

Supporting Information

Adsorption and reduction of hexavalent chromium on magnetic greigite (Fe₃S₄)-CTAB: Leading role of Fe(II) and S(-II)

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Text S1

The pseudo first-order reaction model

The pseudo first-order reaction model can be expressed as Eq. S1:

$$\ln (C/C_0) = -k_1 t \quad (\text{S1})$$

k_1 is the rate constant of pseudo-first order kinetics (min^{-1}), and t is the contact time (min). C ($\text{mg}\cdot\text{L}^{-1}$) and C_0 ($\text{mg}\cdot\text{L}^{-1}$) are the concentration of Cr(VI) in aqueous solution at t min and 0 min, respectively.

The pseudo first and second-order adsorption models

The pseudo first-order adsorption model can be expressed as Eq. S1:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (\text{S1})$$

k_1 is the equilibrium rate constant of pseudo-first order kinetics (min^{-1}), and t is the contact time (min). The parameters q_t ($\text{mg}\cdot\text{g}^{-1}$) and q_e ($\text{mg}\cdot\text{g}^{-1}$) are the concentration of Cr(VI) adsorbed onto adsorbents at time t (min) or equilibrium time, which can be determined according to the mass balance equation:

$$q_t = (C_0 - C_t) \times V/m \quad (\text{S2})$$

$$q_e = (C_0 - C_e) \times V/m \quad (\text{S3})$$

where C_0 , C_t or C_e ($\text{mg}\cdot\text{L}^{-1}$) are the initial concentrations, concentration at t min, and equilibrium concentration of Cr(VI) in the solution, respectively. V (L) is the total volume of the reaction solution, and m (g) is the weight of the adsorbent.

According to Eq. S1, values of $\ln[(q_e - q_t)/q_e]$ should show a linear correlation with reaction time t , and the reaction rate constant k_1 can be determined from the slope of the linear plot.

The linear form of the pseudo second-order adsorption model can be expressed as Eq. S4:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (\text{S4})$$

where k_2 is the rate constant of the pseudo-second-order adsorption kinetics (g/mg/min).

Langmuir and Freundlich Isotherm analysis

The Langmuir model can be expressed as Eq. S5:

$$\frac{1}{q_e} = \frac{1}{ab} \times \frac{1}{C_e} + \frac{1}{b} \quad (\text{S5})$$

q_e and C_e correspond to the equilibrium concentration of Cr(VI) in the sorbent ($\text{mg}\cdot\text{g}^{-1}$) and solution ($\text{mg}\cdot\text{L}^{-1}$), respectively. b is the Langmuir constant related to maximum monolayer capacity, a is the Langmuir constant related to energy of adsorption. $1/q_e$ versus $1/C_e$ shows a linear relationship, and the rate constants can be calculated from the slope and intercept of their linear plot. In general, Langmuir isotherm is applied based on the hypothesis of monolayer adsorption on sorbents.

The Freundlich model can be expressed as Eq. S6:

$$q_e = K_F C_e^n \quad (\text{S6})$$

After modification, Eq. S6 can be transformed to Eq. S7 as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (\text{S7})$$

where K_F is an unit capacity parameter related to the adsorption capacity, and n is a dimensionless parameter of surface intensity. Both of their value can be obtained by plotting the line with $\ln q_e$ versus $\ln C_e$. The Freundlich isotherm is generally used to describe the heterogeneous adsorption on sorbents with uniform energy.

