

### Data analysis

The initial adsorption rate ( $h$ ) equation was as follows.

$$h = k_2 q_e^2$$

The normalized standard deviation (NSD) and average relative error (ARE), indicating the validity of kinetic models, are defined as:

$$NSD = 100 \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left[ \frac{(q_{ti}^{exp} - q_{ti}^{cal})}{q_{ti}^{exp}} \right]^2}$$
$$ARE = \frac{100}{N} \sum_{i=1}^N \left| \frac{(q_{ti}^{exp} - q_{ti}^{cal})}{q_{ti}^{exp}} \right|$$

where  $q_{ti}^{exp}$  and  $q_{ti}^{cal}$  (mg/g) are experimental and calculated Cr(VI) adsorbed on MnS@biochar at time  $t$  and  $N$  is the number of measurements made. The smaller NSD and ARE values reveal more accurate estimation of  $q_t$  values. The governing equations of the three models are integrated by applying the boundary conditions  $q = 0$  at  $t = 0$

The Marquardt's percent standard deviation (MPSD) and the hybrid error function (HYBRID) indicated the validity of adsorption isotherm:

$$MPSD = 100 \sqrt{\frac{1}{N-P} \sum_{i=1}^N \left( \frac{q_{ei}^{exp} - q_{ei}^{cal}}{q_{ei}^{exp}} \right)^2}$$
$$HYBRID = \frac{100}{N-P} \sum_{i=1}^N \left| \frac{(q_{ei}^{exp} - q_{ei}^{cal})^2}{q_{ei}^{exp}} \right|$$

where  $q_{ei}^{exp}$  is the data from the batch experiment  $i$  (mg/g),  $q_{ei}^{cal}$  is the estimated value from the isotherm for corresponding  $q_{ei}^{exp}$  (mg/g),  $N$  is the number of observations in experimental isotherm, and  $P$  is the number of parameters in regression model. The smaller MPSD and HYBRID values indicate more accurate estimation of  $q_e$  values.

### Figures

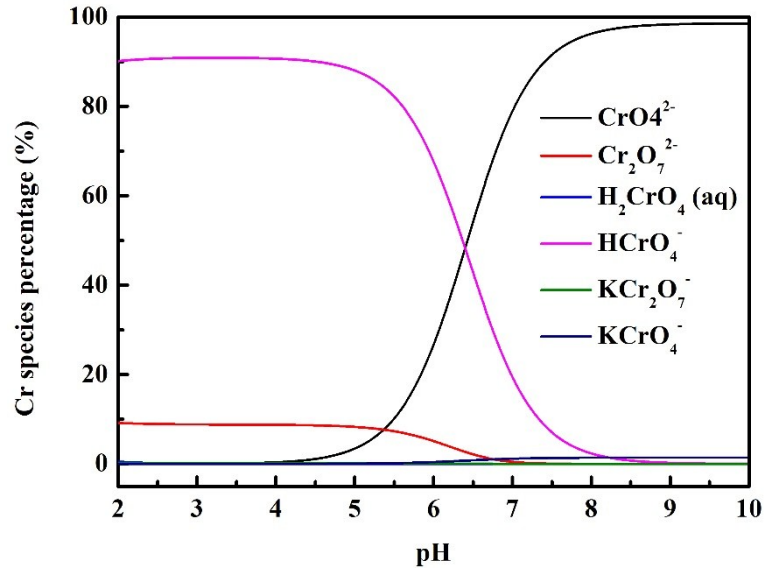


Fig. S1 Cr species percentage as the function of pH (Condition:  $C_{Cr(VI)}=150$  mg/L)

