Supporting Information

The Effects of Formation Modes of Ferrihydrite-Low Molecular Weight Organic Matter Composites on the Adsorption of Cd(II)

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This supplemental information contains 5 figures and 14 tables. This document contains 10 pages including this cover page.

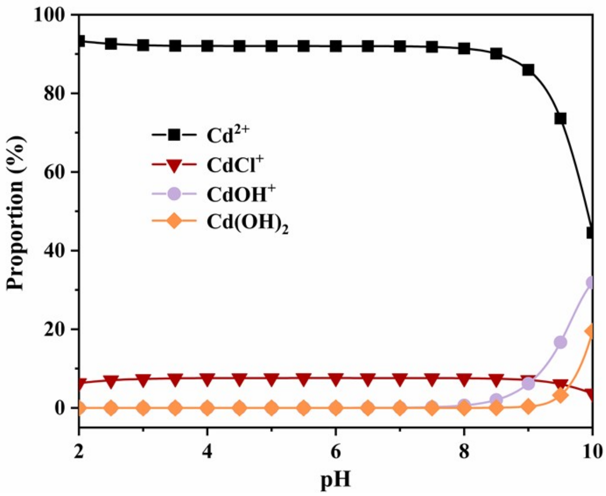

Fig. S1. The main species of Cd (calculated by the Visual Minteq3.1) in solution. (Background electrolyte was 1.0 mM NaCl, Cd concentration was 2.0 mg L^{-1}.)

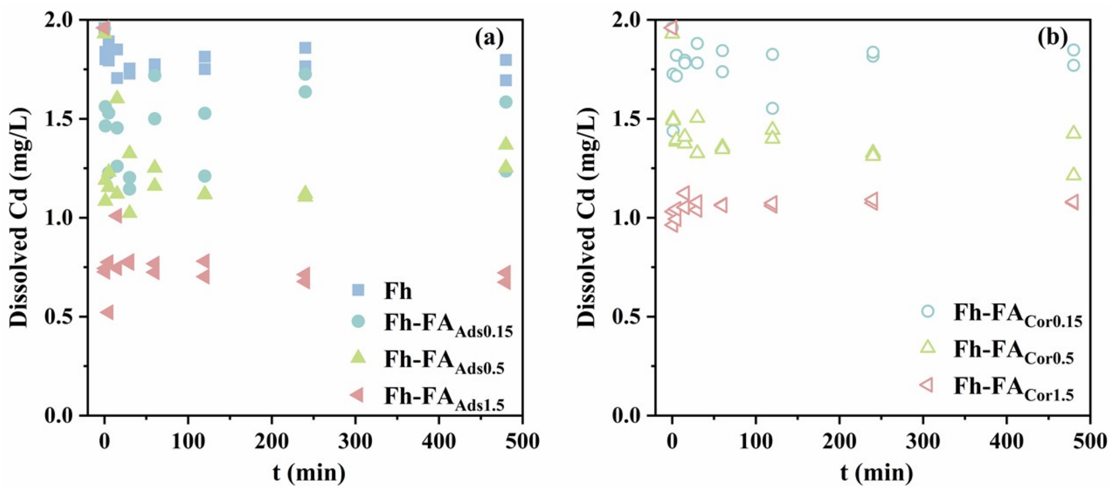

Fig. S2. Adsorption kinetics of Cd(II) on adsorption composites (a) and coprecipitates (b). (pH was 5.5–6.5, background electrolyte was 1.0 mM NaCl, Cd concentration was 1.95 mg L^{-1}, and adsorbent concentration was 0.2 g/L.)