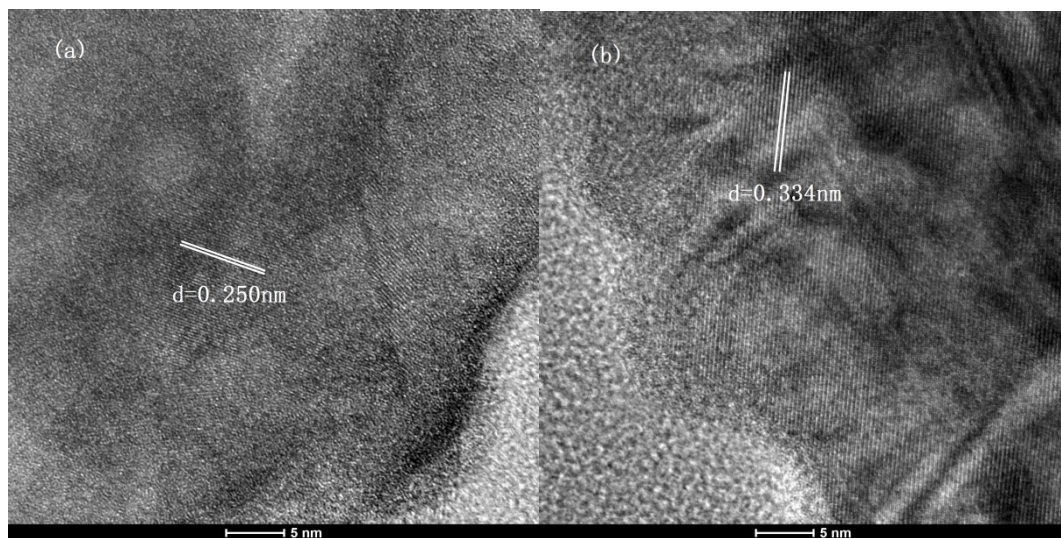


Figure S1. HRTEM images of Cr(VI)-treated $\text{Fe}_3\text{S}_4\text{-CTAB}_{0.75}$

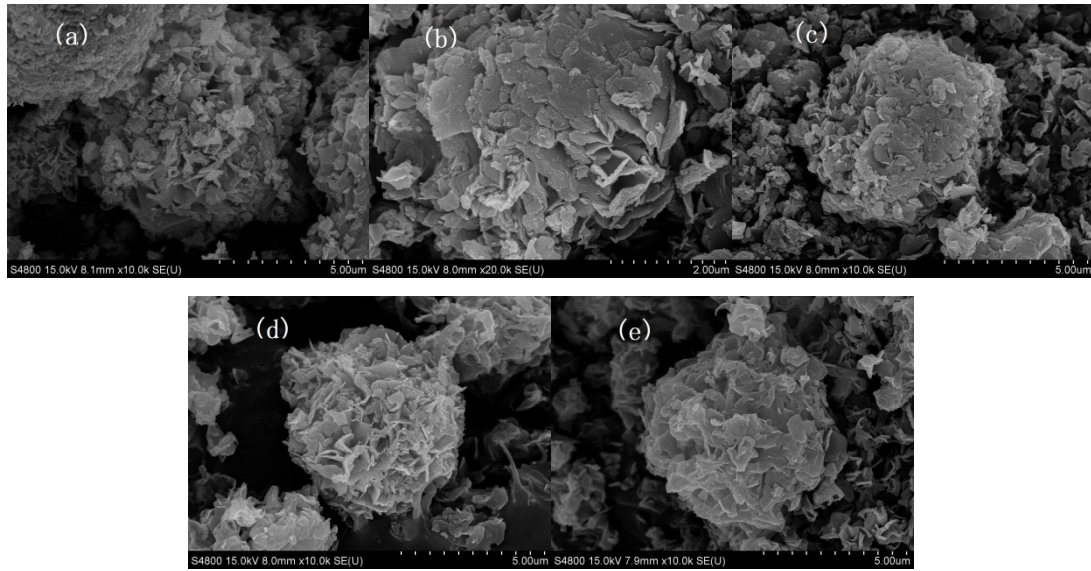


Figure S2. SEM of (a) Fe_3S_4 , (b) $\text{Fe}_3\text{S}_4\text{-CTAB}_{0.25}$, (c) $\text{Fe}_3\text{S}_4\text{-CTAB}_{0.50}$, (d) $\text{Fe}_3\text{S}_4\text{-CTAB}_{0.75}$ and (e) $\text{Fe}_3\text{S}_4\text{-CTAB}_{1.00}$

