Supplementary Information

Purification As(III) through oxidation of siderite and As(III) by dissolved oxygen: Behavior and Mechanism

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Text S1 Chemicals

Chemicals used in all experiments included sodium bicarbonate ($NaHCO_3$), ferrous sulfate heptahydrate ($FeSO_4·7H_2O$), sodium hydroxide (NaOH), nitric acid (HNO_3), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), hydrofluoric acid (HF), boric acid (H_3BO_3), sodium citrate, N-hydroxyethylpiperazine-1-ethanesulfonic acid, hydroxyl ammonium chloride, phenanthrozine, 1,10-phenanthroline, ethanol, potassium iodine (KI), sodium benzoate (BA), *p*-hydroxybenzoic acid (*p*-HBA), acetonitrile, trifluoroacetic acid (TFA) and potassium bromide (KBr). All were purchased from Sinopharm Co., Ltd. Ultrapure water was used in the experiments.

Text S2 Siderite preparation

Siderite was synthesized following previous methods.[1-3] Briefly, 0.05 mol of ferrous sulfate heptahydrate ($FeSO_4·7H_2O$) and 0.1 mol sodium bicarbonate ($NaHCO_3$) were mixed in 50 mL ultrapure water. After reaction for 24 h at 200 ℃ and 15 MPa, the produced precipitate was centrifuged at 6000 r/min for 10 min, filtered with 0.22 μm filter membrane, and washed with deoxygenated water for several times. Subsequently, the synthesized siderite was dried in an anoxic glovebox (COY-7000220A, COY, USA) for about five days, which was grounded to powder of 200 mesh for subsequent As(III) removal experiment.

Text S3 Total Fe and total Fe(II) measurement

Specifically, for total Fe(II) measurement, siderite suspensions (0.2 mL in volume) were sampled at selected time with a 1 mL syringe and injected into black centrifuge tubes. Hydrofluoric acid and sulfuric acid were added followed by boiling for 30 min to thoroughly dissolve siderite. 1,10-phenanthroline (10% in ethanol) was added as a color-developing agent. After color development, absorbance at 510 nm was recorded by a UV-vis spectrophotometer (UV-2550, SHIMADZU). For total Fe measurement, Fe(III) was pre-reduced into Fe(II) by 10% sodium citrate in the 1 N HCl solution, followed by the same measurement as Fe(II).[4,5]

Text S4 Dissolved Fe and dissolved Fe(II) measurement

For dissolved Fe(II) measurement, the samples were acidified with 1 mol/L HCl. After addition of 1 mL of Ferrozine agent (1 g/L), the absorbance at 562 nm was recorded by a UV-vis spectrophotometer (UV-2550, SHIMADZU). For dissolved Fe measurement, Fe(III) was pre-reduced by hydroxyl ammonium chloride (m/v=10%) in 1 mol/L HCl into dissolved Fe(II), followed by the same measurement of dissolved Fe(II). Then, dissolved Fe(III) was obtained by subtracting dissolved Fe(II) from dissolved Fe.[6]

References

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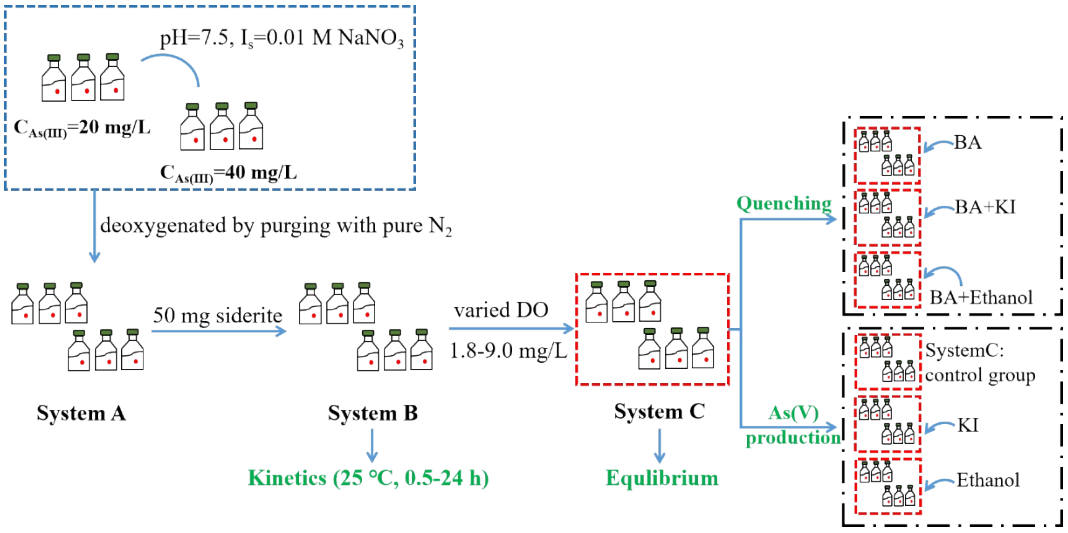