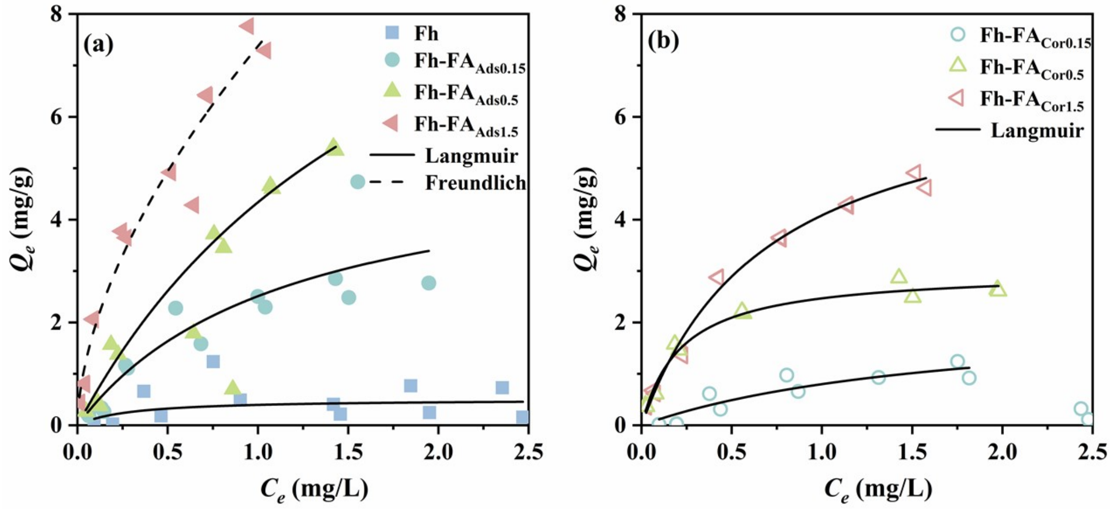

Fig. S3. Adsorption isotherm results of Cd(II) on adsorption composites (a) and coprecipitates (b). (pH was 5.5–6.5, background electrolyte was 1 mM NaCl, and adsorbent concentration was 0.2 g L^{-1}.)

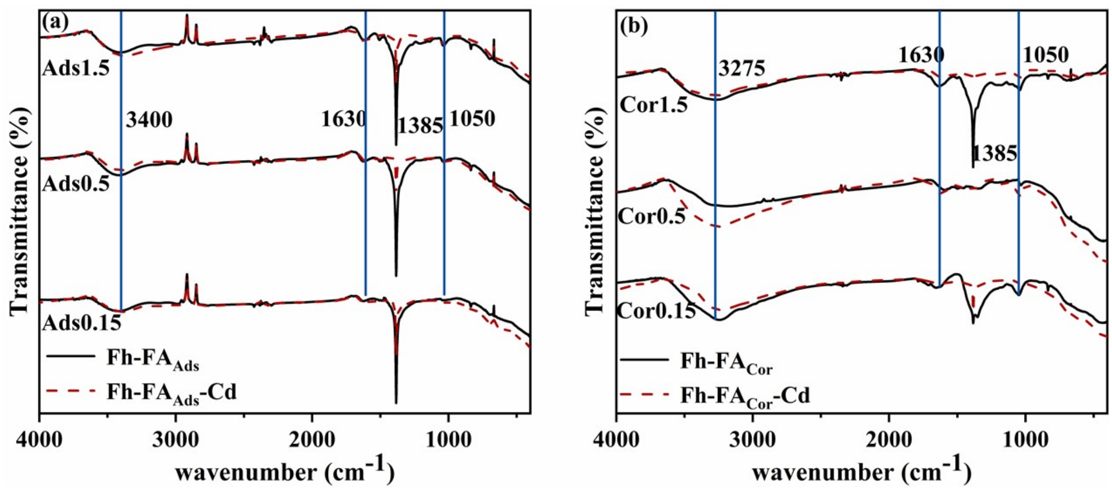

Fig. S4. FTIR spectra of adsorption composites (a) and coprecipitates (b) before and after reaction with Cd(II). Cd(II) initial concentration is 2.0 mg L^{-1}.

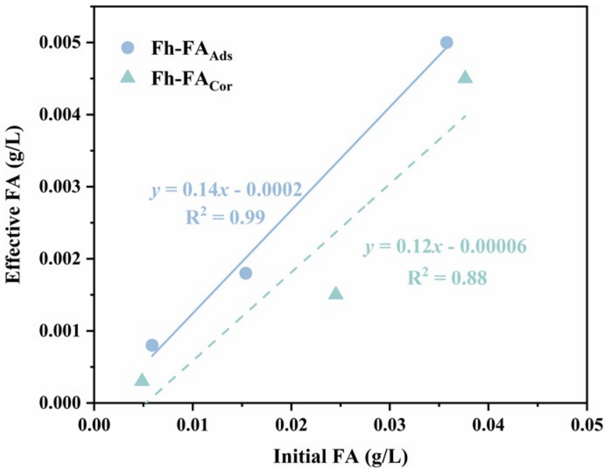

Fig. S5. The relationship between the model effective concentration of FA and the initial concentration in the composites.

Table S1. Elemental composition and fulvic acid (FA) content of the materials

Materials	C content（mg g^{-1}）	FA content (mg g^{-1})	C/Fe molar ratios of product
FA	415.85±1.44		
Fh-$FA_{Ads0.15}$	14.39±0.04	29.41	0.14
Fh-$FA_{Ads0.5}$	38.06±0.15	76.88	0.40
Fh-$FA_{Ads1.5}$	87.50±1.61	178.84	1.05
Fh-$FA_{Cor0.15}$	12.01±0.86	24.25	0.12
Fh-$FA_{Cor0.5}$	52.03±0.19	122.60	0.49
Fh-$FA_{Cor1.5}$	92.08±0.03	188.20	1.12

Note: The C/Fe molar ratios of product was calculated using the chemical formula of Ferrihydrite (Fh) ($Fe_5HO_8 \cdot 4H_2O$) [1].

