Removal of Cr(VI) from wastewater by Fe-Mn oxides loaded sludge biochar

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Adsorption models

Adsorption kinetic models

The pseudo-first-order model (Eq. 1), the pseudo-second-order model (Eq. 2), Elovich model (Eq. 3), the intraparticle diffusion model (Eq. 4) and Film diffusion model (Eq. 5) were used for fitting analysis.

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

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

$$q_t = \beta \ln(\alpha\beta) + \beta \ln(t) \quad (3)$$

$$q_t = K_{id} t^{1/2} + C_i \quad (4)$$

$$\ln(1 - F) = K_{fd} t + C_{fd} \qquad F = \frac{q_t}{q_e} \quad (5)$$

where q_e and q_t are the adsorption capacity at the equilibrium time and time "t" time (mg/g), respectively; k_1 and k_2 represent adsorption rate constant of the pseudo-first-order (min^{-1}) and the pseudo-second-order (g/mg·min), respectively; α and β are the initial absorbance (mg/g·min) and desorption constant (g/mg), respectively; K_{id} [mg/(g·$min^{1/2}$)] is rate constants of intra-particle diffusion; C_i is constant of the intra-particle diffusion model. K_{fd} and C_{fd} are rate constant and constant of film diffusion model, respectively.

Adsorption isotherm models

The Langmuir model (Eq. 6, and Eq. 7), Freundlich model (Eq. 8), Temkin model (Eq. 9) and Sips model (Eq. 10) were used to fit these data.

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}, \quad (6)$$

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

$$q_e = K_f C_e^{1/n} \quad (8)$$

$$q_e = \frac{RT}{b_T} \ln(A_T C_e)$$

（9）

$$q_e = \frac{Q_m (K_s C_e)^{1/m}}{1 + (K_s C_e)^{1/m}} \quad (10)$$

where q_e is the adsorption capacity at equilibrium (mg/g); C_e is the concentration of Cr(VI) ions at adsorption equilibrium (mg/L); q_{max}, K_L and R_L are the maximum adsorption capacity of Cr(VI) ions (mg/g), Langmuir equilibrium constant (L/mg) and separation factor, respectively; K_f and n represent the Freundlich affinity coefficient ($mg^{1-n} \cdot L^n/g$) and Freundlich constant related to the surface site heterogeneity, respectively; A_T (1/g) and b_T (kJ/mol) are Temkin constants; R is the global constant of gases, and T is the absolute temperature (K); K_s (L/mg), C_s and m are Sips constants.

Additionally, to ensure the correctness of the fit of the non-linear kinetic model, the chi-square test will be used to check how well the model fits. Obtained by judging the sum squares differences between the experimental and the calculated data, with each squared difference is divided by its corresponding value (calculated from the models). Small χ^2 value indicates its similarities while a larger number represents the variation of the experimental data.

The thermodynamic investigation of Cd(II) removal at different temperatures (288 K, 298 K, and 308 K). The thermodynamic parameters for the removal process were calculated using Eq. (11) and Eq. (12), and the relevant parameters were listed in Table 3.

$$\ln K^0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (11)$$

$$\Delta G^0 = -RT \ln K^0 \quad (12)$$

where, R is the gas constant (8.314 kJ/mol). K^0 is the equilibrium constant and T is the Kelvin temperature (K). The ΔG^0, ΔH^0 and ΔS^0 represent the standard free energy (kJ/mol), enthalpy (J/mol), and entropy (J/mol), respectively. The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the linear regression curve of $\ln K^0$ versus $1/T$ (Fig. S2d).

Characterization

Pore structure parameters were measured by a specific surface area analyzer (BET, Tristar II Plus 2.02, USA) and analyzed by BET method. Scanning electron microscopy with energy dispersive spectrometer (SEM-EDS, JSM-7500F, JEOL, Japan). The material composition of the samples was surveyed by a X diffraction analyzer (XRD, D8X, Bruker, Germany). A X-ray photoelectron spectrometer (XPS, Escalab 250Xi, Thermo Fisher Scientific, USA) was used to analyze the elemental composition and valence changes of the samples. The functional groups were investigated using a Fourier Transform Infrared Spectroscopy (FTIR, Nicolet-460, Thermo Fisher, USA). The zeta potential of different pH solution was measured by using a zeta potential analyzer (Zetasizer, Malvern, UK).