Fig. S1 Sketch of batch experiments of As(III) adsorption and oxidation on siderite

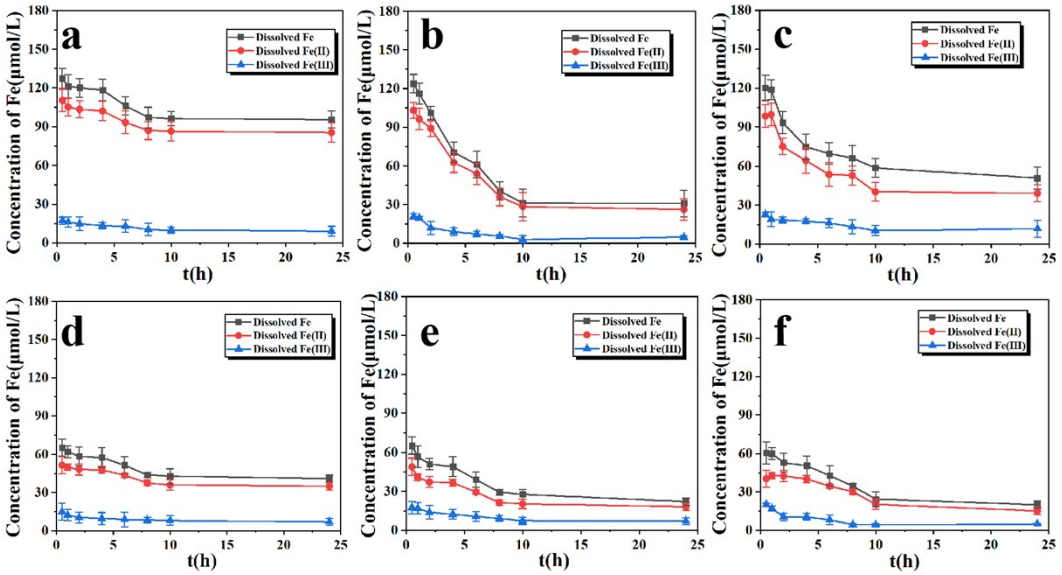

Fig. S2 Changes of dissolved Fe species in solutions with initial As(III) concentration of 20 mg/L (DO concentration of 1.8 mg/L (a), 4.6 mg/L (b), and 9.0 mg/L (c)) and 40 mg/L (DO concentration of 1.8 mg/L (d), 4.6 mg/L (e), and 9.0 mg/L (f))

