Supporting Information

A New Carbon/Ferrous Sulfide/Iron Composite Prepared by an in Situ Carbonization Reduction Method from Hemp (*Cannabis sativa* L.) Stems and Its Cr(VI) Removal Ability

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The related chemical equations:

$$FeSO_4 + 4CO = FeS + 4CO_2 \quad (1)$$

$$FeSO_4 + 2C = FeS + 2CO_2 \quad (2)$$

$$FeS + 5\ FeSO_4 = 2Fe_3O_4 + 6SO_2 \quad (3)$$

$$[1-(2x/5)]FeS + 2x/5SO_2 = Fe_{1-x}S + x/5\ Fe_3O_4 \quad (4)$$

$$Fe_3O_4 + 4CO = 3Fe + 4CO_2 \quad (5)$$

$$Fe_3O_4 + 2C = 3Fe + 2CO_2 \quad (6)$$

$$Fe_{1-x}S = (1-x)FeS + xS \quad (7)$$

$$Fe_{1-x}S + xFe = FeS \quad (8)$$

$$HCrO_4^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \quad (9)$$

$$\text{Surface-C-e}^- \leftrightarrow \text{Surface-CO}_x\text{H} \quad (10)$$

$$FeS + H^+ \leftrightarrow Fe^{2+} + HS^- \quad (11)$$

$$3Fe^{2+} + HCrO_4^- + 7H^+ \leftrightarrow 3Fe^{3+} + Cr^{3+} + 4H_2O \quad (12)$$

$$Fe + HCrO_4^- + 7H^+ \leftrightarrow Fe^{3+} + Cr^{3+} + 4H_2O \quad (13)$$

$$2HCrO_4^- + 3HS^- + 11H^+ \leftrightarrow 3S + 2Cr^{3+} + 8H_2O \quad (14)$$

$$8HCrO_4^- + 3HS^- + 29H^+ \leftrightarrow 3SO_4^{2-} + 8Cr^{3+} + 20H_2O \quad (15)$$

$$xCr^{3+} + (1-x)Fe^{3+} + 3H_2O \leftrightarrow (Cr_xFe_{1-x})(OH)_3\ (s) + 3H^+ \quad (16)$$

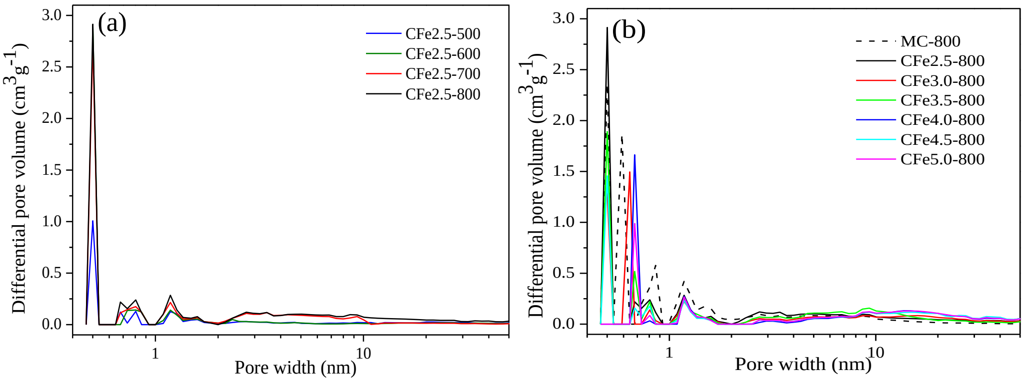

Figure S1. The pore size distributions of as-prepared samples (a) with 2.5 mmol of $FeSO_4$ at different temperatures and (b) with various $FeSO_4$ dosages at 800 °C.