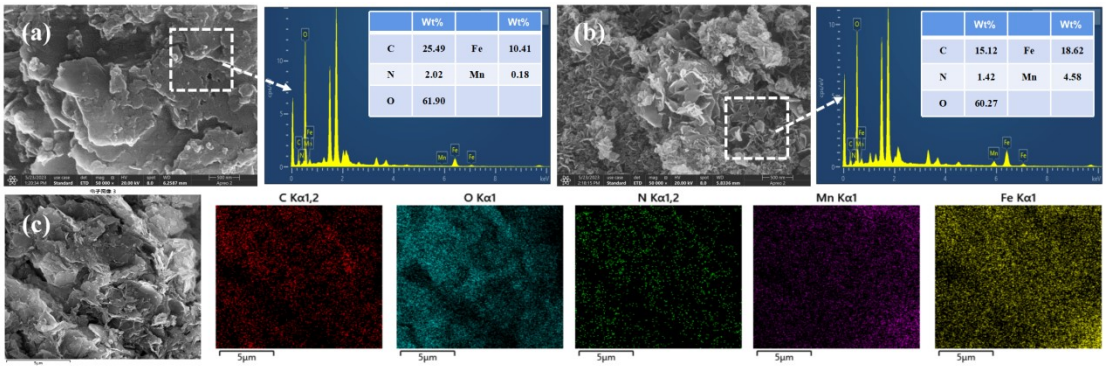

Fig. S1 SEM-EDS analysis of BC and FMBC (a: BC, b: FMBC and c: surface elements mapping of FMBC).