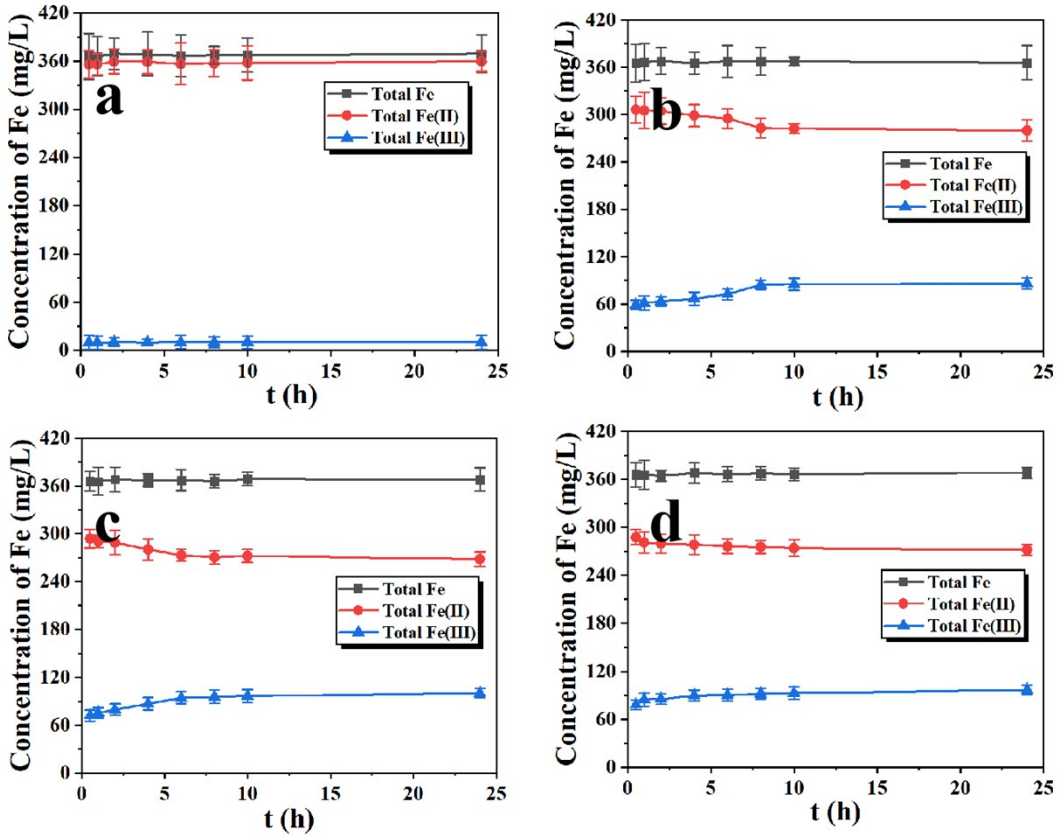

Fig. S3 Changes in concentrations of total Fe species in the ternary system with initial As(III) concentration of 20 mg/L (Solid/Liquid = 1 g/L, I = 0.05 M $NaNO_3$, initial pH = 7.5, without DO (a), DO concentrations of 1.8 mg/L (b), 4.6 mg/L (c), and 9.0 mg/L (d))

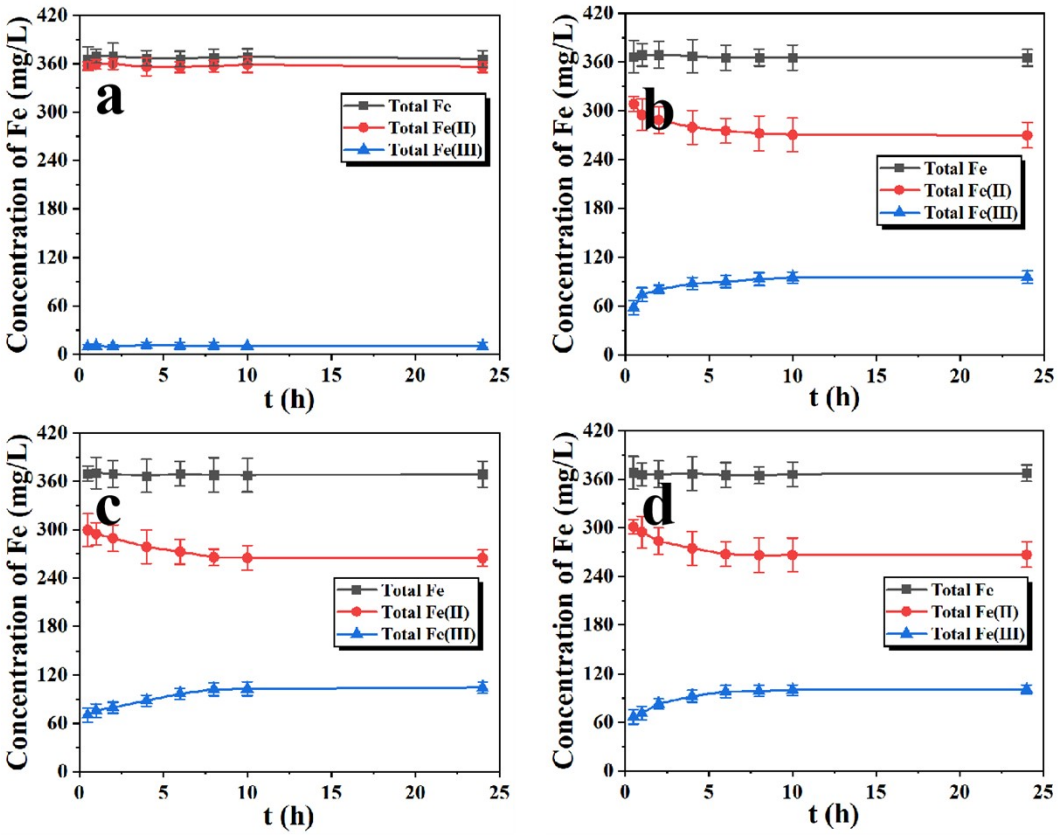

Fig. S4 Changes in concentrations of total Fe species in the ternary system with initial As(III) concentration of 40 mg/L (Solid/Liquid = 1 g/L, I = 0.05 M $NaNO_3$, initial pH = 7.5, without DO (a), DO concentration of 1.8 mg/L (b), 4.6 mg/L (c), and 9.0 mg/L (d))

