

Supporting Information

Highly efficient antimonate removal from water by pyrite/hematite bi-mineral: performance and mechanism studies

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Characterization. XPS measurements were conducted on a VG Scientific ESALAB Mark II spectrometer. FTIR analysis was carried out with a VERTEX 70 FTIR device using the KBr method. The morphology was characterized by SEM (JEOL JSM 7401). XRD analysis was done using a Max-III A X-ray diffractometer with Cu K α radiation ($\lambda=1.5418$ Å). The inductively coupled plasma (ICP) (Agilent, USA) was applied to determine the Sb concentration.

Data analyses. The Sb(V) removal efficiency was obtained by Eq. (S1):

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (\text{S1})$$

where C_t (mg/L) and C_0 (mg/L) are the residual and initial Sb(V) concentration, respectively.

The FeS₂/ α -Fe₂O₃'s Sb(V) adsorption capacity (Q_e) was obtained by Eq. (S2):

$$Q_e = \frac{(C_0 - C_e) \times V}{W} \quad (\text{S2})$$

where W (mg) is the FeS₂/ α -Fe₂O₃ mass; V (mL) is the solution volume; C_e and C_0 (mg•L⁻¹) are equilibrium and initial Sb(V) concentration, respectively; Q_e (mg•g⁻¹) is the equilibrium adsorption capacity.

The Freundlich and Langmuir isotherm models are shown in the following equations, respectively:

$$\lg Q_e = \frac{1}{n} \lg C_e + \lg K_f \quad (\text{S3})$$

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \quad (\text{S4})$$

where Q_e (mg•g⁻¹) is the equilibrium Sb(V) adsorption capacity; C_e (mg•L⁻¹) is equilibrium Sb(V) concentration; Q_{\max} (mg•g⁻¹) is the maximum sorption capacity; K_f

$(\text{mg}^{(n-1)/n} \cdot \text{L}^{1/n} \cdot \text{g}^{-1})$ is Freundlich constant; n is a sorption intensity constant; K_L ($\text{L} \cdot \text{mg}^{-1}$) is Langmuir constant.

The Weber's intraparticle diffusion (Eq.(S5)), pseudo-second-order (Eq.(S6)) and pseudo-first-order (Eq.(S7)) models were employed to analyze the sorption data.

$$Q_t = k_i t^{0.5} + c \quad (\text{S5})$$

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{h_0}, \text{ where } h_0 = k_2 Q_e^2 \quad (\text{S6})$$

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (\text{S7})$$

where k_i ($\text{mg/g min}^{0.5}$) is the Weber's intraparticle diffusion model's rate constant; h_0 ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$) represents the initial sorption rate; k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) and k_1 (min^{-1}) are sorption rate constants; Q_e and Q_t ($\text{mg} \cdot \text{g}^{-1}$) are the amount of Sb(V) adsorbed on $\text{FeS}_2/\alpha\text{-Fe}_2\text{O}_3$ or pyrite at equilibrium and t , respectively.

The linear equation of the D-R isotherm¹ model is given in Eq(S7):

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (\text{S8})$$

where ε ($\varepsilon = RT \ln(1 + 1/C_e)$) is the Polanyi potential; β (mol^2/kJ^2) is the activity coefficient; q_m (mol/g) and q_e (mol/g) are the maximum sorption capacity and the amount of metal ions adsorbed on adsorbent, respectively. The free energy (E ; kJ/mol) is defined by Eq.(S8)².

$$E = \frac{1}{\sqrt{2\beta}} \quad (\text{S9})$$

The temperature-dependent adsorption isotherms can deduce the thermodynamic parameters for Sb(V) sorption on $\text{FeS}_2/\alpha\text{-Fe}_2\text{O}_3$, the ΔG^0 , ΔH^0 and ΔS^0 are shown in the following equations (Eqs. (S9) and (S10)).³⁻⁵

$$\Delta G^0 = -RT \ln K \quad (\text{S10})$$

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (\text{S11})$$

where K is the dimensionless equilibrium coefficient; $T(\text{K})$ is temperature in Kelvin; R ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) is the universal gas constant. K can be calculated from Eq. (S11)⁶:

$$K = K_L \times C_w \quad (\text{S12})$$

where K_L is the Langmuir constant, C_w ($1 \times 10^6 \text{ mg}\cdot\text{L}^{-1}$) is the water concentration.

