

1 **Mechanistic insights into Cr(VI) removal by acid modified**
2 **biochar via coupled redox and complexation processes**

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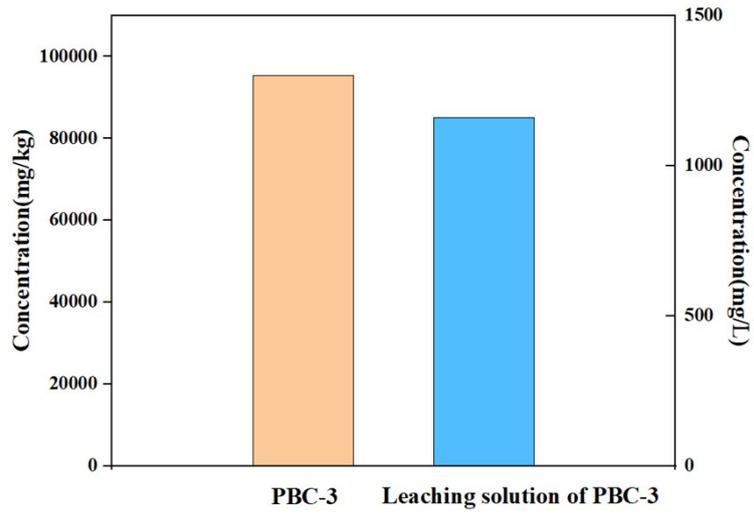
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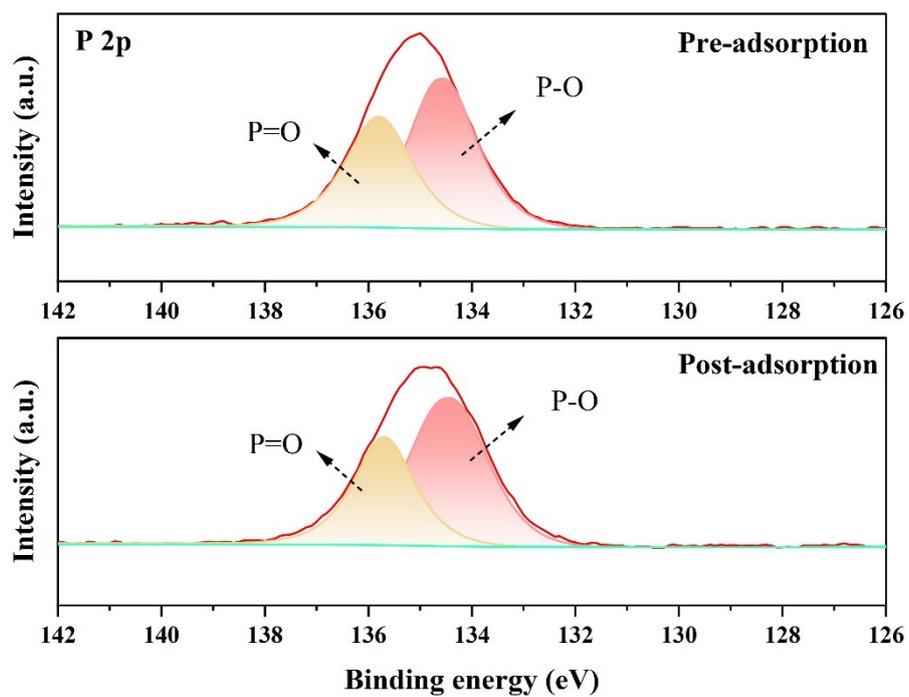
47 adsorbents.



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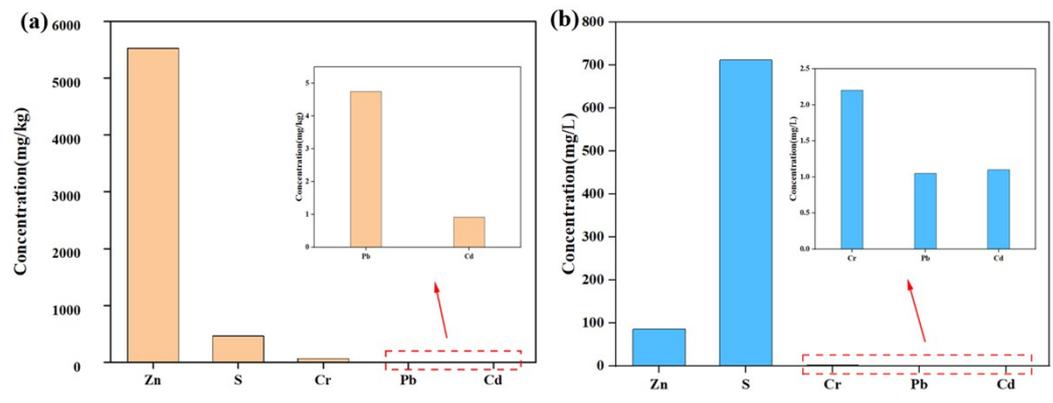
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Figure S1. Contents of P in PBC-3 and its leaching solution.



