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Synergistic Adsorption of Cd(II) with Sulfate/Phosphate on Ferrihydrite: An *in Situ* ATR-FTIR/2D-COS Study

Supporting Information

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This supporting information includes 18 pages, 5 tables, and 8 figures: (page)

S1. Two-Dimensional Correlation Spectroscopy (2D-COS)

The 2D-COS is performed according to the theory of Noda.[34-35] A set of one-dimentional spectra collected under external perturbation (e.g. time, concentration, pH) is transformed into a 2D correlation spectrum, which consists of two orthogonal components: synchronous and asynchronous plots. The former represents the simultaneous or coincidental changes of two separate spectral intensity variations during the interval, while the latter represents out-of-phase changes.

A synchronous plot is symmetric with respect to the diagonal and including diagonal peaks (auto peaks) and off-diagonal peaks (cross peaks). The auto peaks are always positive and reveal the major changes in spectral intensities during the perturbation. Thus, any region of a spectrum which changes intensity to a great extent under perturbation will show strong autopeaks, while those remaining near constants develop little or no autopeaks. Cross-peaks can be positive (when intensities at two separate wavenumbers increase or decrease simultaneously) or negative (when increase in intensity at one wavenumber is coupled to the decrease in intensity at another wavenumber).

Unlike a synchronous plot, an asynchronous plot is asymmetric with respect to the diagonal line and consists exclusively of cross peaks, which develops only if the intensities of two spectral features change out of phase with each other. This feature is very useful in enhancing the resolution and separating the overlapped bands arising from different species. On the other hand, the sequential order of intensity changes between two bands at v_1 and v_2 could also be obtained from the sign of synchronous correlation peak Φ (v_1, v_2) and asynchronous correlation peak Ψ (v_1, v_2) according to the well-established principles. In brief, when Φ (v_1, v_2) and Ψ (v_1, v_2) have the same sign, the change in the spectral intensity at v_1 band occurs prior to that at v_2, while the order is reversed if Φ (v_1, v_2) and Ψ (v_1, v_2) have the opposite sign. The changes at v_1 and v_2 occur simultaneously if Ψ (v_1, v_2) is zero. Thus, the sequential order of different species could also be speculated based on the sequential order of different bands.

In this study, the collected time resolved spectra were subjected to the 2D correlation analysis using the 2Dshige code (https://sites.google.com/site/shigemorita/home/2dshige.). From inspection of the regular spectra, we believe that the auto peaks appearing below 960 and above 1180 cm^{-1} in the sulfate spectra, and peaks below 880 and above 1160 cm^{-1} in the phosphate spectra are caused by baseline changes in this region and will not be further discussed, since the asynchronous plot is sensitive to all changes in the spectra including baseline or noise.

Figure S1. XRD pattern of Fh.

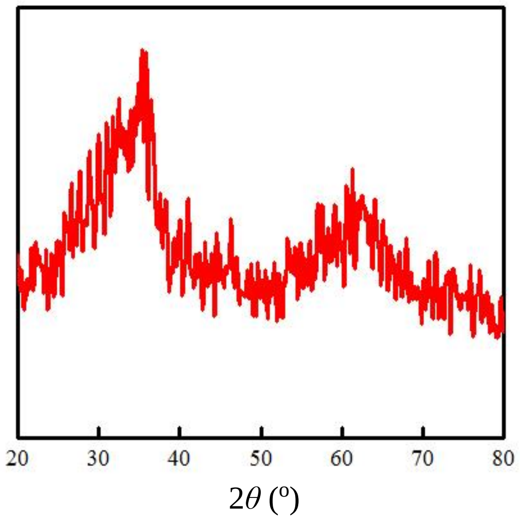

Figure S2. MINTEQ calculation results of saturation index of the potential Cd solid phases in the Cd, Cd+P (A), and Cd+S solutions (B). (The concentration of Cd(II) was 0.2 mM, and that of oxyanions was 2 mM.)