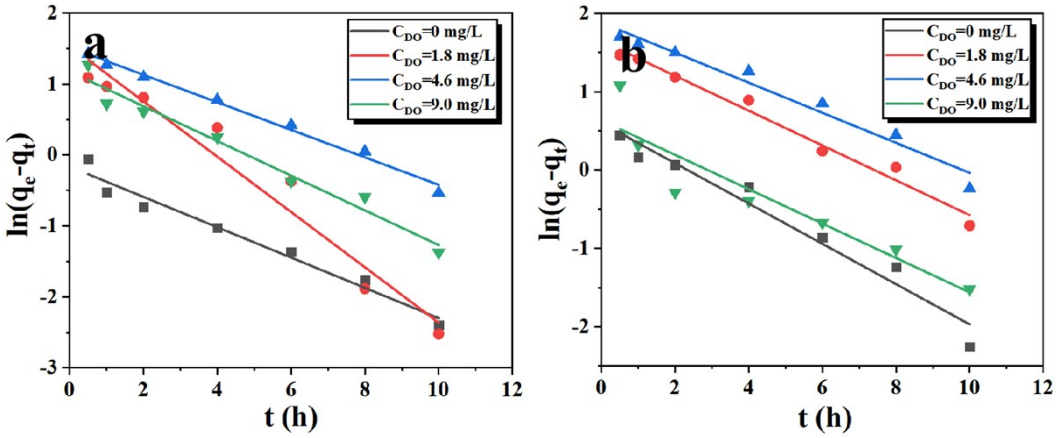

Fig. S5 The pseudo-first-order kinetic models of As(III) adsorption onto siderite (initial As(III) concentrations of 20 mg/L (a) and 40 mg/L (b))

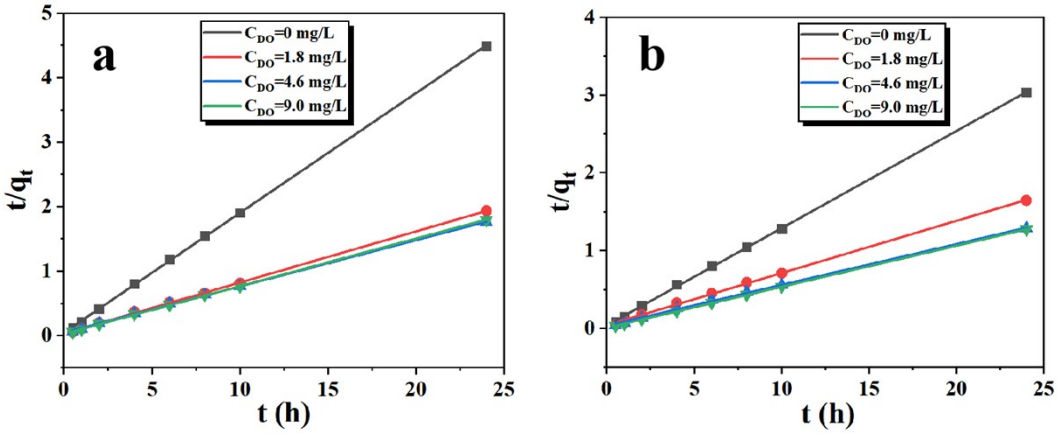

Fig. S6 The pseudo-second-order kinetic models of As(III) adsorption onto siderite (initial As(III) concentrations of 20 mg/L (a) and 40 mg/L (b))