According to Eq. (S11), the ΔS^0 and ΔH^0 parameters can be calculated from the intercept and slope.

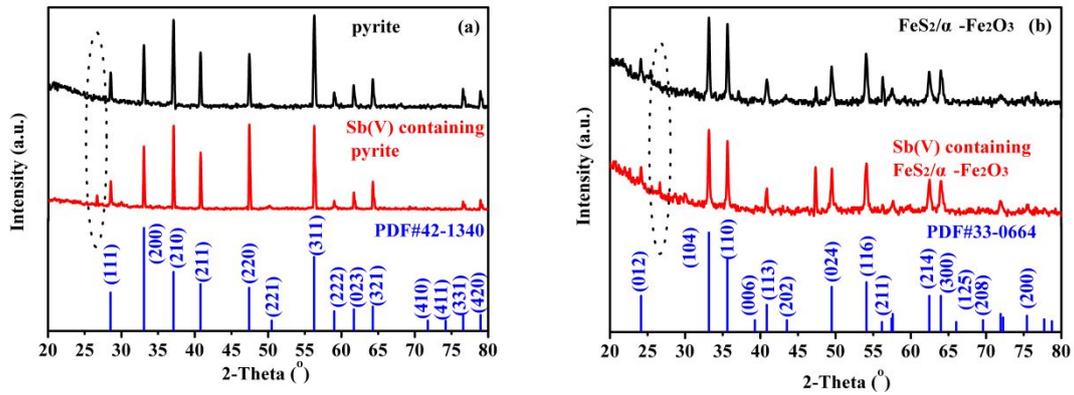


Figure S1. XRD of pyrite, Sb(V) containing pyrite (a), FeS₂/α-Fe₂O₃ and Sb(V) containing FeS₂/α-Fe₂O₃ (b).

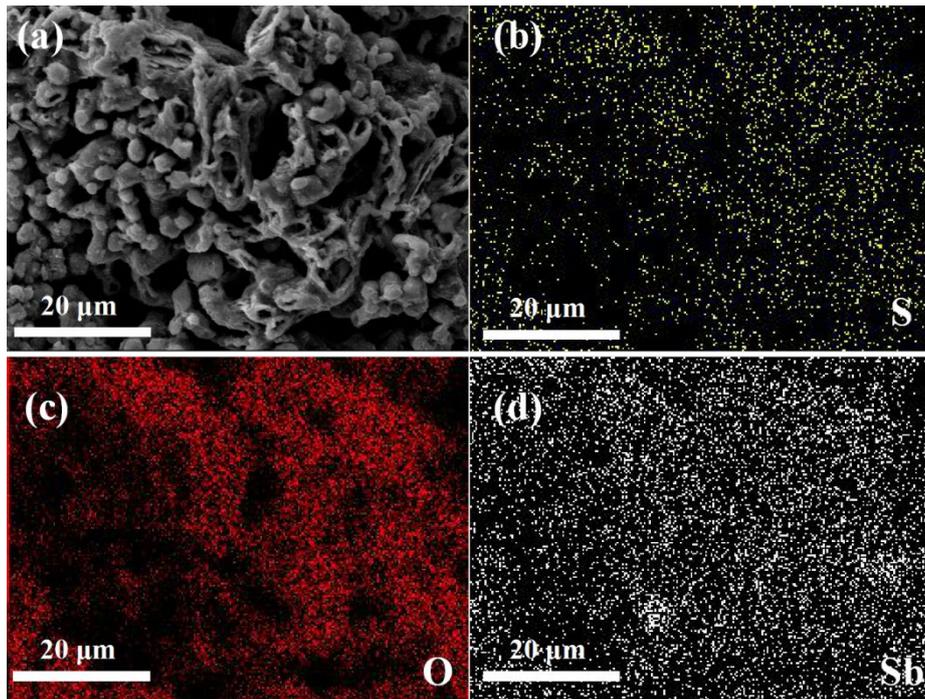


Figure S2. SEM (a) and corresponding EDS mapping images (b, c, d) of Sb(V) laden $\text{FeS}_2/\alpha\text{-Fe}_2\text{O}_3$.