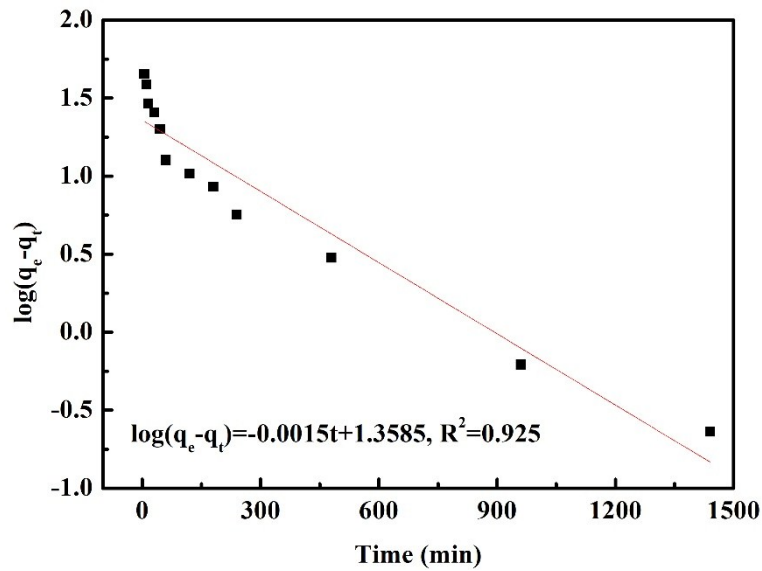
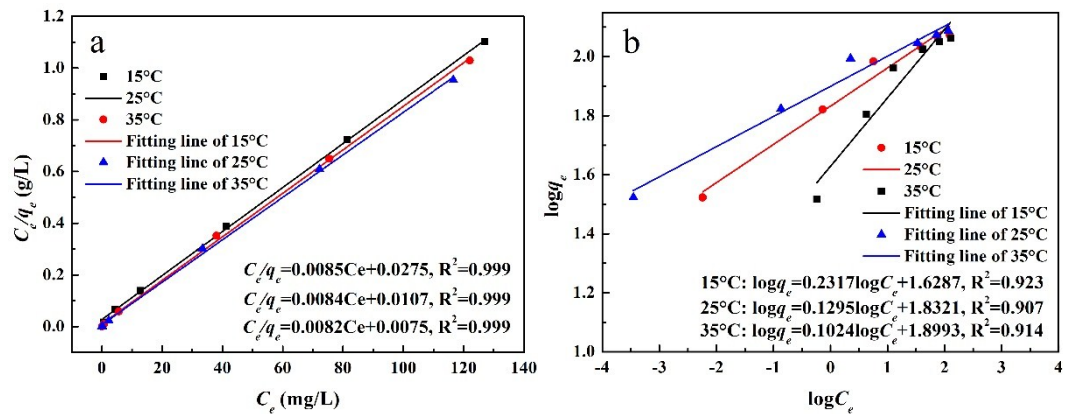


Fig. S2 The pseudo first-order kinetic model fitting line



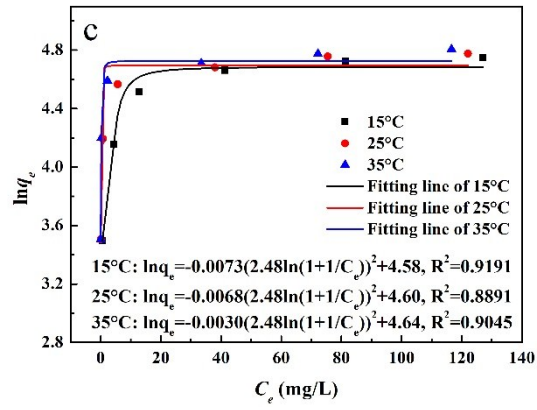


Figure S3 The fitting results of adsorption isotherms models (a: Langmuir model, b: Freundlich model, c: Dubinin-Radushkuvich model)

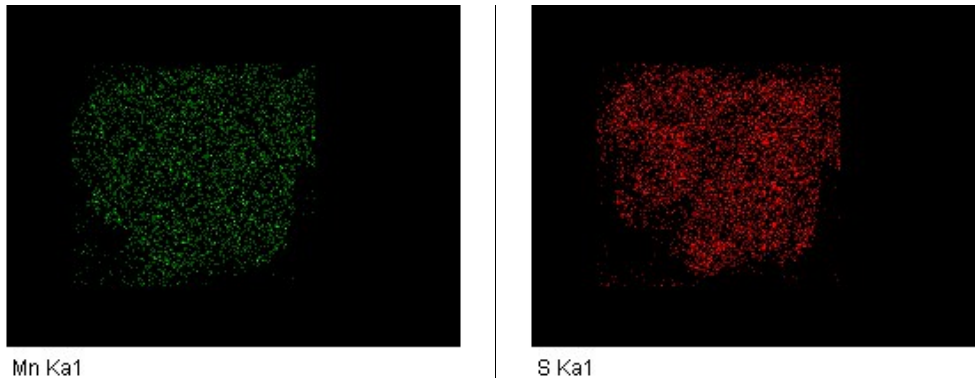
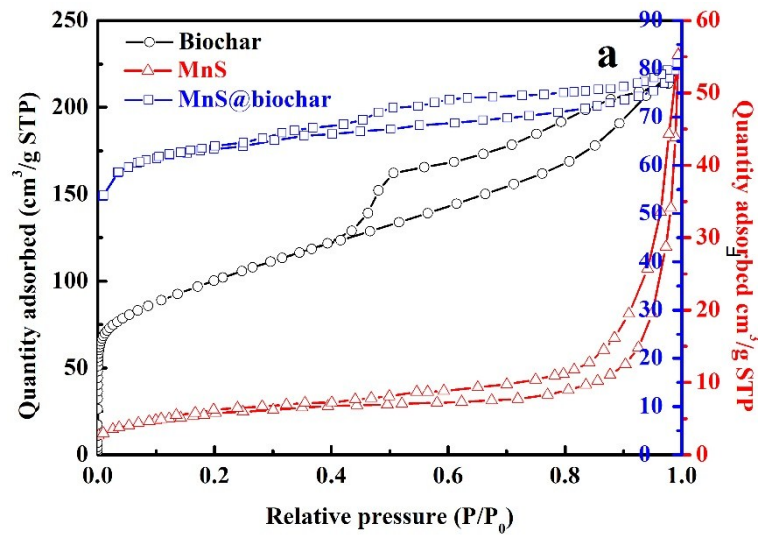