52

53 **Figure S2.** XPS spectrum P2p fine spectrum of PBC-3 before and after adsorption.



55

56 **Figure S3.** Contents of Zn, S, Cr, Pb and Cd in PBC-3 (a) and its leaching solution

57

(b).

59 **Text S1. Materials and reagents**

60 NaNO_3 , NaCl , Na_2SO_4 , and ethanol ($\text{C}_2\text{H}_5\text{OH}$) were purchased from Guangdong
61 Guanghua Sci-Tech Co., Ltd. (Guangdong, China). HCl , H_2SO_4 , and $\text{K}_2\text{Cr}_2\text{O}_7$ were
62 obtained from Sichuan Xilong Science Co., Ltd. (Sichuan, China). NaOH , H_3PO_4 and
63 $\text{C}_3\text{H}_6\text{O}$ were purchased from Chengdu Kelong Chemical Co., Ltd. (Sichuan, China).
64 Diphenylcarbazide ($\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$) was obtained from Tianjin Damao Chemical Reagent
65 Factory. (Tianjin, China). Humic acid ($\text{C}_9\text{H}_9\text{NO}_6$) and fulvic acid ($\text{C}_{14}\text{H}_{12}\text{O}_8$) were
66 purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai,
67 China). All the above reagents are analytical grade. Furthermore, the lake water was
68 collected from the Little West Lake at Northwest A&F University (Shaanxi, China),
69 and the river water was obtained from Weihe (Shaanxi, China).

71 **Text S2. Characterization of chemical properties of biochar**

72 The morphological characteristics of biochar before and after modification were
73 determined by scanning electron microscope (FESEM, NanoSEM 450, FEI). The
74 functional groups of biochar before modification and after modification, before
75 adsorption and after adsorption were examined using the Fourier transform infrared
76 spectroscopy (FTIR, Vetex70, Bruker) in the range of 4000–400 cm^{-1} and X-ray
77 photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher Scientific). The
78 biochar before and after modification of straw and tire were degassed using Brunauer
79 Emmett Teller (BET, Micromeritics ASAP2020 HD88, USA) at 120°C, and then N₂
80 isothermal adsorption-desorption method was used to test the biochar. The Cr2p
81 Raman spectra of modified biochar before and after adsorption of Cr(VI) were
82 analyzed by Raman spectrometer (Roman, Horiba LabRam HR Evolution) at an
83 excitation wavelength of 532 nm.¹

85 **Text S3. Adsorption kinetic modeling**

86 The obtained data were fitted using the pseudo-first-order and the pseudo-second-
87 order kinetic and the intra-particle diffusion models expressed by Eqs. (1)-(3):^{2, 3}

88
$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

89
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

90
$$q_t = k_p t^{0.5} + C \quad (3)$$

91 where q_e and q_t ($\text{mg}\cdot\text{g}^{-1}$) are the adsorption capacity of the adsorbent at adsorption
92 equilibrium and time t . k_1 is a pseudo-first-order reaction rate constant, k_2 is the
93 pseudo-second-order reaction rate constant, k_p is the intraparticle diffusion rate
94 constant, t (h) is the adsorption time, C it is a constant ($\text{mg}\cdot\text{g}^{-1}$) related to the
95 thickness of the boundary layer.⁴

97 **Text S4. Adsorption Isotherm Analysis**

98 The adsorption isotherm model could be used to describe the relationship between
99 the adsorbent and the adsorbate in the solution under equilibrium state. The Cr(VI)
100 solution with initial concentration of 10, 20, 30, 40, 50 mg·L⁻¹ was prepared, and
101 three experimental groups were set up. The other experimental conditions were
102 consistent with the above. Two commonly used isotherms were investigated which
103 are Langmuir, and Freundlich,⁵ and the corresponding expressions used and are given
104 by Eqs. (4) and (5):

105
$$q_e = (q_m \cdot K_L \cdot C_e) / (1 + K_L \cdot C_e) \quad (4)$$

106
$$q_e = K_F \cdot C_e^{1/n} \quad (5)$$

107 whereby q_e (mg·L⁻¹) is the equilibrium concentration of Cr(VI) in solution, q_m
108 (mg·g⁻¹) is the maximum adsorption capacity of the adsorbent for Cr(VI), C_e (mg·g⁻¹)
109 is the amount of Cr(VI) adsorbed per unit mass of adsorbent at adsorption equilibrium.
110 K_L is the Langmuir constant related to the affinity of the adsorption site, K_F is the
111 Freundlich constant, $1/n$ is adsorption index.⁶