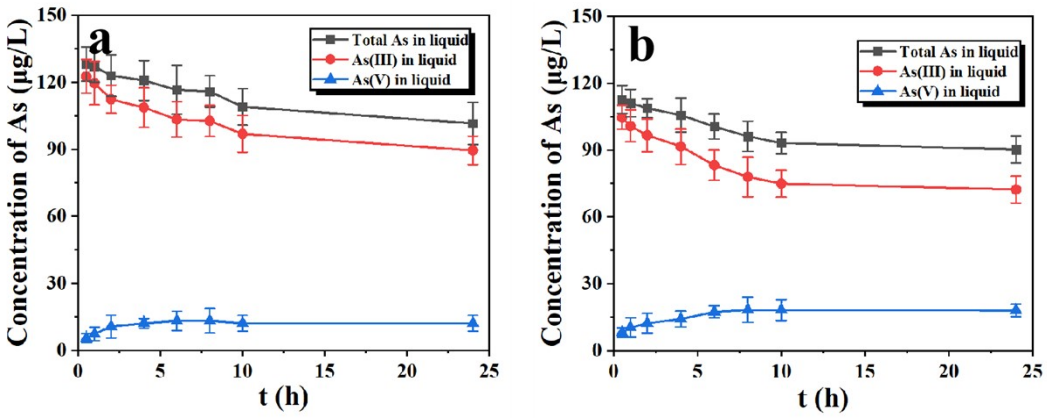

Fig. S7 Concentrations of dissolved As(III) and As(V) in the ternary system with DO concentration of 9.0 mg/L (Solid/Liquid = 1 g/L, I = 0.05 M $NaNO_3$, initial pH = 7.5, initial As(III) concentrations of 20 mg/L (a) and 40 mg/L (b))

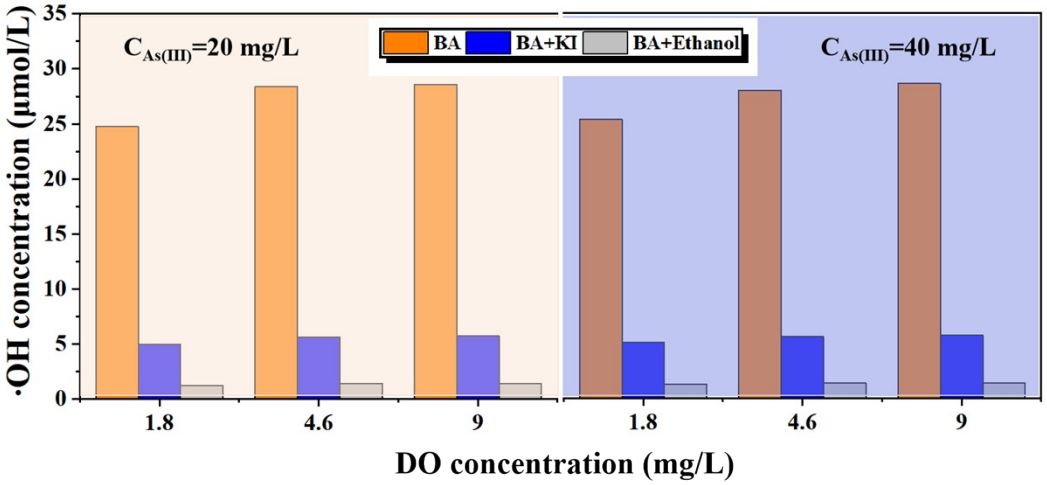

Fig. S8 Concentrations of •OH generated in the ternary systems with different DO concentrations (Solid/Liquid = 1 g/L, t = 24 h, I = 0.05 M $NaNO_3$, initial pH = 7.5, BA is the scavenger of •OH, while KI and ethanol are quenchers of •OH)

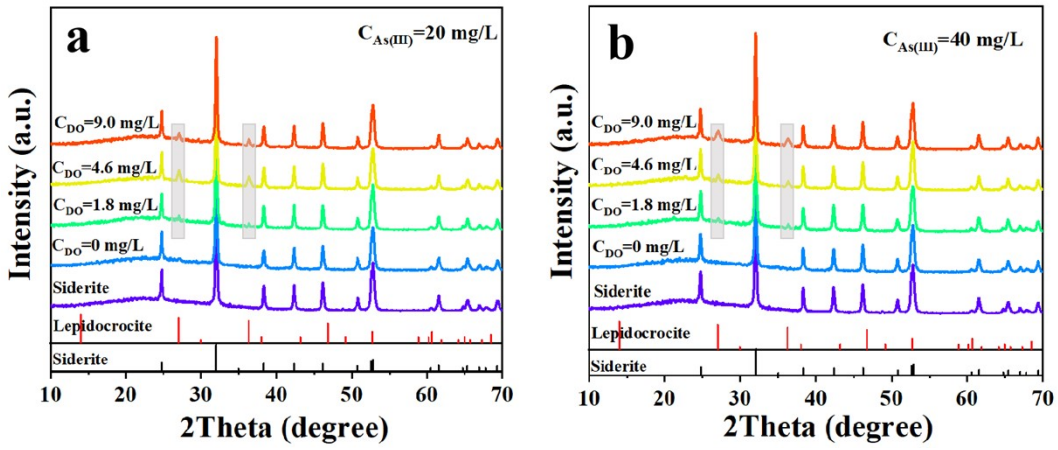

Fig. S9 The XRD of siderite and reacted siderite (initial As(III) concentrations of 20 mg/L (a) and 40 mg/L (b))

