Pyrolysis temperature-driven structural evolution of wheat straw biochar and enhanced adsorption mechanisms for Cr(VI)

Jiajia He[ǀ], Bo Meng[ǀ], Haiyang Qi, Haoyu Fan, Miao Long, Mengjin Yu, Xianming Bao[*], Lichao Zhang[**]

Anhui Province Key Laboratory of Pollutant Sensitive Materials and Environmental Remediation,

Huaibei Normal University, Huaibei, 235000, PR China

[ǀ] Jiajia He and Bo Meng contributed equally to this paper.
[*] Corresponding Author.
[**] Corresponding Author.
E-mail address: xmbao96@126.com (X. Bao), moerboy6@163.com (L. Zhang).

SI. 1 Determination of Cr(VI) Concentration: Diphenylcarbazide (DPCI) Method

The DPCI reagent was prepared as follows: 0.2 g of diphenylcarbazide was weighed using an analytical electronic balance and dissolved in 50 mL of acetone. The solution was transferred into a 100 mL brown volumetric flask, diluted to the mark with deionized water, and mixed thoroughly. The reagent was stored in a refrigerator at 4 °C in the dark. It should not be used if the solution turns dark.

For the determination, 0.5 mL of sulfuric acid (1:1, v/v) and 0.5 mL of phosphoric acid (1:1, v/v) were added to the sample solution, followed by the addition of 2 mL of the DPCI solution. Under acidic conditions, Cr(VI) reacted with DPCI to form a violet-red complex. After standing for 10 min, the absorbance was measured at 540 nm (UV-vis spectrophotometer).

SI. 2 Background Ion Experiment

To investigate the influence of potassium salts on Cr(VI) adsorption, a background ion experiment was conducted. Biochar samples (0.1 g) were added to 30 mL of Cr(VI) solution with an initial concentration of 80 mg/L, containing varying concentrations of K^+ (0, 0.005, 0.02, and 0.1 mol/L) prepared from KCl. The mixtures were shaken at 120 rpm and 25 ± 0.5 °C for 24 h. After adsorption, the residual Cr(VI) concentration was measured, and the adsorption capacity was calculated. The results showed that as the K^+ concentration increased from 0 to 0.1 mol/L, the adsorption capacity of WS300 decreased from 9.34 mg/g to 6.35 mg/g, and that of WS500 decreased from 12.20 mg/g to 6.66 mg/g, indicating that the presence of potassium salts inhibited Cr(VI) adsorption.

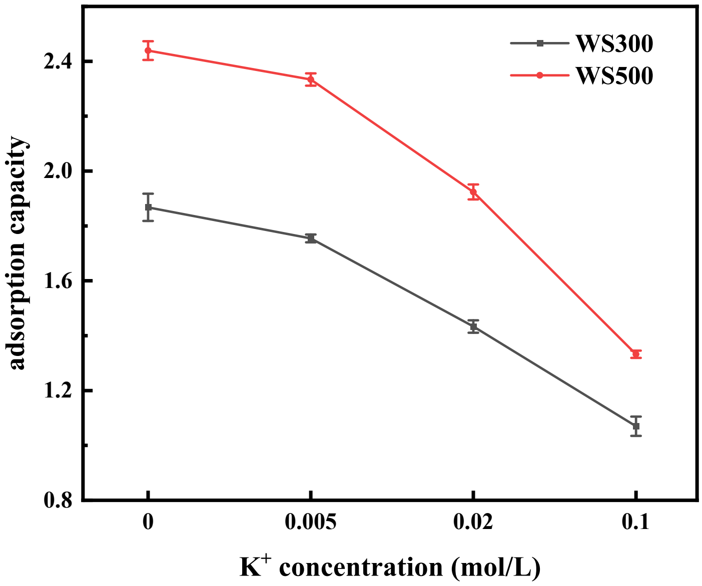

Fig. S1. Effect of K^+ concentration on Cr(VI) adsorption capacity of biochar samples WS300 and WS500 (initial Cr(VI) concentration: 80 mg/L, biochar dosage: 0.1 g, solution volume: 30 mL, K^+ concentration range: 0-0.1 mol/L).

SI. 3 Control XPS Analysis of $K_2Cr_2O_7$

To verify the reliability of Cr speciation analysis and to evaluate whether X-ray-induced reduction occurred under the measurement conditions, a control experiment was performed by analyzing a pure $K_2Cr_2O_7$ solid sample. The Cr 2p spectrum of this reference sample is presented in Fig. S2. Two distinct peaks were observed at binding energies of 579.9 eV and 588.4 eV, corresponding to the Cr $2p_{3/2}$ and Cr $2p_{1/2}$ spin–orbit components of Cr(VI), respectively. Notably, no peaks characteristic of Cr(III) were detected in the spectrum. This result demonstrates that under the XPS measurement conditions used in this study, X-ray-induced reduction of Cr(VI) to Cr(III) is negligible.