Table S2. Fitting results of parameters of the adsorption isotherm models

Adsorbent	Langmuir			Freundlich		
	Q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_f ((mg g^{-1})/(mg L^{-1})$^{1/n}$)	1/n	R^2
Fh	0.51	3.52	0.15	0.36	0.31	0.10
Fh-$FA_{Ads0.15}$	5.40	0.87	0.80	2.37	0.63	0.78
Fh-$FA_{Ads0.5}$	12.77	0.51	0.99	4.22	0.77	0.98
Fh-$FA_{Ads1.5}$	10.47	2.03	0.95	7.38	0.58	0.96
Fh-$FA_{Cor0.15}$	2.18	0.58	0.82	0.75	0.73	0.79
Fh-$FA_{Cor0.5}$	3.01	4.58	0.98	2.26	0.35	0.90
Fh-$FA_{Cor1.5}$	6.95	1.43	0.99	3.93	0.56	0.97

Table S3. 2D-FTIR-COS results on the assignment and sign of each cross-peak in synchronous and asynchronous (in parentheses) maps of Fh-$FA_{Ads0.15}$-Cd

Position (cm^{-1})	Peak assignment	Sign	
		3400	1385
3400	-OH		
1385	R-COO-Fe	+(-)	
500	Fe-O-Fe	+(-)	+(+)

Table S4. 2D-FTIR-COS results on the assignment and sign of each cross-peak in synchronous and asynchronous (in parentheses) maps of Fh-FA$_{Ads0.5}$-Cd

Position (cm^{-1})	Peak assignment	Sign	
		3400	1385
3400	-OH		
1385	R-COO-Fe	+(-)	
500	Fe-O-Fe	+(-)	+(-)

Table S5. 2D-FTIR-COS results on the assignment and sign of each cross-peak in synchronous and asynchronous (in parentheses) maps of Fh-FA$_{Ads1.5}$-Cd

Position (cm^{-1})	Peak assignment	Sign	
		3400	1385
3400	-OH		
1385	R-COO-Fe	+(+)	
500	Fe-O-Fe	+(-)	+(-)

Table S6. 2D-FTIR-COS results on the assignment and sign of each cross-peak in synchronous and asynchronous (in parentheses) maps of Fh-FA$_{Cor0.15}$-Cd

Position (cm^{-1})	Peak assignment	Sign		
		3400	1630	1050
3400	-OH			
1630	COO$^-$	+(+)		
1050	alcoholic C-O	+(-)	+(-)	
450	Fe-O-Fe	+(-)	+(-)	+(-)

Table S7. 2D-FTIR-COS results on the assignment and sign of each cross-peak in synchronous and asynchronous (in parentheses) maps of Fh-$FA_{Cor0.5}$ -Cd

Position (cm^{-1})	Peak assignment	Sign		
		3400	1630	1050
3400	-OH			
1630	COO^-	+(+)		
1050	alcoholic C-O	+(-)	+(-)	
500	Fe-O-Fe	+(+)	+(+)	+(+)

Table S8. 2D-FTIR-COS results on the assignment and sign of each cross-peak in synchronous and asynchronous (in parentheses) maps of Fh-$FA_{Cor1.5}$-Cd

Position (cm^{-1})	Peak assignment	Sign		
		3275	1630	1050
3275	-OH			
1630	COO^-	+(-)		
1050	alcoholic C-O	+(-)	+(-)	
450	Fe-O-Fe	-(+)	-(+)	-(+)

Table S9. The contents of Fh, FA and dissolved organic carbon (DOC) in adsorption isotherm experiments

Composites type	Fh (g/L)	FA (g/L)	DOC (mg C L^{-1})
Fh-$FA_{Ads0.15}$	0.164	0.006	1.09
Fh-$FA_{Ads0.5}$	0.153	0.015	2.17
Fh-$FA_{Ads1.5}$	0.134	0.036	6.59
Fh-$FA_{Cor0.15}$	0.163	0.005	1.07
Fh-$FA_{Cor0.5}$	0.171	0.024	1.59
Fh-$FA_{Cor1.5}$	0.132	0.037	6.72

Table S10. Input concentrations of Fh and FA of composites with different C/Fe molar ratios in surface complexation models

Composites type	Effective Fh (g/L)	Effective FA (g/L)	DOC (mg C L^{-1})*
Fh-$FA_{Ads0.15}$	0.158	0.0008	0.50
Fh-$FA_{Ads0.5}$	0.139	0.0018	1.67
Fh-$FA_{Ads1.5}$	0.106	0.0050	6.00
Fh-$FA_{Cor0.15}$	0.158	0.0003	0.50
Fh-$FA_{Cor0.5}$	0.150	0.0015	1.00
Fh-$FA_{Cor1.5}$	0.103	0.0045	6.20

*: the input DOC concentration was subtracted from the background DOC concentration in ultrapure water.