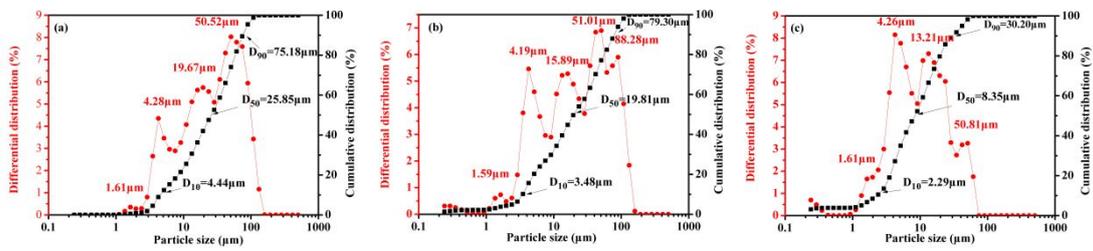


Figure S3. Particle size distribution of FeS_2 (a), $\alpha\text{-Fe}_2\text{O}_3$ (b) and $\text{FeS}_2/\alpha\text{-Fe}_2\text{O}_3$ (c).

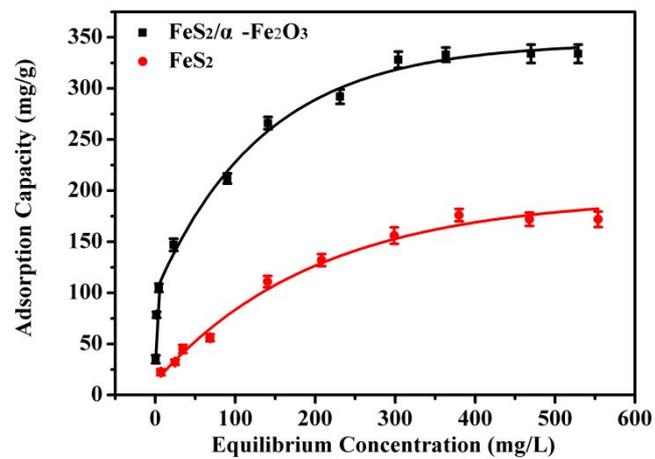


Figure S4. The Sb(V) adsorption isotherms of FeS₂/α-Fe₂O₃ and pyrite (25 °C).

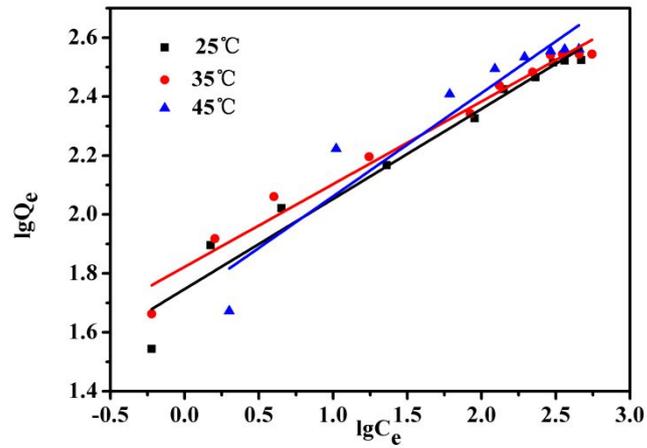


Figure S5. Freundlich plots for Sb(V) removal by FeS₂/α-Fe₂O₃.

