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Synergistic adsorption of Cd(II) with sulfate/phosphate on ferrihydrite: An in situ ATR-FTIR/2D-COS study

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19 **Abstract**

20 Elucidation of the co-adsorption characteristics of heavy metal cations and oxyanions on
21 (oxyhydr)oxides can help to better understand their distribution and transformation in many
22 geological settings. In this work, batch adsorption experiments in combination with *in situ* attenuated
23 total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) were applied to explore the
24 interaction mechanisms of Cd(II) with sulfate or phosphate at the ferrihydrite (Fh)–water interface,
25 and the two-dimensional correlation spectroscopic analysis (2D-COS) was used to enhance the
26 resolution of ATR-FTIR bands and the accuracy of analysis. The batch adsorption experiments
27 showed enhanced adsorption of both sulfate (S) and phosphate (P) on Fh when co-adsorbed with
28 Cd(II); additionally, the desorbed percentages of Cd(II) were much lower in the P+Cd adsorption
29 systems than those in the S+Cd adsorption systems. The spectroscopic results suggested that in the
30 single adsorption systems, sulfate primarily adsorbed as outer-sphere complexes with a small amount
31 of bidentate inner-sphere complexes, while the dominant adsorbed species of phosphate were largely
32 the bidentate nonprotonated inner-sphere complexes, although there was significant pH-dependence.
33 In the co-adsorption systems, the synergistic adsorption of Cd(II) and sulfate was dominantly
34 attributed to the electrostatic interaction, as well as the formation of Fe–Cd–S (i.e., Cd-bridged)
35 ternary complexes. In contrast, Fe–P–Cd (i.e., phosphate-bridged) ternary complexes were found in
36 all of the co-adsorption systems of phosphate and Cd(II); furthermore, electrostatic interaction should
37 also contribute to the co-adsorption process. Our results show that *in situ* ATR-FTIR in combination
38 with 2D-COS can be an efficient tool in analyzing the co-adsorption mechanisms of anions and heavy
39 metal cations on iron (oxyhydr)oxides in ternary adsorption systems. The co-existence of Cd(II) with
40 sulfate or phosphate can be beneficial for their accumulations on Fh, and phosphate is more efficient
41 than sulfate for the long-term immobilization of Cd(II).

42 **Keywords:** Cadmium; Phosphate; Sulfate; Ferrihydrite; Synergistic adsorption; ATR-FTIR; 2D-COS

43

44 **1. Introduction**

45 Iron (oxyhydr)oxides can significantly affect the speciation and distribution of contaminants,
46 nutrients, and other solutes in water–rock systems through adsorption processes and thus control the
47 geochemical cycle of many elements.¹⁻⁶ The complexity of natural geomedial media implies that the
48 adsorption of multiple components may occur simultaneously. In recent years, the co-adsorption of
49 heavy metal cations and oxyanions has attracted interest in geochemistry and environmental science.⁷⁻
50 ¹¹ Although a few studies have shown that the adsorption of heavy metal cations and oxyanions on
51 iron (oxyhydr)oxides can be inhibited by each other,⁷ synergistic adsorption is observed more often
52 in the co-adsorption studies.

53 The underlying mechanisms of the co-adsorption are rather complex and they are significantly
54 affected by factors such as solution conditions, the nature and density of the sorbent species, and the
55 surface structure of the selected iron (oxyhydr)oxides.⁹⁻¹¹ For example, arsenate and Zn(II) formed
56 ternary complexes on goethite (Gt) surfaces at low adsorbed density, whereas they formed adamite-
57 like surface precipitates at high density.¹² In addition, sulfate and Pb(II) primarily formed ternary
58 complexes at low pH values and high Pb(II) concentrations, while dominant electrostatic interactions
59 were postulated at high pH values and low Pb(II) concentrations.¹³ It is worth noting that oxyanions
60 having strong affinities to mineral's surface and complexing strongly with metals in solution often
61 form surface ternary complexes in the co-adsorption systems. For instance, phosphate and arsenate,
62 commonly regarded as strong ligands to the surfaces, are mostly reported to form ternary complexes
63 or surface precipitates in the co-adsorption systems.¹⁴⁻¹⁶ On the other hand, sulfate, which rarely forms
64 ligand–metal complexes in solution, is thought to be adsorbed with heavy metal cations through
65 electrostatic interaction and/or $\equiv\text{FeOHMSO}_4$ ternary complexes formation.^{13, 17} One can speculate
66 that the mobility of heavy metal cations could be varied in the environment enriched with different

67 anions due to the differences in the synergistic adsorption characteristic. However, comparison
68 studies and discussions on the co-adsorption characteristics as related to properties of anions are
69 insufficient.