Figure S4 EDS analysis of F-MnS@biochar



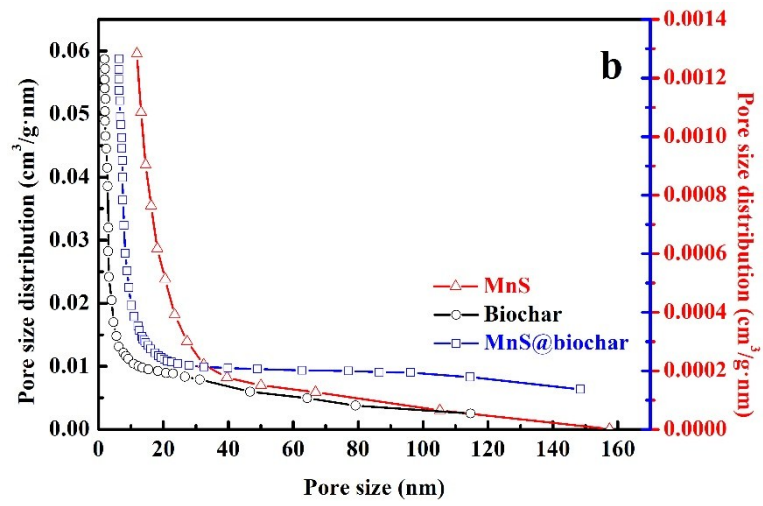


Fig. S5 The specific surface areas (a) and porous structures (b) of MnS, biochar, and

F-MnS@biochar

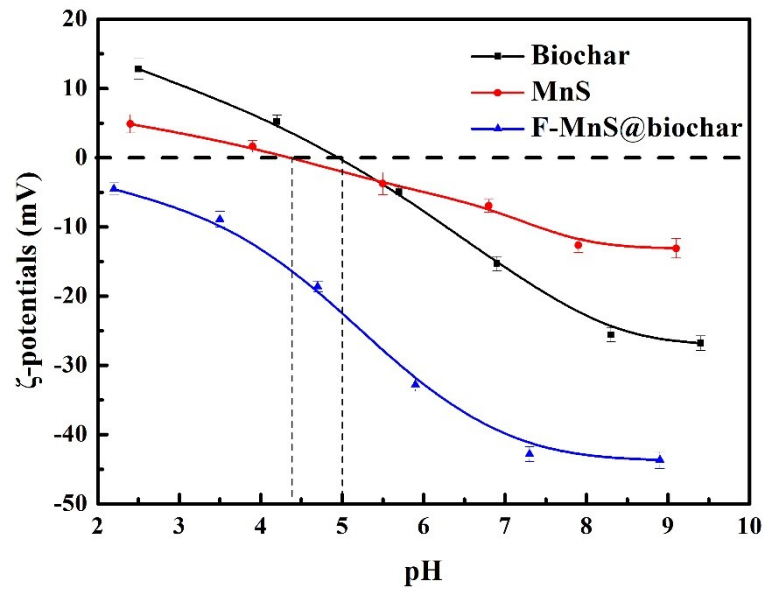
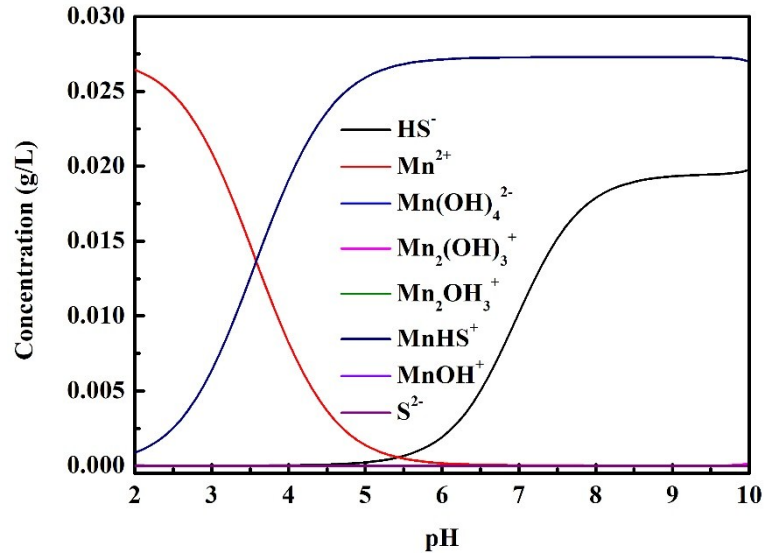