113 **Text S5. Systematic investigation of key factors governing adsorption efficiency**

114 The effect of solution pH was done in the pH range of (2.0 to 8.0) and it was
115 adjusted using $0.1 \text{ mol}\cdot\text{L}^{-1}$ of NaOH and HCl. The effect of the biochar dosage was
116 investigated between (1.5 to 5 g/L) whereas the effect of ionic strength (NaCl,
117 Na_2SO_4 , NaNO_3) was evaluated within the range of 100-500 $\text{mg}\cdot\text{L}^{-1}$. All experimental
118 procedures were conducted in triplicate under consistent ambient conditions
119 maintained at 25°C .

121 **Text S6. Reusability and complex water matrix effects on Cr(VI) adsorption**

122 The straw and waste TWPs-based modified biochar was investigated for four
123 cycles of the adsorption/desorption process. A Cr(VI) solution with an initial
124 concentration of $30 \text{ mg}\cdot\text{L}^{-1}$ was prepared. Then, 20 mL aliquots were transferred into
125 30 mL brown glass bottle. The initial pH of the solution was adjusted to 2.0, followed
126 by the addition of 1.5 g/L of PBC-3. The mixtures were oscillated at 120 rpm in a
127 thermostatic shaker at 25°C . At predetermined time intervals, samples were collected
128 and filtered, and the Cr(VI) concentration in the filtrate was measured after 24 h.
129 After adsorption, the modified biochar was filtered, rinsed with deionized water and
130 anhydrous ethanol, and desorbed at 120°C for 24 h before being reused for subsequent
131 adsorption cycles. This adsorption-desorption process was repeated four times.

132 Cr(VI) solutions with an initial concentration of $30 \text{ mg}\cdot\text{L}^{-1}$ were prepared using
133 deionized water, tap water, lake water, and river water, respectively. Additional
134 Cr(VI) solutions ($30 \text{ mg}\cdot\text{L}^{-1}$) containing humic acid (HA) or fulvic acid (FA) at
135 concentrations of 0, 10, 20, 30, 40, and $50 \text{ mg}\cdot\text{L}^{-1}$ were also prepared. For each
136 experiment, 20 mL of the solution was transferred into a 30 mL narrow-mouth brown
137 bottle. The initial pH was adjusted to 2.0, and $1.5 \text{ g}\cdot\text{L}^{-1}$ of PBC-3 was added. The
138 mixtures were shaken at 120 rpm in a thermostatic oscillator at 25°C . At designated
139 time intervals, samples were filtered, and the Cr(VI) concentration in the filtrate was
140 measured after 24 h.

142 **Table S1.** Pore structure parameters of biochar

Name	Specific surface area (m²·g⁻¹)	Porosity (cm³·g⁻¹)	Average pore size (nm)
BC-3	30.10	0.07	7.81
PBC-3	132.33	0.12	24.20

143

145 **Table S2.** The model parameters related to the adsorption of Cr(VI) by modified
 146 biochar

Kinetic Model		Parameter	
Pseudo-first order kinetic model	$q_{e,1}(\text{mg/g})$	k_1	R_1^2
	10.08	0.670	0.968
Pseudo-second-order kinetic model	$q_{e,2}(\text{mg/g})$	k_2	R_2^2
	10.85	0.087	0.984
Intra-particle diffusion model	k_{1d1}	$C_1(\text{mg/g})$	R_1^2
	6.077	-1.097	0.826
	k_{1d2}	$C_2(\text{mg/g})$	R_2^2
	0.805	7.198	0.999
	k_{1d3}	$C_3(\text{mg/g})$	R_3^2
	0.238	9.002	0.997

149 **Table S3.** The adsorption isotherm model parameters of modified biochar for Cr(VI)

Model	Parameter		
Langmuir	R^2	K_L	$Q_m(mg/g)$
	0.994	0.410	14.59
Freundlich	R^2	K_F	n
	0.928	5.345	2.832

152 **Table S4.** Maximum adsorption capacities for Cr(VI) on PBC-3 compared with other
153 adsorbents.

Adsorbent	pH	Adsorption capacity(mg/g)	Reference
PBC-3	2	10.85	Present study
Apple wood biochar	2	5.14	7
Pineapple peel biochar	4	7.44	8
Soybean stoverbiochar	3	6.48	9
Oak wood and oak bark biochar	2	4.93	10
Amino-functionalized biochar	3	3.80	11

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