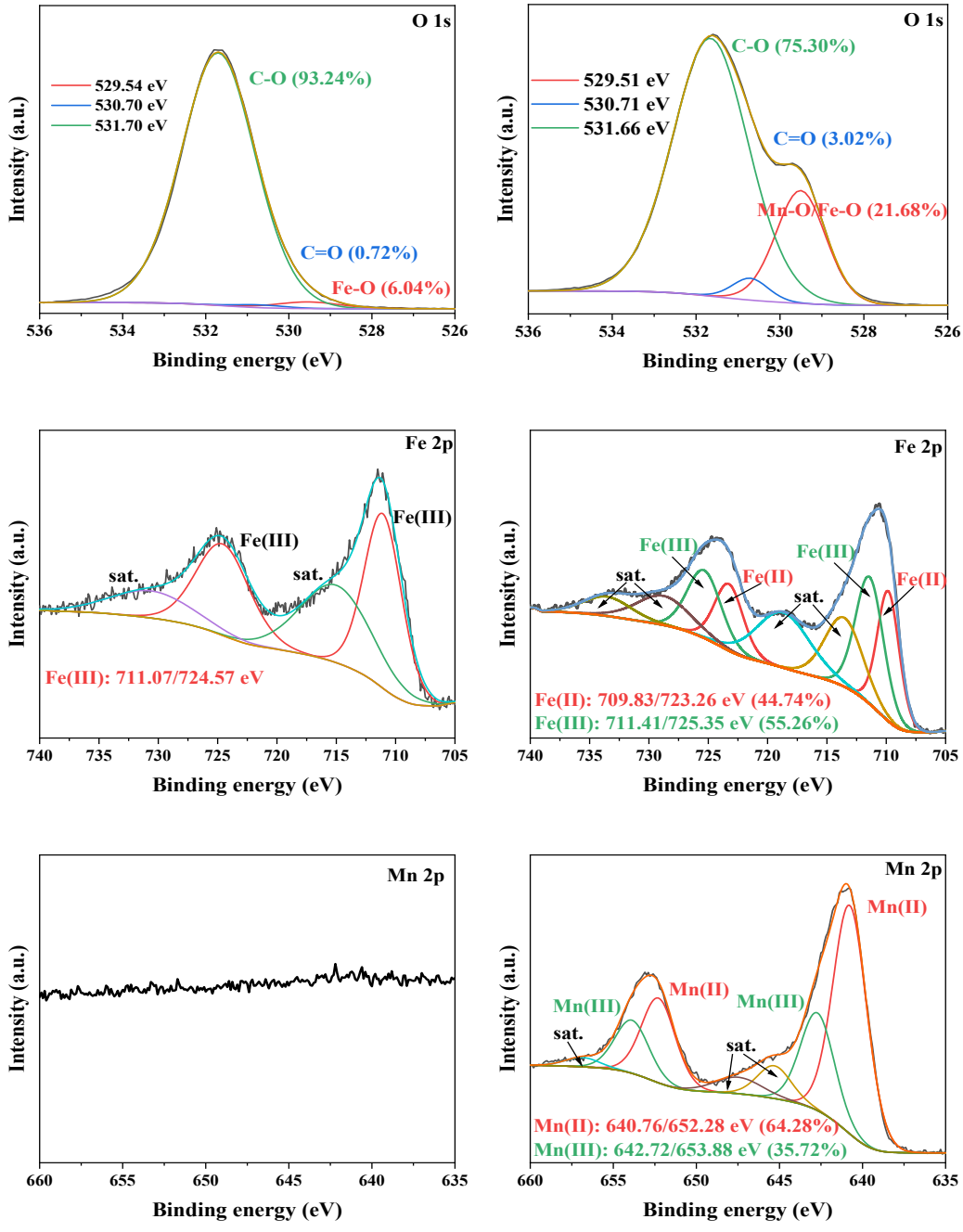

Fig. S2 XPS High-resolution mapping of O 1s, Fe 2p and Mn 2p in BC (a, c and e) and FMBC (b, d and f).

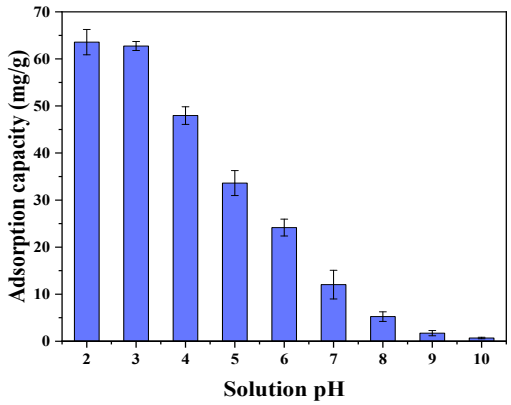

Fig. S3 Influence of solution pH on removing Cr(VI) for BC.

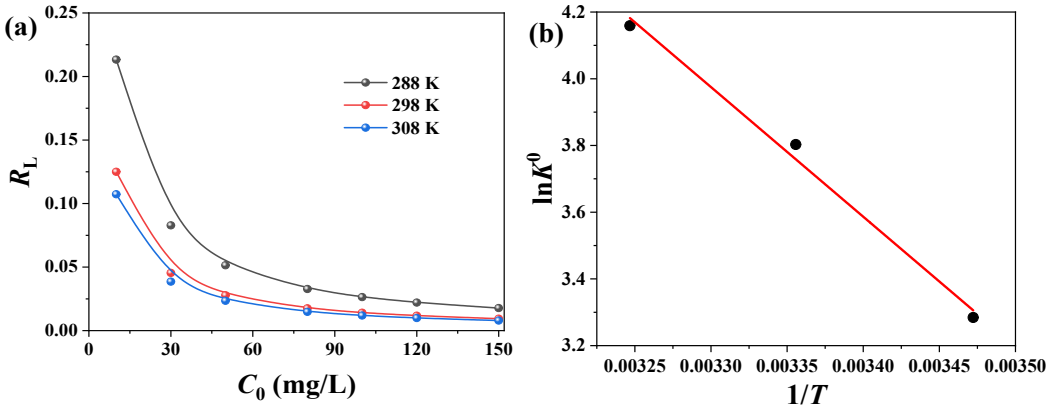

Fig. S4 The R_L value of FMBC (a) and lot of lnK^0 versus 1/T for the estimation of thermodynamic parameters (b).

Table S1 Properties of electroplating wastewater and mineral dissolving wastewater

	Electroplating wastewater	Mineral dissolving wastewater
	Concentration (mg/L)	Concentration (mg/L)
pH	2.19	6.76
Total Cr	43.70	1.54
Cr(VI)	40.21	1.35
Cu	2.89	0.32
Zn	19.48	0.53
Pb	3.04	0.89
Cl^-	315.61	112.63

SO2- 4	115.94	68.09
NH+ 4	60.18	35.42
PO3- 4	7.03	2.87

Table S2 Intra-particle diffusion and liquid film diffusion model for Cr(VI) removal by FMBC

Model	Parameter	Fitting result
Intra-particle diffusion	C_1	12.595
	K_{d1} (mg/g·min$^{1/2}$)	15.140
	R2 1	0.930
	C_2	74.866
	K_{d2} (mg/g·min$^{1/2}$)	3.475
	R2 2	0.929
	C_3	111.626
	K_{d3} (mg/g·min$^{1/2}$)	0.285
	R2 3	0.981
Liquid film diffusion	K_{fd}	-0.025
	C_{fd}	-0.579
	R^2	0.990