhang, H. W.; Shi, H. J.; Chen, J. Y.; etc. Elemental Mercury Removal from Syngas at High-temperature Using Activated Char Pyrolyzed from Biomass and Lignite. *Korean J. Chem. Eng.* **2016**, *33* (11), 3134-3140. DOI: 10.1007/s11814-016-0182-7

(SI15) Fan, B. G.; Jia, L.; Wang, Y. L.; etc. Study on Adsorption Mechanism and Failure Characteristics of CO₂ Adsorption by Potassium-Based Adsorbents with Different Supports. *Materials* **2018**, *11*(12), 2424-2444.

(SI16) Jia, L.; Li, B.; Xu, L.; etc. Effect of Different Preparation Conditions on Mercury Adsorption Characteristics and Kinetics of Biochar. *Chin. J. of Environ. Eng.* 2018, *12* (1), 134-144.

(SI17) He, N. Study on Adsorption Performance and Kinetics of Gaseous Elemental Mercury on Modified Biomass Char. T. M.S. Thesis, Nanjing Normal University, Nanjing, Jiangsu, China, 2014.

(SI18) Fu, S. M. Study on Mercury Removal Performance and Kinetics of Calciumbased Adsorbent Modified by Biomass Ash. T. M.S. Thesis, Nanjing Normal University, Nanjing, Jiangsu, China, 2018.

(SI19) Xu, W. Study on Mercury Removal from Coal-Fired Flue Gas by Metal Oxides/Halides Modified Bio-Chars. T. M.S. Thesis, Jiangsu University, Nanjing, Jiangsu, China, 2018.

(SI20) Zhou, Q.; Duan, Y. F.; Mao, Y. Q.; etc. Kinetics and Mechanism of Activated Carbon Adsorption for Mercury Removal. *Proc. Chin. Soc. Elect. Eng.* **2013**, *33* (29), 10-17+2.