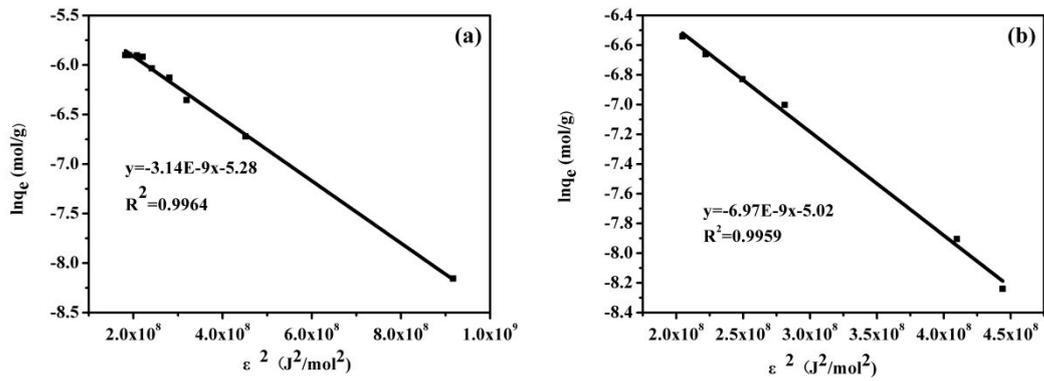


Figure S6. The D-R isotherm plots of Sb(V) removal by $FeS_2/\alpha-Fe_2O_3$ (a) and pyrite (b), respectively.

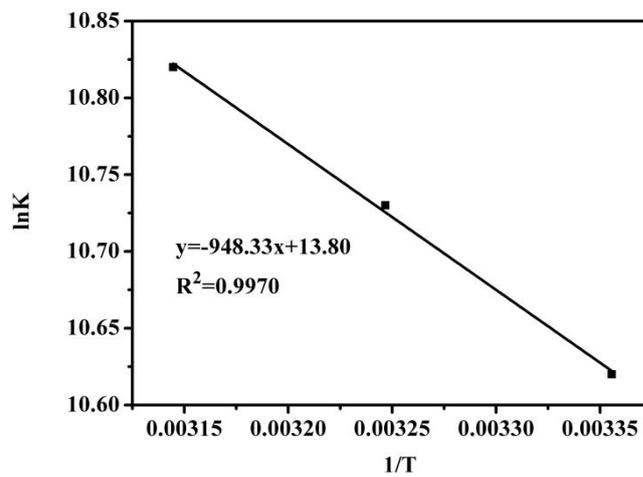


Figure S7. Relationship of $\ln K$ vs $1/T$ obtain for the Sb(V) removal by $FeS_2/\alpha-Fe_2O_3$.