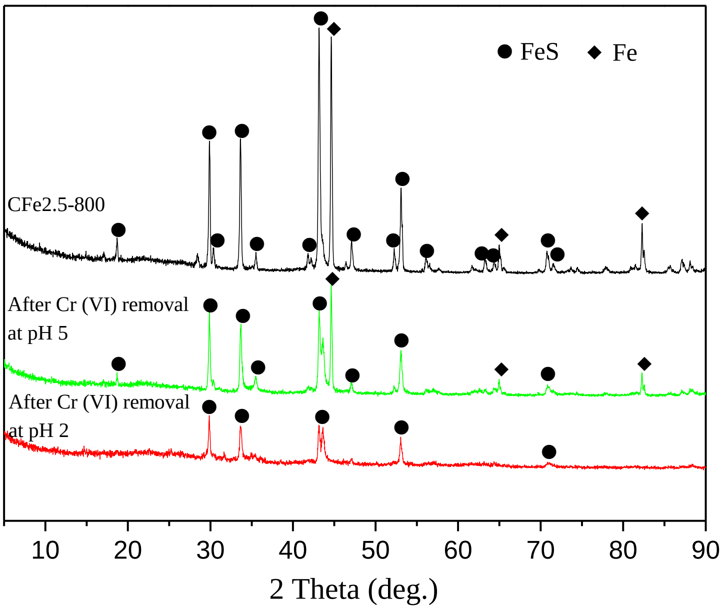

Figure S2. XRD patterns of the C/FeS/Fe composite prior to and after Cr(VI) removal at pH 5 and pH 2.

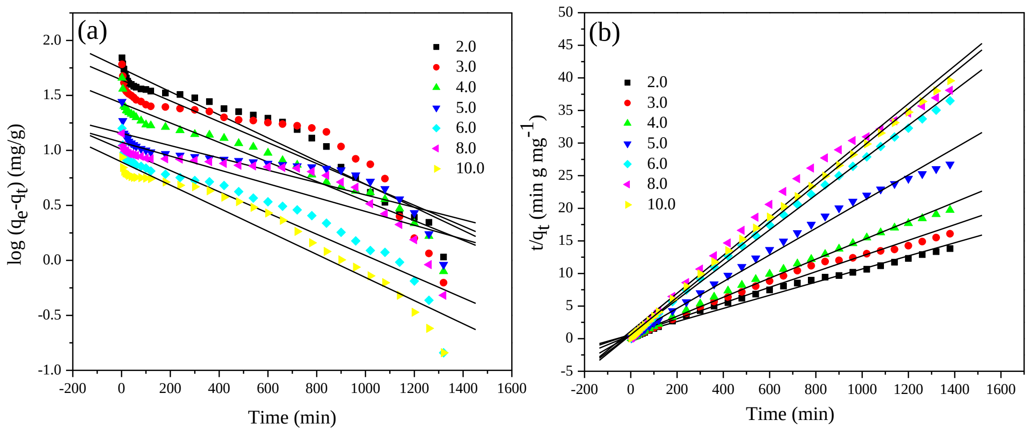

Figure S3. (a) Pseudo-first-order and (b) pseudo-second-order kinetic models for the removal of Cr(VI) by a C/FeS/Fe composite under different pH. (Initial concentration, 100 mg/L; carbon dosage, 1.0 g/L)

The removal kinetics are investigated by two commonly used models, namely, pseudo-first-order and pseudo-second-order models. The linear form of the two equations can be expressed as

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (17)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (18)$$

where q_e and q_t (mg g^{-1}) are respectively the amounts of Cr(VI) removal at equilibrium and at time t (min), and k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constants. The plot of $\log(q_e-q_t)$ versus t gives a linear plot, which allows computation of q_e and k_1 in pseudo-first-order model, and the parameters q_e and k_2 in pseudo-second-order model can be estimated from the linear plot t/q_t versus t.

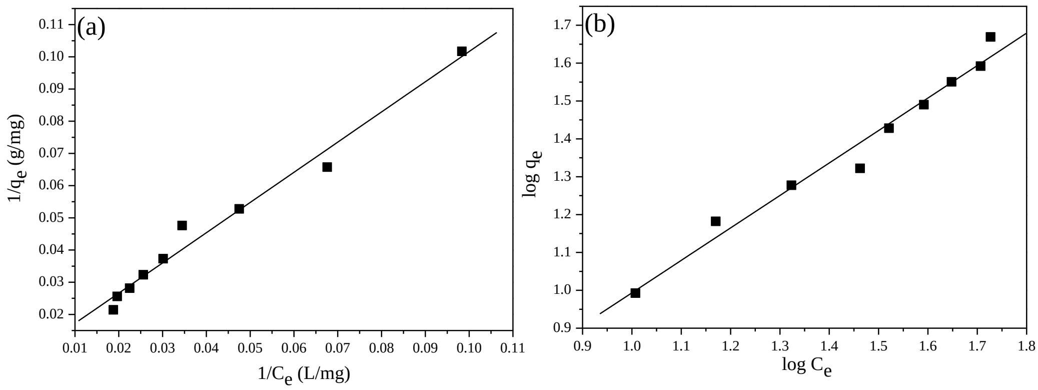

Figure S4. Linear plots of (a) Langmuir isotherm and (b) Freundlich isotherm for Cr(VI) removal on a C/FeS/Fe composite at different initial concentrations. (Carbon dosage, 1.0 g/L; pH=5)