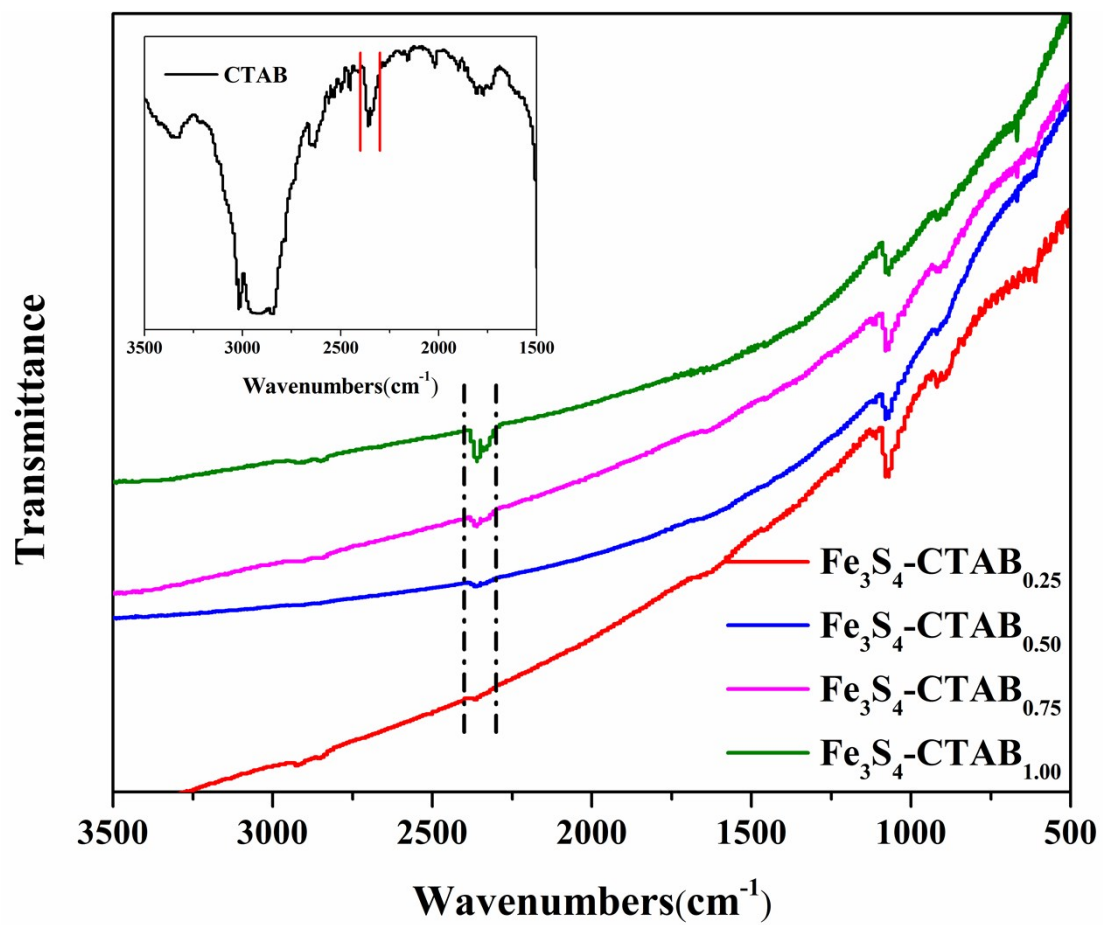


Figure S3. FTIR spectra of Fe_3S_4 -CTAB_{0.25}, Fe_3S_4 -CTAB_{0.50}, Fe_3S_4 -CTAB_{0.75}, Fe_3S_4 -CTAB_{1.00}