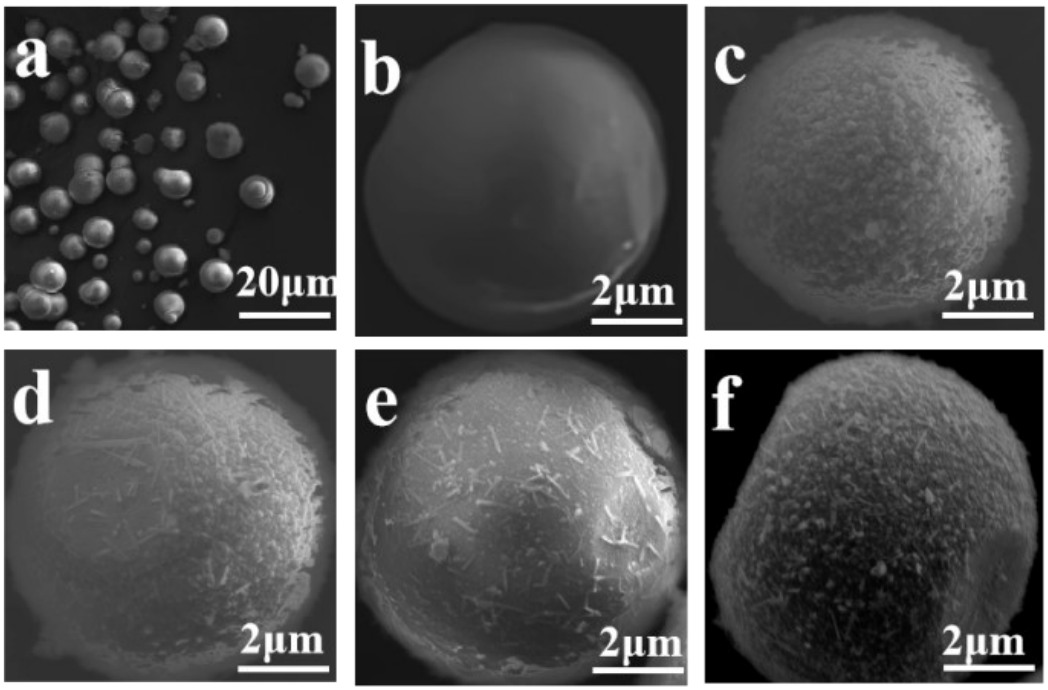

Fig. S10 SEM images of siderite (a, b) and reacted siderite with initial As(III) concentration of 20 mg/L (without DO (c), DO concentrations of 1.8 mg/L (d), 4.6 mg/L (e) and 9.0 mg/L (f))