Fig. S6  $\zeta$ -potentials of biochar, MnS, and F-MnS@biochar



**Fig. S7** MnS hydrolysis as the function of pH (Condition:  $C_{\text{MnS}}=1.5$  g/L)

## Tables

**Table S1** The fitting parameters of pseudo first-order model and pseudo second-order model used for simulating Cr(VI) adsorption kinetic data

Model	$k_1/k_2$	$q_e$	$h_1/h_2$	$R^2$	NSD	ARE
PFO	0.0035	22.83	0.08	0.925	62.1	55.3
PSO	0.0306	98.04	9.02	0.999	11.6	8.7

**Table S2** The Cr(VI) removal amounts of different biochar materials

Material	$Q_e$	Ref.
CMC-FeS@biochar	130.5 mg/g	1
ZVI-biochar	17.8 mg/g	2
Fe-biochar	67.44 mg/g	3
$\beta$ -FeOOH/SYBK	37.04 g kg <sup>-1</sup>	4
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -NH <sub>2</sub> -biochar	27.2 mg/g	5
Fe <sub>3</sub> O <sub>4</sub> @biochar	25.27 mg/g	6

**Table S3** Regression parameters of adsorption isotherm data of Cr(VI) onto MnS@biochar by Langmuir, Freundlich, Redlich-Peterson, and Dubinin-Radushkevich models

Temperature	Model	Parameters	MPSD	HYBRID
15° C	Langmuir	$q_m=117.65; b=0.3091; R^2=0.999$	9.51	4.88
	Freundlich	$n=4.3159; k_2=42.53; R^2=0.923$	44.75	21.91
	Redlich-Peterson	$K_R=93.34; \alpha = 1.27; \beta= 0.9083; R^2=0.977$	4.86	1.48
	Dubinin-Radushkevich	$q_m = 97.51 \text{ mg/g}; K_D = 0.0073; E= 8.28$	38.95	17.24
25° C	Langmuir	$q_m=119.05; b=0.7850; R^2=0.999$	17.35	3.26
	Freundlich	$n=7.7220; k_2=67.94; R^2=0.907$	38.26	18.73
	Redlich-Peterson	$K_R=23178; \alpha = 310; \beta= 0.8985; R^2=0.982$	3.17	0.63
	Dubinin-Radushkevich	$q_m = 99.48 \text{ mg/g}; K_D = 0.0068; E= 8.57$	42.33	15.45
35° C	Langmuir	$q_m=121.95; b=1.0933; R^2=0.99109$	14.02	5.23
	Freundlich	$n=9.7656; k_2=79.30; R^2=0.914$	40.55	19.28
	Redlich-Peterson	$K_R=362792; \alpha = 4280; \beta= 0.9207; R^2=0.981$	5.42	2.19
	Dubinin-Radushkevich	$q_m = 103.54 \text{ mg/g}; K_D = 0.0030; E= 12.91$	40.59	16.23

**Table S4** XPS results of F-MnS@biochar, and R-MnS@biochar (%)

Samples	O1s				S2p		
	C-O	-OH	C=O	M=O	S(VI)/S(IV)	S(-II)*	S(-II)#
F-MnS@biochar	22.3	60.8	16.9	-	7.6	12.8	79.6
R-MnS@biochar	-	42.7	35.6	21.7	15.3	11.9	72.8
Samples	Mn2p				Cr2p		
	Mn(II)	Mn(III)	Mn(IV)	Me=O	Cr <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> S <sub>3</sub>	Cr(VI)
F-MnS@biochar	91.6	-	8.4	-	-	-	-
R-MnS@biochar	62.8	29.7	7.5	21.7	24.5	42.8	32.7

### References:

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2. Dong H, Deng J, Xie Y, et al. Stabilization of nanoscale zero-valent iron (nZVI) with modified biochar for Cr(VI) removal from aqueous solution. *Journal of Hazardous Materials*, 2017, 332:79-86.
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5. Shi S, Yang J, Liang S, et al. Enhanced Cr(VI) removal from acidic solutions using biochar modified by  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$  particles. *Science of the Total Environment*, 2018, 628–629: 499-508.
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