and

pure

CTAB

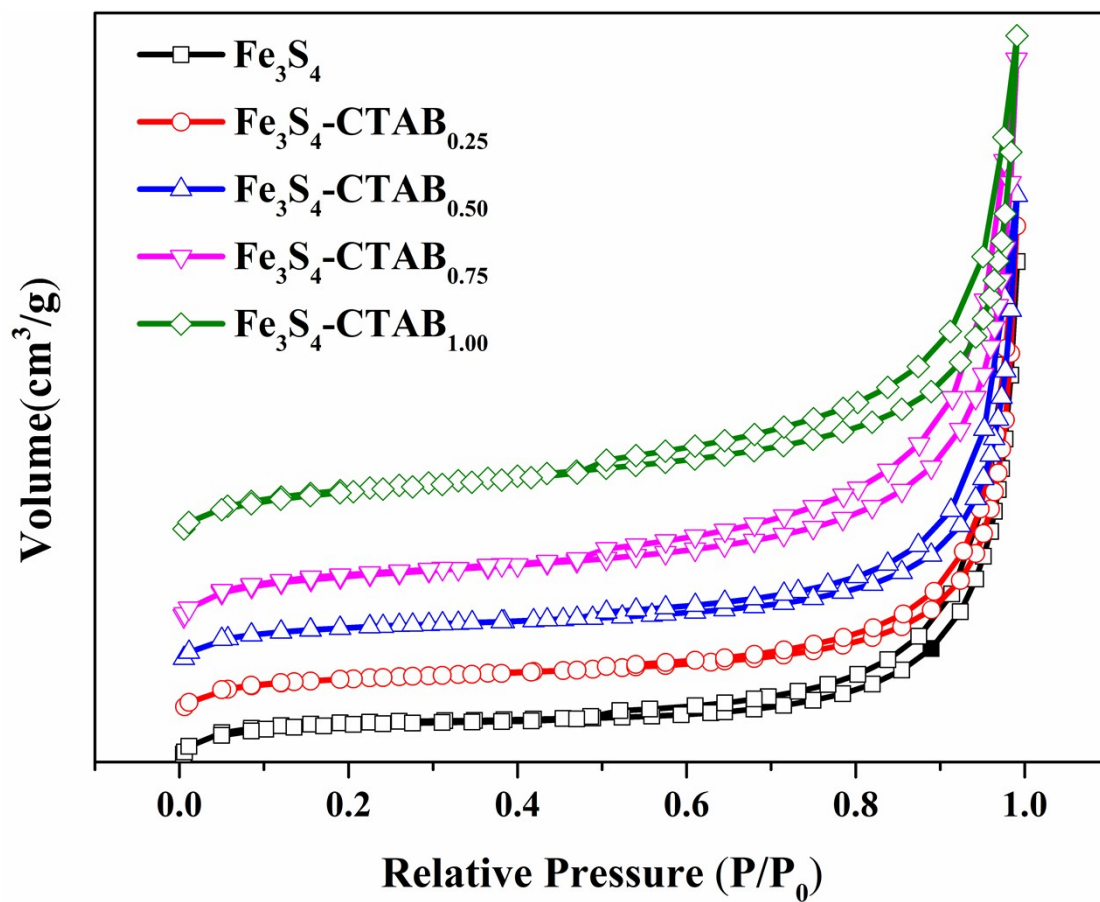


Figure S4. N₂ adsorption-desorption isotherm of Fe₃S₄, Fe₃S₄-CTAB_{0.25}, Fe₃S₄-CTAB_{0.50}, Fe₃S₄-CTAB_{0.75} and Fe₃S₄-CTAB_{1.00}