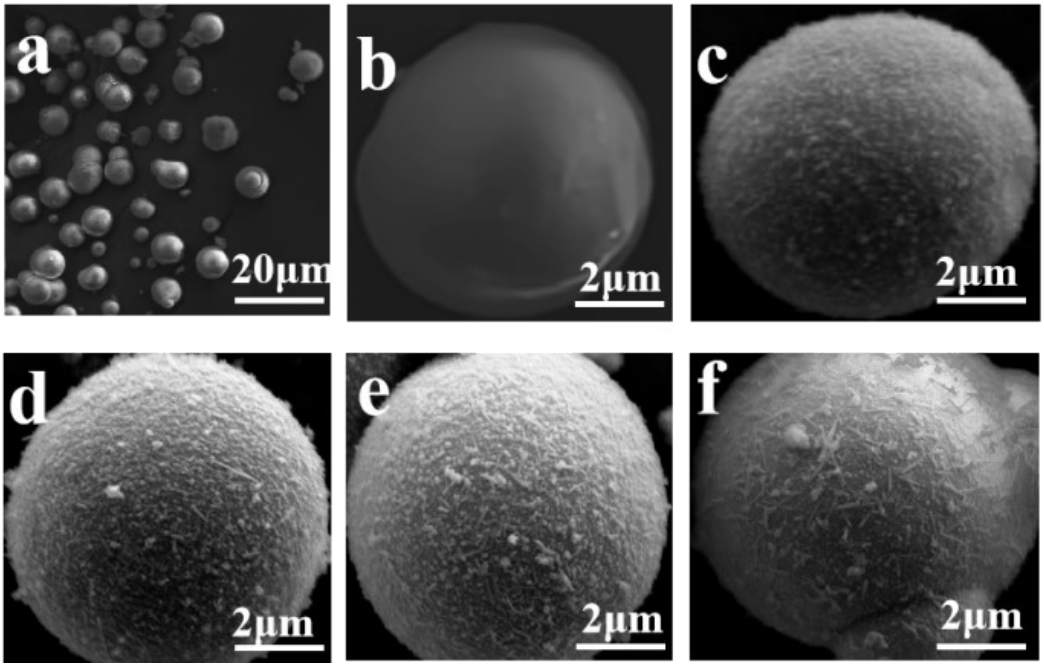

Fig. S11 SEM images of siderite (a, b) and reacted siderite with initial As(III) concentration of 40 mg/L (without DO (c), DO concentrations of 1.8 mg/L (d), 4.6 mg/L (e) and 9.0 mg/L (f))

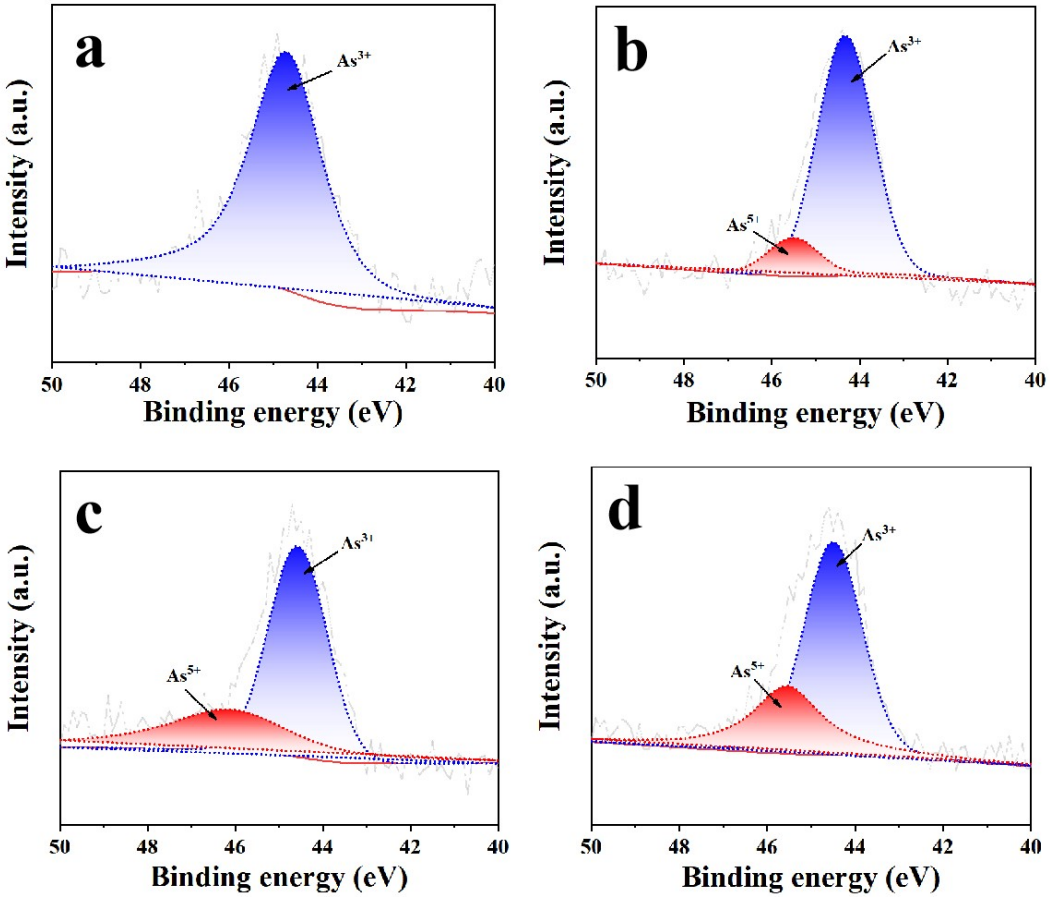

Fig. S12 The XPS of As 3d in reacted siderite from the ternary system with initial As(III) concentration of 20 mg/L (without DO (a), DO concentrations of 1.8 mg/L (b), 4.6 mg/L (c) and 9.0 mg/L (d))