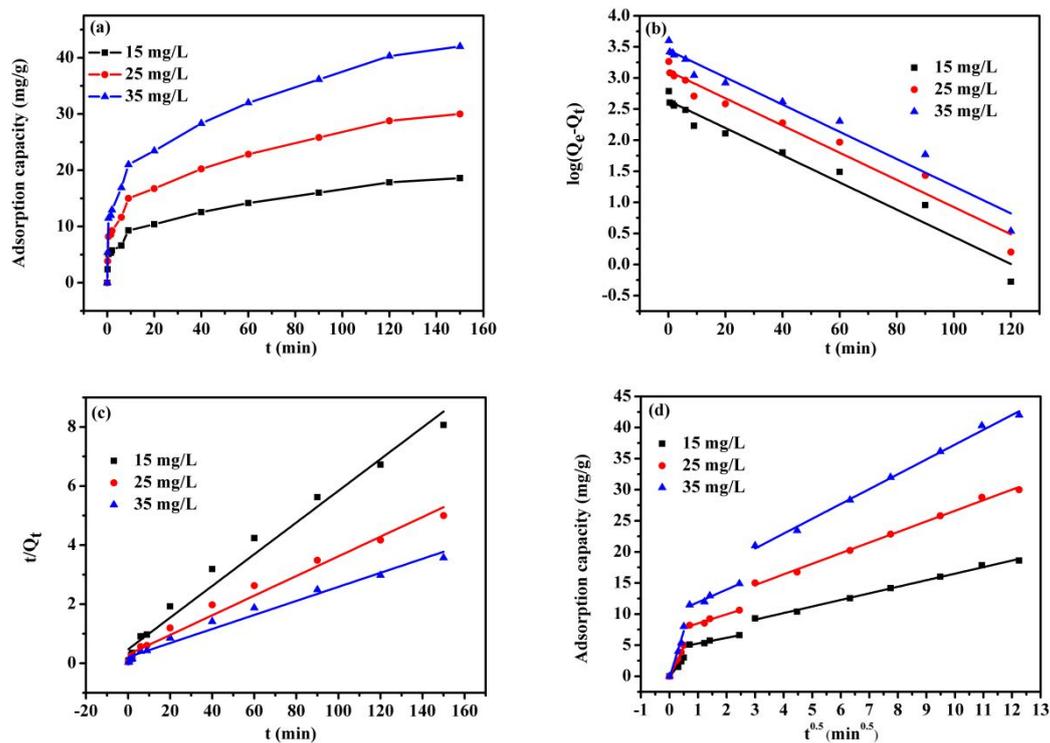


Figure S8. Adsorption of Sb(V) on FeS₂ as a function of (a) contact time. The fitting plots of the (b) pseudo-first-order, (c) pseudo-second-order kinetic model and (d) intraparticle diffusion model.

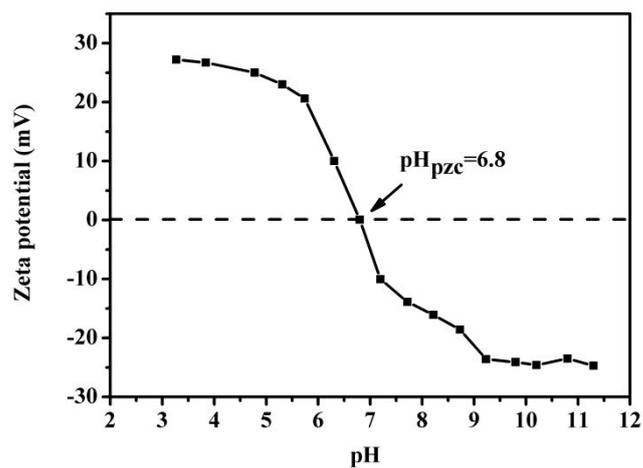


Figure S9. Zeta potential of FeS₂/α-Fe₂O₃.

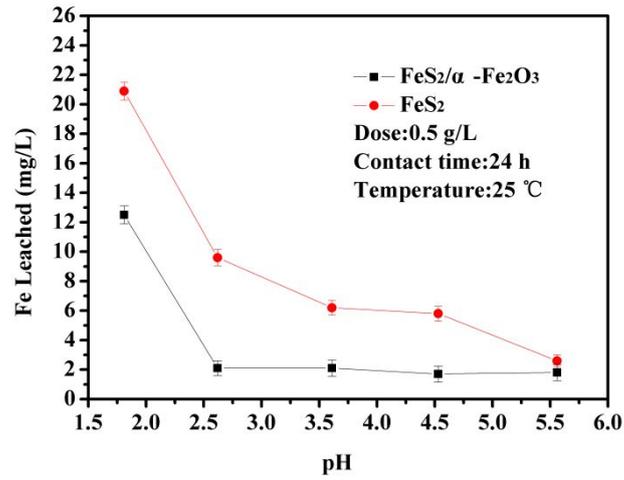


Figure S10. Iron leaching of FeS₂/α-Fe₂O₃ and FeS₂ at different pH.