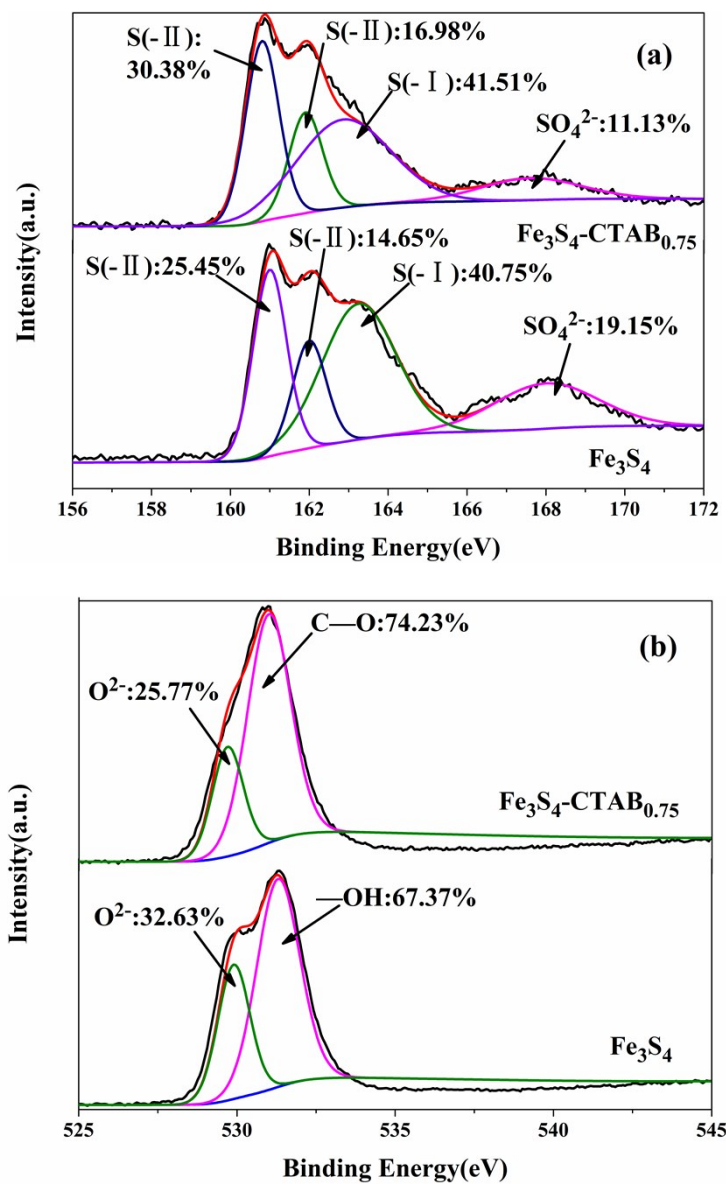


Figure S5. XPS spectra of (a) the S 2p region and (b) the O 1s region of Fe_3S_4 and $\text{Fe}_3\text{S}_4\text{-CTAB}_{0.75}$ sample.

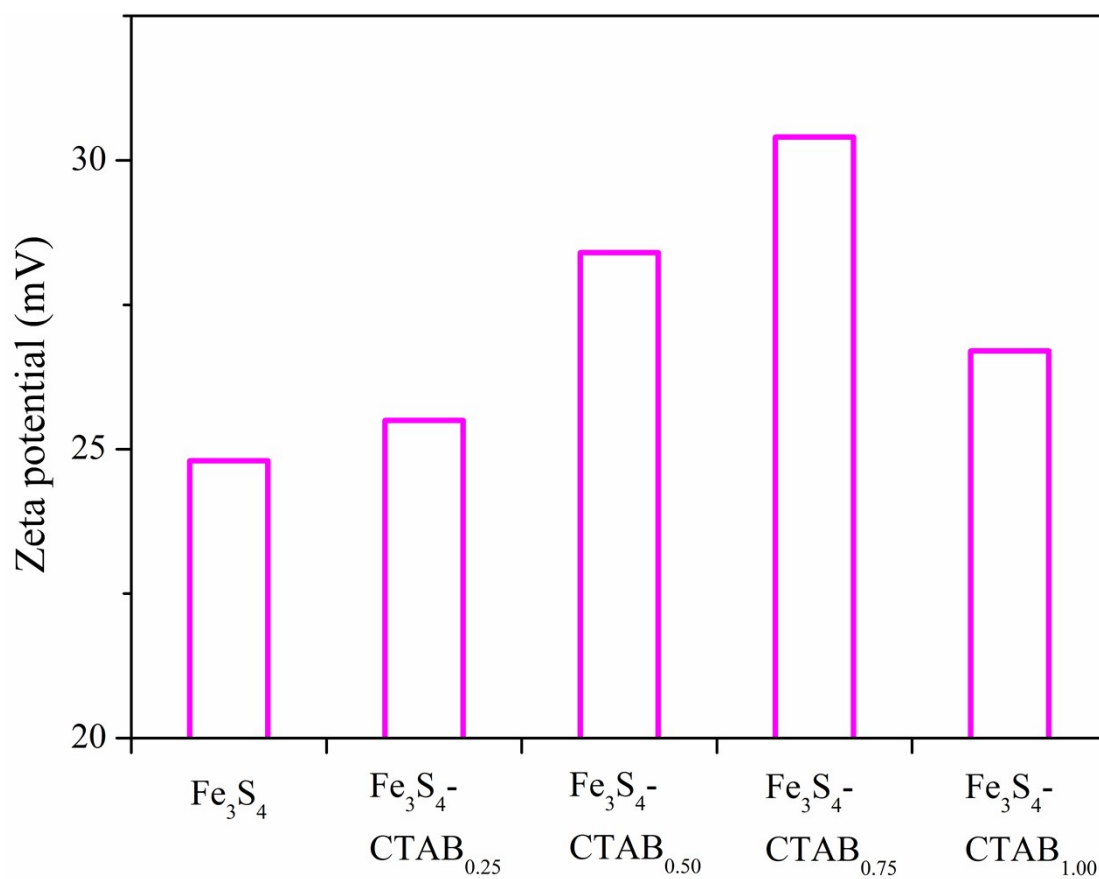


Figure S6. Zeta potentials of Fe_3S_4 , $\text{Fe}_3\text{S}_4\text{-CTAB}_{0.25}$, $\text{Fe}_3\text{S}_4\text{-CTAB}_{0.50}$, $\text{Fe}_3\text{S}_4\text{-CTAB}_{0.75}$ and $\text{Fe}_3\text{S}_4\text{-CTAB}_{1.00}$ in deionized water (pH=2.0).