Table S11. CD-MUSIC model parameters of Fh

Model parameters	Fh*
Specific surface area (m^2/g)	650
Site density ≡$FeOH^{0.5-}$ (sites/nm^2)	6.25
Site density ≡$Fe_3O^{0.5-}$ (sites/nm^2)	1.55
C_{in} (F/m^2)	1.15
C_{out} (F/m^2)	0.90

*: the parameters of ferrihydrite were adopted from [2].

Table S12. Surface complexation reaction between Fh and Cd(II)

Ferrihydrite-Cd	(ΔZ_0, ΔZ_1, ΔZ_2)	log*K*
$FeOH^{0.5-}+H^+=FeOH_2^{0.5+}$	(1, 0, 0)	8.10
$FeOH^{0.5-}+Na^+=FeOHNa^{0.5+}$	(0, 1, 0)	-0.60
$FeOH^{0.5-}+H^++Cl^-=FeOH_2Cl^{0.5-}$	(1, -1, 0)	7.65
$Fe_3O^{0.5-}+H^+=Fe_3OH^{0.5+}$	(1, 0, 0)	8.10
$Fe_3O^{0.5-}+Na^+=Fe_3ONa^{0.5+}$	(0, 1, 0)	-0.60
$Fe_3O^{0.5-}+H^++Cl^-= Fe_3OHCl^{0.5-}$	(1, -1, 0)	7.65
$2FeOH^{0.5-}+Cd^{2+}+H_2O=(FeOH)_2CdOH+H^+$	(0.5, 0.5, 0)	-2.35 (99%) [a]
	(0.5, 0.5, 0)	0.68 (1%) [a]

[a]: the LogK values were adopted from [3].

Table S13. The optimized complexation constant of Fh-Cd

Composites type	$\log K_{Fh\text{-}Cd(99\%)}$
Fh-$FA_{Ads0.15}$	-0.35
Fh-$FA_{Ads0.5}$	-0.2
Fh-$FA_{Ads1.5}$	-0.2
Fh-$FA_{Cor0.15}$	-1.1
Fh-$FA_{Cor0.5}$	-2.15
Fh-$FA_{Cor1.5}$	-1

Table S14. NICA-Donnan model parameters of FA and surface complexation reactions between FA and Cd(II)

NICA-Donnan model parameters [a]				
Functional group	Site density (mol/kg)	p	nH	b
carboxyl	5.88	0.57	0.66	0.57
Phenolic hydroxyl	1.86	0.59	0.76	
Surface complexation reaction				$\log K$ [b]
$R\text{-}COO^- + H^+ = R\text{-}COOH$				2.34
$R\text{-}COO^- + Cd^{2+} = R\text{-}COOCd^+$				-0.97
$R\text{-}O^- + H^+ = R\text{-}OH$				8.60
$R\text{-}O^- + Cd^{2+} = R\text{-}OCd^+$				0.5

[a]: the NICA-Donnan model parameters of FA; [b]: the LogK values were adopted from [4, 5].

References

1. K. M. Towe and W. F. Bradley, *Mineralogical constitution of colloidal "hydrous ferric oxides"*, *Journal of Colloid and Interface Science*, 1967, **24**, 384-392.
2. C. Tiberg, C. Sjostedt, I. Persson and J. P. Gustafsson, *Phosphate effects on copper(II) and lead(II) sorption to ferrihydrite*, *Geochimica et Cosmochimica Acta*, 2013, **120**, 140-157.
3. Y. Liang, L. Tian, Y. Lu, L. Peng, P. Wang, J. Lin, T. Cheng, Z. Dang and Z. Shi, *Kinetics of Cd (II) adsorption and desorption on ferrihydrite: experiments and modeling*, *Environmental Science: Processes & Impacts*, 2018, **20**, 934-942.
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5. C. J. Milne, D. G. Kinniburgh, W. H. Van Riemsdijk and E. Tipping, *Generic NICA-Donnan model parameters for metal-ion binding by humic substances*, *Environmental Science & Technology*, 2003, **37**, 958-971.