The linear form of Langmuir plot is given as

(19)

where C_e (mg L^{-1}) is the equilibrium concentration, q_e (mg g^{-1}) is the removed amount at equilibrium, and q_m (mg g^{-1}) and b are Langmuir constants related to adsorption capacity and adsorption energy. The Freundlich model is an empirical equation with its form expressed as

$$\log q_e = \log K_f + (\frac{1}{n})\log C_e \quad (20)$$

where q_e (mg g^{-1}) is the removed amount at equilibrium, K_f and n are the Freundlich constants related to adsorption capacity and the adsorption intensity, respectively.

Table S1. The total mass fraction of iron compounds and iron for as-prepared samples.

Samples	Iron compounds and iron loaded on carbon	Total mass fraction (wt.%)
CFe2.5-500	$Fe_3O_4/Fe_{1-x}S/FeS$	18.8
CFe2.5-600	$Fe_3O_4/Fe_{1-x}S/FeS$	22.9
CFe2.5-700	$Fe_{1-x}S/FeS/Fe$	30.6
CFe2.5-800	FeS/Fe	40.4
CFe3.0-800	FeS/Fe	43.8
CFe3.5-800	FeS/Fe	49.4
CFe4.0-800	FeS/Fe	56.9
CFe4.5-800	FeS/Fe	60.1
CFe5.0-800	FeS/Fe	65.2

Table S2. Surface elemental composition of the C/FeS/Fe composite before and after Cr(VI) removal at pH 5 and 2.

Samples with different treatments	Atom ratio detected by XPS (%)				
	C	O	Fe	S	Cr
CFe2.5-800	84.8	12.5	0.910	1.80	-
CFe2.5-800-pH5	77.5	18.5	0.810	1.65	1.58
CFe2.5-800-pH2	67.3	26.3	1.70	2.72	1.97

Table S3. Kinetic parameters for the removal of Cr(VI) by a C/FeS/Fe composite under different pH.

pH	$q_{e, exp}$ (mg g^{-1})	Pseudo-first-order			Pseudo-second-order		
		k_1 (min^{-1})	$q_{e, cal}$ (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e, cal}$ (mg g^{-1})	R^2
2.0	97.9	0.00242	55.5	0.938	0.000163	97.3	0.989
3.0	83.8	0.00219	43.7	0.815	0.000206	83.2	0.985
4.0	68.0	0.00205	26.8	0.940	0.000388	67.6	0.996
5.0	46.7	0.00336	10.4	0.854	0.00115	46.4	0.999
6.0	37.8	0.00222	10.2	0.907	0.00111	37.4	0.998
8.0	34.9	0.00145	11.9	0.750	0.000663	34.4	0.988
10.0	31.2	0.00242	7.84	0.945	0.00140	31.2	0.999

Table S4. Langmuir and Freundlich isotherm parameters for the removal of Cr(VI) on a C/FeS/Fe composite.

Isotherms	Parameters	Values
	q_{m} (mg g^{-1})	127
Langmuir	b	0.00840
	R^2	0.979
	K_f	1.37
Freundlich	n	1.17
	R^2	0.974

Table S5. The removal capacity of Cr(VI) by some reported materials.

Adsorbent	q_m (mg g^{-1})	pH	Sorbent dose (g L^{-1})	Reference
Mackinawite (tetragonal FeS)	240	5	0.6	[22]
Magnetite-coated activated carbon	57.37	2	1	[24]
Fe-modified *Trapa natans* husk activated carbon	11.83	Natural state	1.5	[35]
Montmorillonite-supported magnetite	15.3	Not given	5	[57]
Spent tea	44.9	4	3	[69]
Iron-containing bamboo charcoal	33.1	5	2	[70]
N-doped porous carbon with magnetic particles	30.96	3	1	[71]
Cobalt-coated bamboo charcoal	45.45	5	2	[72]
Diatomite-supported magnetite	69.2	Not given	5	[73]
C/FeS/Fe composite	127.1	5	1	This wok