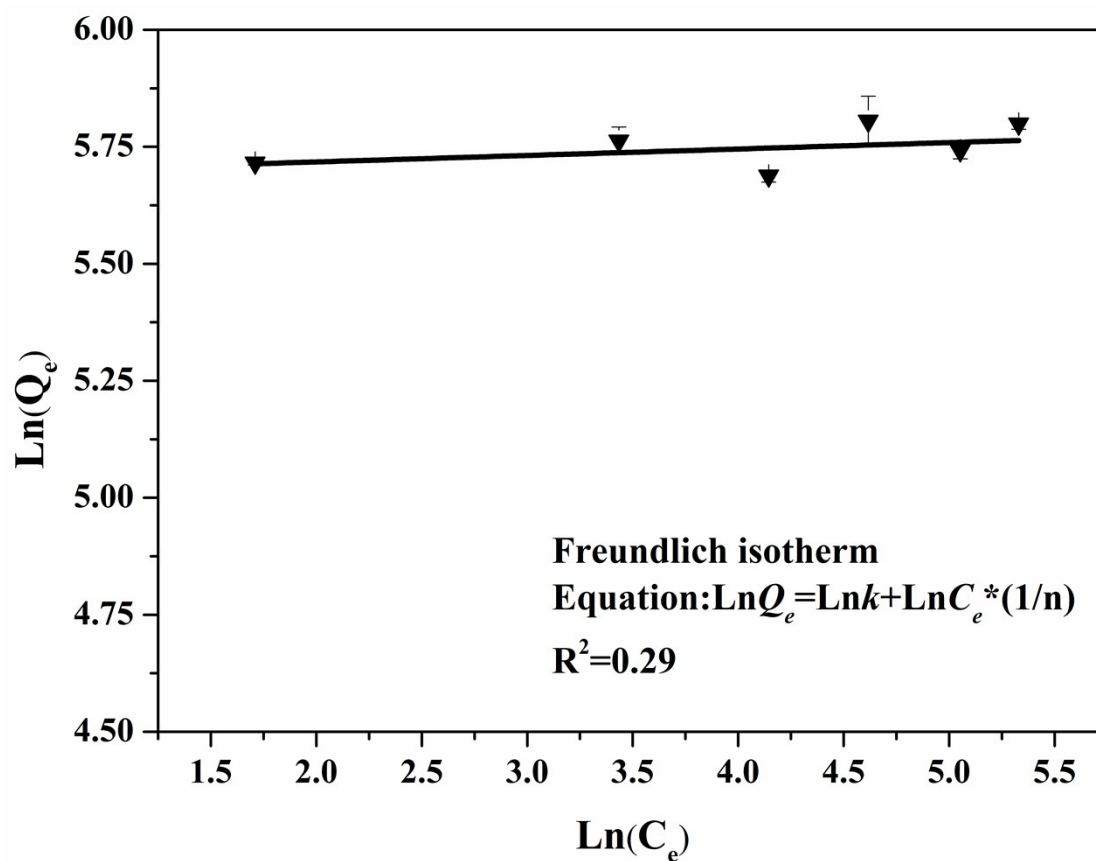


Figure S7. Freundlich isotherm of Cr(VI) adsorption. The reactions were carried out at initial Cr(VI) concentrations of of 100-300 mg·L⁻¹ with 0.3 g·L⁻¹ Fe₃S₄-CTAB_{0.75}, with pH₀=2.0.