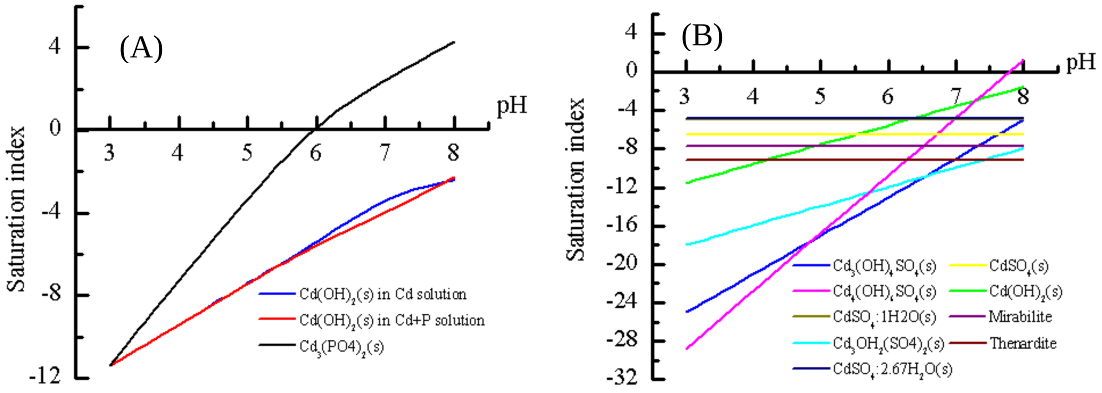

Figure S3. ATR-FTIR spectra of sulfate (100 μM) in the absence or presence of Cd(II) (50 μM) under different solution pH (A); The calculated sulfate speciation diagram in the presence of Cd(II) using visual MINTEQ (B).

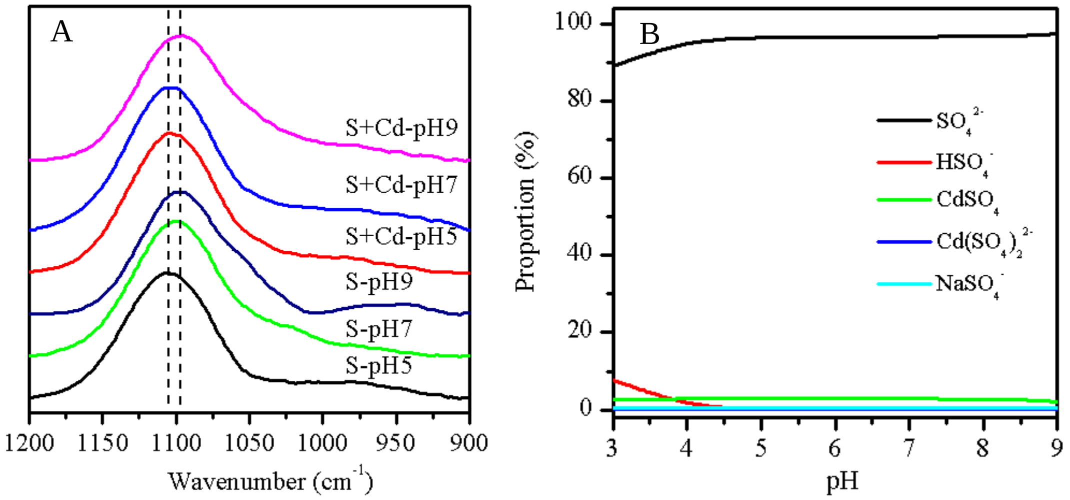

Figure S4. Curve fitting of sulfate infrared spectra at the water-Fh interface at pH 5−9 in S and S+Cd systems.

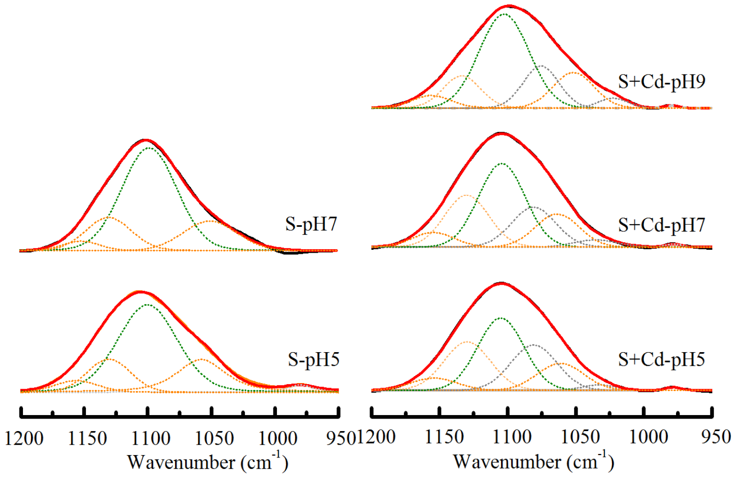

Figure S5. Gran plot for Fh dispersion.