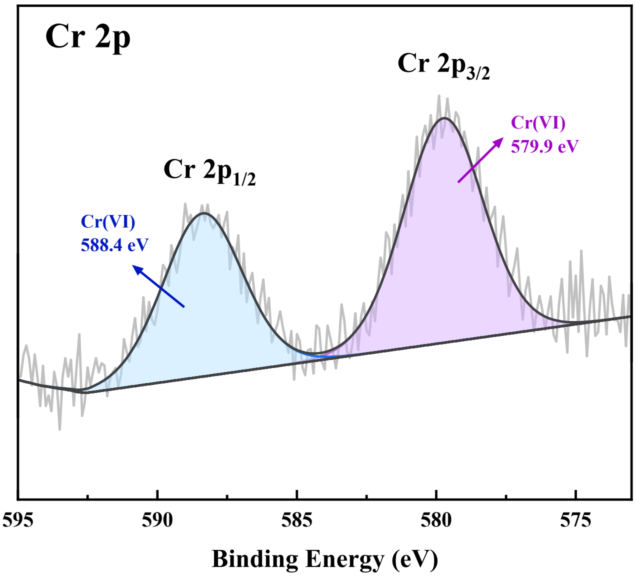

Fig. S2. Cr 2p XPS spectrum of pure $K_2Cr_2O_7$ reference sample.

SI. 4 Diffuse reflectance spectroscopy (DRS) Analysis of Post-Reaction Biochar

To evaluate the presence of chromium species on the biochar surface after adsorption, DRS was performed on the post-reaction samples. Pure $K_2Cr_2O_7$ and $CrCl_3 \cdot 6H_2O$ solid powders were first analyzed as positive controls to validate the method, and their DRS spectra exhibited characteristic absorption features corresponding to Cr(VI) and Cr(III), respectively, confirming the capability of the instrument and method to detect chromium species.

However, for the biochar sample after adsorption (WS500-Cr), no discernible chromium-related signals were observed. To further verify this result, a control sample was prepared by spiking the biochar with a Cr^{3+}/Cr^{6+} mixed solution at a concentration of 20 mg/g (WS500+Cr(III)+Cr(VI)). Even in this artificially enriched sample, no characteristic peaks for chromium were detected. This may be due to the strong background absorption of the biochar matrix, which could overshadow the relatively weak characteristic absorption signals of chromium species. Therefore, under the present experimental conditions, DRS did not yield detectable chromium signals from the biochar samples.

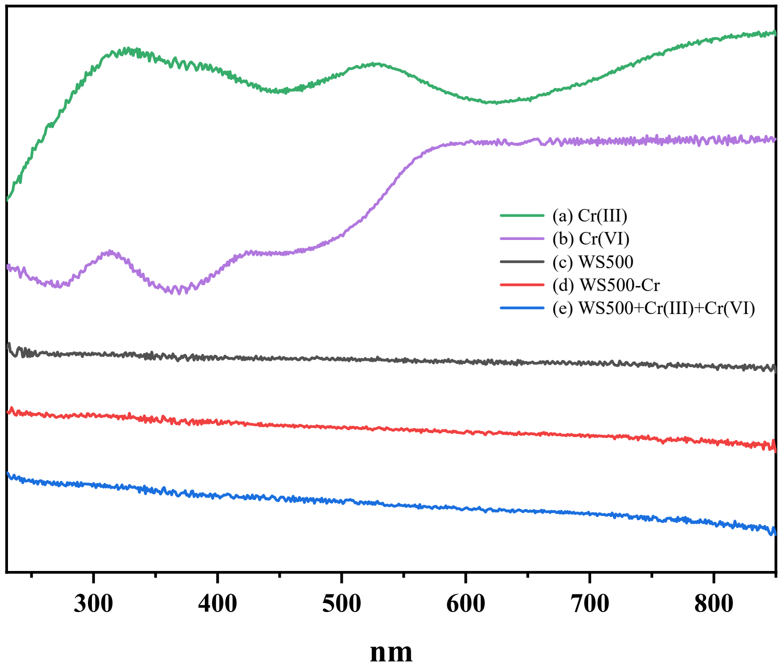

Fig. S3. DRS spectra of reference chromium compounds and biochar samples: (a) pure $CrCl_3 \cdot 6H_2O$; (b) pure $K_2Cr_2O_7$; (c) WS500; (d) WS500-Cr (post-adsorption biochar sample); (e) WS500+Cr(III)+Cr(VI) (biochar spiked with Cr^{3+}/Cr^{6+} mixed solution at 20 mg/g).