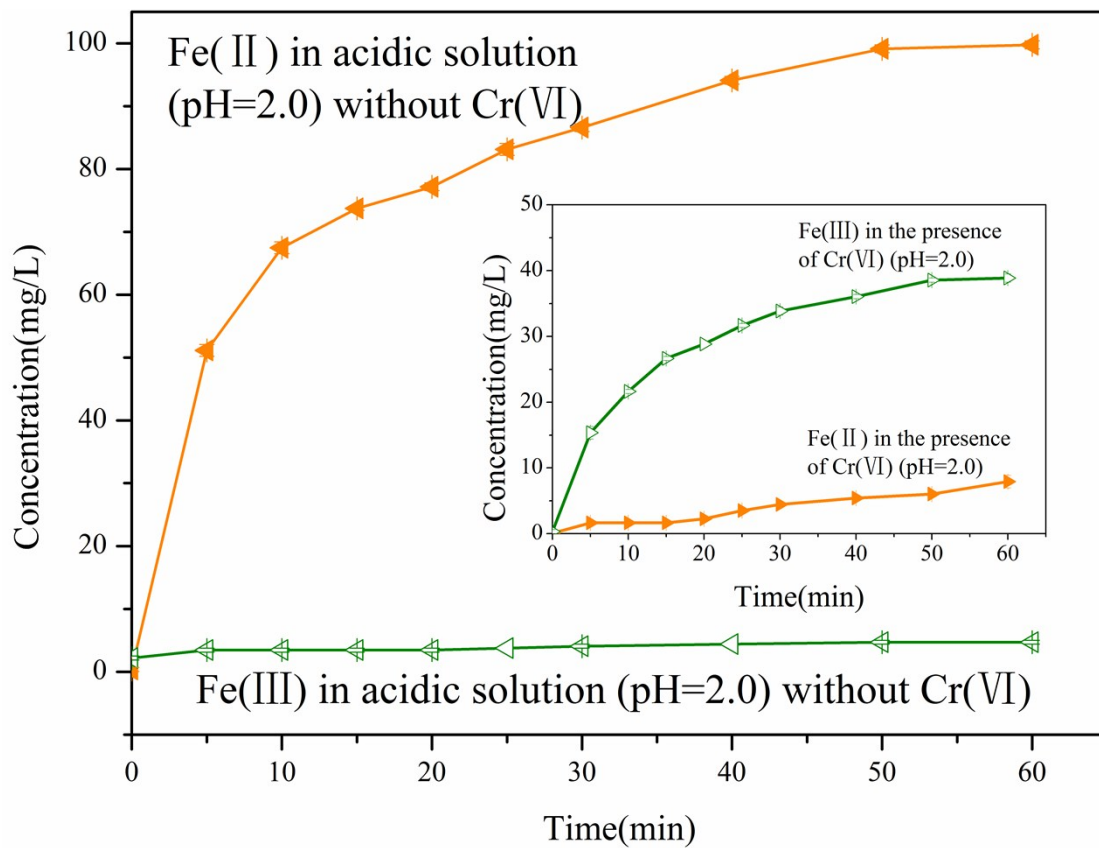


Figure S8. Release of dissolved Fe(II) and Fe(III) from $\text{Fe}_3\text{S}_4\text{-CTAB}_{0.75}$ in acidic solution (pH=2.0) without Cr(VI) and in the presence of Cr(VI) (pH=2.0).

Table S1 XPS results based on curve fitting for Fe 2p, S 2p, and Cr 2p peaks before and after the reaction.

Elements		Species	Relative fraction (%)
Fe	Before	Fe(II) and Fe ⁰	59.84
		Fe(III)	40.16
	After	Fe(II)	49.85
		Fe(III)	50.15
S	Before	S(- II)	47.36
		S(- I)	41.51
		S(VI)	11.13
	After	S(- II)	24.25
		S _n ²⁻ (n>2)	48.17
		S(VI)	27.57
Cr	After	Cr ₂ O ₃	23.23
		Cr(OH) ₃	40.72
		Cr(III)-containing material	36.05

Table S2 Pseudo-first-order reaction kinetics for Cr(VI) removal by sorbents

Synthesis	Kinetic constant, k (10^{-2} min^{-1})	Coefficient of determination, R^2
Fe_3S_4	1.380	0.887
$\text{Fe}_3\text{S}_4\text{-CTAB}_{0.25}$	1.867	0.953
$\text{Fe}_3\text{S}_4\text{-CTAB}_{0.50}$	3.503	0.953
$\text{Fe}_3\text{S}_4\text{-CTAB}_{0.75}$	4.454	0.988
$\text{Fe}_3\text{S}_4\text{-CTAB}_{1.00}$	3.150	0.978