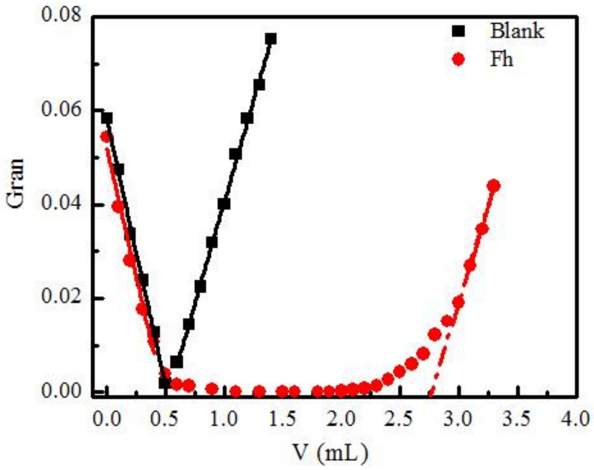

Figure S6. ATR–FTIR spectra of phosphate (100 μM) in the absence or presence of Cd(II) (50 μM) under different solution pH (A); The calculated phosphate speciation diagram in the presence of Cd(II) using visual MINTEQ (B).

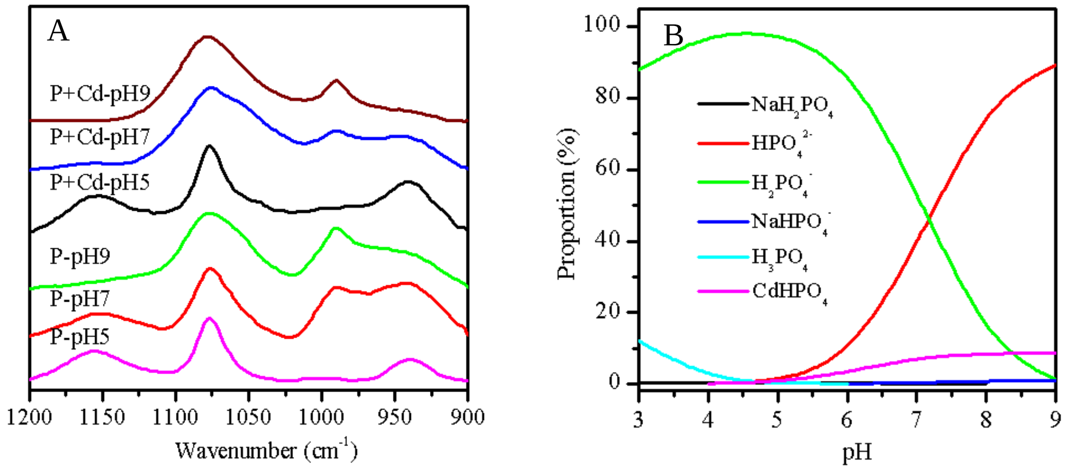

Figure S7. Curve fitting of phosphate infrared spectra at the water-Fh interface at pH 5−9 in P systems (A) and P+Cd systems (B).