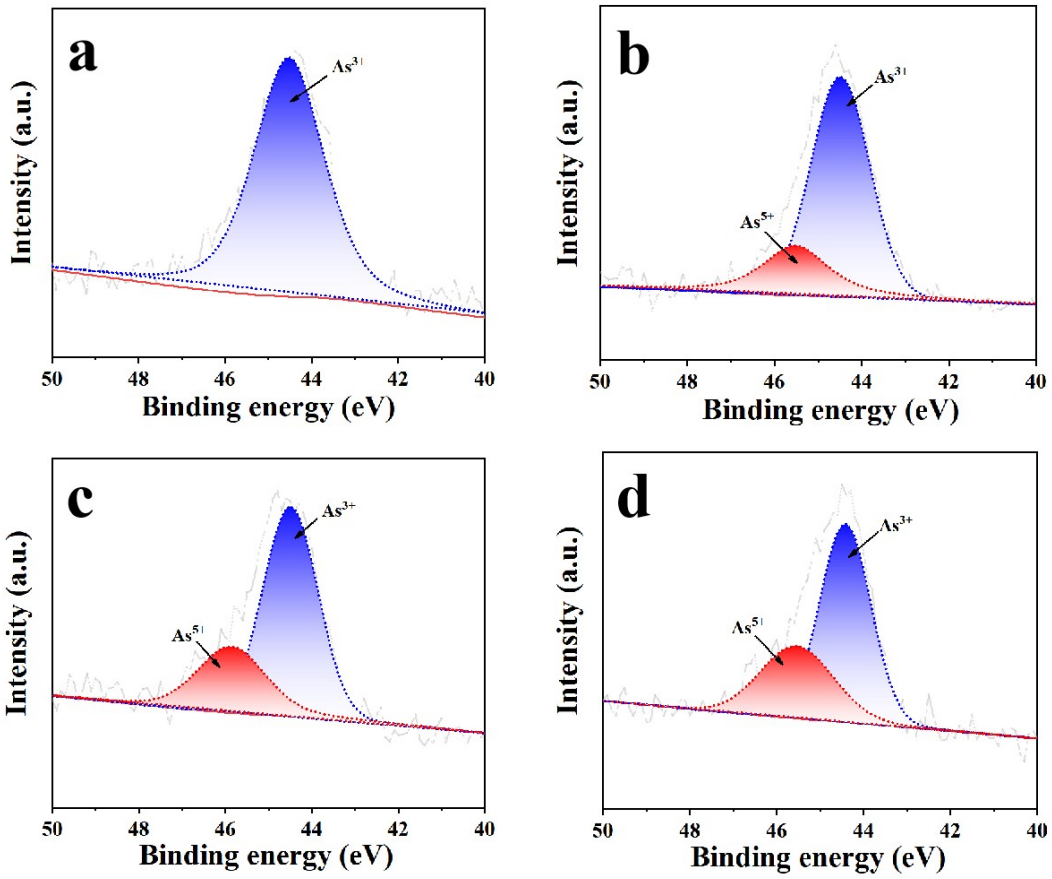

Fig. S13 The XPS of As 3d in reacted siderite in the ternary system with initial As(III) concentration of 40 mg/L (without DO (a), DO concentrations of 1.8 mg/L (b), 4.6 mg/L (c) and 9.0 mg/L (d))

Table S1 Kinetic parameters of As(III) adsorption on siderite with the absence and presence of DO

As(III) (mg/L)	DO (mg/L)	Pseudo-first-order			Pseudo-second-order		
		r	k_1	q_m (mg/g)	r	k_2	q_m (mg/g)
20	0	0.964	0.213	0.848	0.999	0.0346	5.38
	1.8	0.946	0.389	4.63	0.999	6.30×10^{-3}	12.6
	4.6	0.988	0.194	4.55	0.998	5.16×10^{-3}	13.9
	9.0	0.962	0.244	3.24	0.999	5.47×10^{-3}	13.5
40	0	0.953	0.257	1.83	0.999	0.0156	7.80
	1.8	0.978	0.222	5.20	0.999	4.52×10^{-3}	14.9
	4.6	0.960	0.192	6.57	0.998	2.75×10^{-3}	19.1
	9.0	0.840	0.219	1.88	0.999	2.79×10^{-3}	18.9

Table S2 Proportions of As(III) and As(V) in different depths of reacted siderite from the ternary system with DO concentration of 9.0 mg/L

As(III) (mg/L)	Depth of siderite (nm)	As(III) proportions (%)	As(V) proportions (%)
20	0	61.29	38.71
	10	64.89	35.11
	20	69.87	30.13
	30	74.98	25.02
	40	79.68	20.32
40	0	65.43	34.57
	10	70.79	29.21
	20	77.76	22.24
	30	86.67	13.33
	40	91.98	8.02