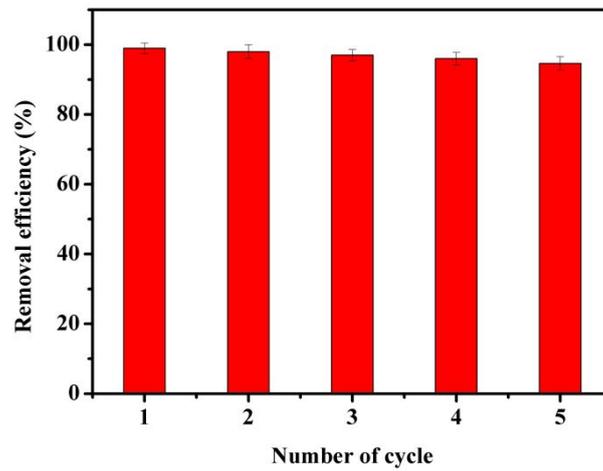


Figure S11. Efficiency of regeneration process of FeS₂/α-Fe₂O₃, under optimum conditions. (Initial Sb(V) concentration, 20 mg/L)

Table S1. The calculated D-R model parameters of Sb(V) removal by FeS₂/α-Fe₂O₃ and FeS₂.

Adsorbent	q_m (mol/g)	β (mol/g)	E (kJ/mol)	R ²
FeS ₂ /α-Fe ₂ O ₃	5.09×10 ⁻³	3.14×10 ⁻⁹	12.62	0.9964
FeS ₂	6.60×10 ⁻³	6.97×10 ⁻⁹	8.47	0.9959

Table S2. Thermodynamic parameters of Sb(V) removal by FeS₂/α-Fe₂O₃.

Adsorbent	Temp. (°C)	Thermodynamics parameters		
		ΔG_0 (kJ/mol)	ΔH_0 (kJ/mol)	ΔS_0 J/mol•K
FeS ₂ /α-Fe ₂ O ₃	25	-26.31		
	35	-27.48	5.00	114.73
	45	-28.58		

Table S3. Kinetic parameters of Sb(V) removal by FeS₂/α-Fe₂O₃ (a) and FeS₂ (b).

Adsorbent & Sb(V) concentration	pseudo-first-order kinetics			pseudo-second-order kinetics			
	K_1 (min ⁻¹)	$Q_{e,cal}$ (mg/g)	R^2	K_2 (g•mg ⁻¹ • min ⁻¹)	$Q_{e,cal}$ (mg/g)	h_0 (mg•g ⁻¹ • min ⁻¹)	R^2
FeS ₂ /α-Fe ₂ O ₃ (15 mg/L)	0.031	23.41	0.9542	1.83×10 ⁻³	32.86	1.97	0.9925
FeS ₂ /α-Fe ₂ O ₃ (25 mg/L)	0.031	29.11	0.9542	1.15×10 ⁻³	54.59	3.43	0.9914
FeS ₂ /α-Fe ₂ O ₃ (35 mg/L)	0.031	54.58	0.9542	7.46×10 ⁻⁴	77.10	4.43	0.9935
FeS ₂ (15 mg/L)	0.021	13.91	0.9642	6.14×10 ⁻³	18.62	2.13	0.9802
FeS ₂ (25 mg/L)	0.021	22.44	0.9642	3.81×10 ⁻³	30.04	3.43	0.9804
FeS ₂ (35 mg/L)	0.021	31.42	0.9642	2.72×10 ⁻³	42.05	4.81	0.9801

Table S4. Kinetic parameters of Weber's intraparticle diffusion model for Sb(V)

removal by FeS₂/α-Fe₂O₃ and FeS₂.

Adsorbent & Sb(V) concentration	Intraparticle diffusion parameters			
	R^2	K_{i1}	K_{i2}	K_{i3}
FeS ₂ /α-Fe ₂ O ₃ (15 mg/L)	0.9962	16.31	1.98	1.10
FeS ₂ /α-Fe ₂ O ₃ (25 mg/L)	0.9962	27.37	12.98	1.84
FeS ₂ /α-Fe ₂ O ₃ (35 mg/L)	0.9963	38.15	4.63	2.57
FeS ₂ (15 mg/L)	0.9746	5.92	0.90	1.06
FeS ₂ (25 mg/L)	0.9506	9.77	1.45	1.71
FeS ₂ (35 mg/L)	0.9950	15.05	2.03	2.39

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