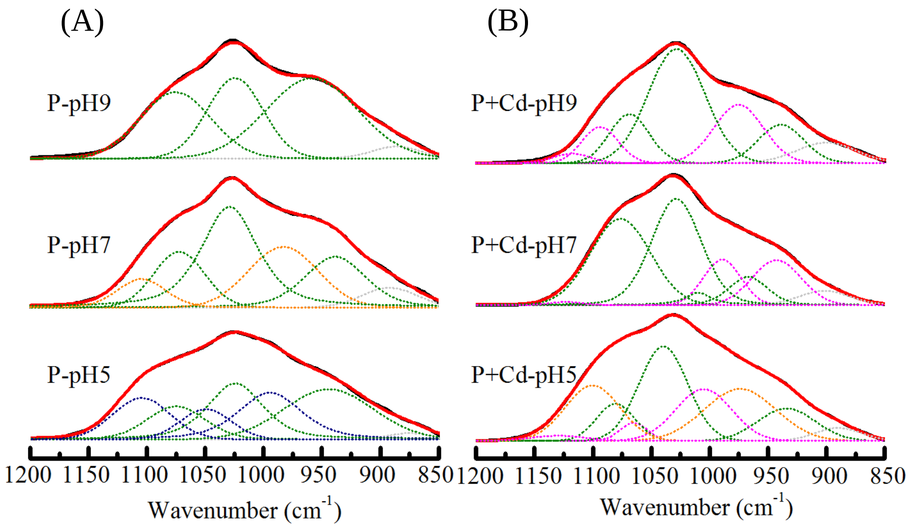

Figure S8. Difference spectra of phosphate (spectra in co-adsorption systems minus that in single adsorption systems)

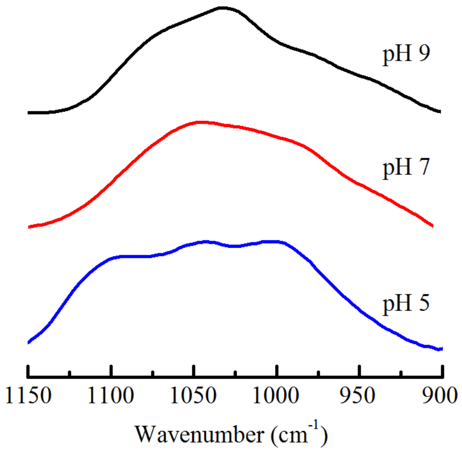

Table S1. Adsorption percentages of phosphate and sulfate in the 2P+Cd and 2S+Cd adsorption systems.

Number	**Adsorption (%)**	
	2P+Cd	**2S+Cd**
1	95.2	84.9
2	98.1	87.4
3	99.3	89.0
4	100	91.0
5	95.0	92.2
6	98.1	98.1
7	99.2	93.0
8	100	91.3

Table S2. The 2D-COS results (data retrieved from Figure 3B) and the assignment of each peak in synchronous (○) and asynchronous; ((-) represents the positive signal, and (+) represents the negative signal) figures of sulfate adsorbed on Fh at pH 7 and 5.

Wavenumber (S-pH 7)	1155	1140	1100	1048
1155			+	
1140			+	
1100	-	-	○	-
1048			+	

Wavenumber (S-pH 5)	1150	1130	1100	1047
1150			+	
1130			+	
1100	-	-	○	-
1047			+	

As shown in the table, the peak at ~1100 cm^{-1} displays asynchronous signal with the other three peaks. In addition, an autocorrelation peak at ~1100 cm^{-1} can also be found in the synchronous plot, indicating a strong change of the intensity of the peak. Thus, two classes of peaks can be identified, and the peak at ~1100 cm^{-1} should be the dominant species. In addition, the asynchronous correlation analysis based on the Noda's rule leads to the sequence of the spectral change ("→" means prior to): 1100→1155/1140(1130)/1048(1047) cm^{-1}, which indicates that sulfate should be adsorbed as outer-sphere complexes prior to the adsorption of bidentate inner-sphere surface complexes.

Table S3. The 2D-COS results of Figure 3D and the assignments of peaks of sulfate adsorbed on Fh in the presence of Cd(II) at pH 9, 7, and 5.

Wavenumber (S+Cd-pH 9)	1155	1130	1105	1075	1050	1030
1155				-		
1130				-		
1105			○	-	-	
1075	+	+	+		+	+
1050			+	-		
1030				-		

Wavenumber (S+Cd-pH 7)	1155	1130	1105	1085	1060	1030
1155			+			
1130			+	+		
1100	-	-	○			-
1085		-			-	
1060				+		
1030			+			

Wavenumber (S+Cd-pH 5)	1160	1130	1105	1085	1060	1020
1160			+			
1130				+		
1105	-		○			+
1085		-			-	
1060				+		
1020			-			

In the S+Cd-pH 9 system, the peak at 1075 cm^{-1} with all the other peaks and the peak at 1105 cm^{-1} with that at 1050 cm^{-1} cannot be in the same class of species. The above deduction in conjunction with the previous studies suggests that peak at 1105 cm^{-1} represents the outer-sphere complexes (species A), peaks at 1150, 1130 and 1050 cm^{-1} can be in the same class of species (species B), and although peak at 1075 cm^{-1} shows synchronous signal with peak at 1030 cm^{-1}, it may be an artifact or a result of uncertainty, and they can be assigned to the C_{3v}

species (species C) according to the previous studies. Therefore, one must be very cautious while using 2D-COS to distinguish the relationship of different peaks, and avoid being misled by artifacts or as a result of uncertainty. The sequence of the spectral change are as follows: 1155, 1130, 1105 and 1050→1075 cm^{-1}, 1105→1050 cm^{-1}, suggesting a sequence of A→B→C. The analysis of the following 2D-COS results follows the same procedure as described here.

At pH 7, the peak at 1105 cm^{-1} should be an individual species (species A), the peaks at 1155, 1130 and 1060 cm^{-1} should be in the same class of species (species B), and the peaks at 1085 and 1030 cm^{-1} should be assigned to another species (species C). Furthermore, a sequence of A→C→B is obtained according to the sequential rule.

However, at pH 5, Species A with a peak at 1105 cm^{-1}, species B with peaks at 1160, 1130 and 1060 cm^{-1}, and species C with peaks at 1085 and 1020 cm^{-1} can be distinguished based on the synchronous signals. In addition, the sequential rule reveals a sequence of C→A→B.

Table S4. The 2D-COS results of Figure 5B and the assignments of peaks of phosphate adsorbed on Fh at pH 9, 7, and 5.

Wavenumber (P-pH 9)	1075	1025	950
1075		+	
1025	-	○	-
950		+	

Wavenumber (P-pH 7)	1100	1075	1035	970	945
1100		+	+		
1075	-		○	-	
1035	-	○	○	-	
970		+	+		
945					

Wavenumber (P-pH 5)	1105	1075	1050	1025	995	945
1105	○			-	○	-
1075		○		○		
1050					○	
1025	+	○		○	+	
995	○		○	-	○	-
945	+				+	

At pH 9, although the peak at 1025 cm^{-1} shows asynchronous signal with peaks at 1075 and 975, we assigned them to be the bands of the same species, whereas at pH 7, two classes of peaks can be recognized according to the asynchronous map: 1100 and 970 cm^{-1} for C_{3v} species (A) and 1075, 1035, and 945 cm^{-1} for C_{2v} species (B). In addition, species B is adsorbed before species A according to the sequential rule. At pH 5, species A with peaks at 1105, 1050, and 995 cm^{-1} and species B with peaks at 1075, 1025, and 945 cm^{-1} can be distinguished, and a sequence of A>B can be obtained.

Table S5. The 2D-COS results of Figure 5D and the assignments of peaks of phosphate adsorbed on Fh in the presence of Cd(II) at pH 9, 7, and 5.

Wavenumber (P+Cd-pH 9)	1118	1090	1070	1033	975	936
1118				+		+
1090			-		-	
1070		+		+		
1033	-		-		-	
975		+		+		+
936	-				-	

Wavenumber (P+Cd-pH 7)	1125	1075	1025	1010	1000	975	945
1125							
1075	+		+				+
1025		-	○	-	+	-	
1010	+		+				
1000		-				-	
975	+		+		+		
945		-					

Wavenumber (P+Cd-pH 5)	1128	1100	1080	1062	1045	995	970	935
1128			+		+			
1100						○		
1080	-					-	-	-
1062				○	+			
1045	-			-		-	-	-
995		○	+		+	○		
970			+		+			
935			+		+			

At pH 9, the peaks at 1090, 1033, 936 cm^{-1} should belong to the same species (A); the peaks at 1118, 1070, and 975 cm^{-1} should be assigned to another species (B). All of the band sequences support the conclusion that species A is adsorbed to the surface of Fh before the adsorption of species B occurs. At pH 7, three species co-exist in the system: the peaks at 1125, 1000, 945 cm^{-1} belong to one species (A); the peaks at 1075, 1025, 975 cm^{-1} belong to the second species (B); the bands at 1075 and 1010 cm^{-1} can be assigned to the third species (C). The obtained adsorption sequence is C>A>B. At pH 5, three co-existing species can still be distinguished: the peaks at 1128, 1062, 995 cm^{-1} belongs to one species (A); the peaks at 1080, 1045, 935 cm^{-1} belongs to the second species (B); and the bands at 1100 and 970 cm^{-1} can be assigned to the third species (C). The obtained adsorption sequence is B>A/C.