70 When considering iron (oxyhydr)oxides minerals, ferrihydrite (Fh) is one of the most important
71 geosorbents because it is ubiquitous in the environment and one of the most reactive minerals with a
72 variety of functional groups, and has an extremely large specific surface area ($> 200 \text{ m}^2/\text{g}$).¹⁸⁻¹⁹ A
73 number of studies suggested mechanisms for the co-adsorption of metal cations and oxyanions on Fh,
74 but no consistent conclusion was ever reached. Swedlund et al.²⁰ used FITEQL simulations to propose
75 that sulfate co-adsorbed with Co(II), Pb(II), and Cd(II) forming cation-bridged ternary complexes. A
76 similar mechanism was proposed for the co-adsorption of Cu(II) and Pb(II) with phosphate, using
77 extended X-ray absorption fine structure (EXAFS) and surface complexation modeling (SCM).¹¹
78 However, many studies are different from these results. Antelo et al.¹⁶ described Fh-PO₄-Ca and
79 Fh-AsO₄-Ca as anion-bridged ternary complexes using SCM. In our previous study, we proposed
80 the formation of phosphate-bridged ternary complexes in the co-adsorption of phosphate and Zn(II)
81 on Fh using X-ray photoelectron spectroscopy (XPS) and *in situ* attenuated total reflectance Fourier
82 transform infrared spectroscopy (ATR-FTIR).²¹ In addition, there are EXAFS and X-ray diffraction
83 (XRD) measurements that support surface precipitation of arsenate and Fe(III) at the surfaces of Fh.²²⁻
84 ²³ These discrepancies suggest that more systematic studies and discussions are necessary to gain a
85 fundamental knowledge of the co-adsorption behaviors of metal cations and oxyanions on Fh.

86 At present, SCM and spectroscopy-based approaches are the main tools employed to explore the
87 synergistic adsorption mechanisms of metal cations and oxyanions on Fh. SCM can provide guidance
88 in predicting the reactivity of ions at mineral-water interfaces by extrapolating from data obtained in
89 batch experiments. EXAFS spectroscopy can provide coordination numbers and bond distances of

90 the adsorbed ions. However, the analysis of EXAFS data is hindered by the difficulties in detecting
91 light elements (e.g., phosphorus or sulfur),²⁴⁻²⁶ and the necessity of analyzing multiple adsorption
92 centers in co-adsorption systems.²⁷ ATR-FTIR spectroscopy can provide real-time measurement of
93 the vibration signals of the ions that are composed of light elements.^{10, 28-32} However, previous
94 analysis of ATR-FTIR data on the adsorption of anions onto iron (oxyhydr)oxides resulted in different
95 interpretations of the results, due to differences in experimental conditions and difficulties in
96 analyzing the overlapped bands. Therefore, a comprehensive discussion of these results is needed to
97 utilize the technique more effectively. Besides, methods for improving the accuracy of data analysis
98 could be helpful. In recent years, two-dimensional correlation spectroscopy (2D-COS), has emerged
99 as a promising technique to aid the interpretation of surface complexes and their corresponding
100 vibrational features.³³⁻³⁷ 2D-COS is also flexible and has been applied to many spectroscopies (IR,
101 NIR, Raman, ultraviolet-visible, fluorescence, and NMR). Thus, ATR-FTIR in combination with 2D-
102 COS is a promising method to provide valuable information for untangling the co-adsorption
103 behaviors of metal cations and oxyanions on mineral surfaces.

104 In the present study, we investigated the co-adsorption of heavy metal cations and oxyanions on
105 iron (oxyhydr)oxide minerals. Sulfate/phosphate and Cd(II) were selected as representative
106 oxyanions and heavy metal cation, respectively, as they are common contaminants in the natural
107 environment. In addition, as phosphate and sulfate have different complex capacities with heavy
108 metal cations and Fh, the comparison study may provide novel information. Batch adsorption
109 experiments and *in situ* ATR-FTIR in combination with 2D-COS were used to provide novel insight
110 into the mechanism of the co-adsorption behaviors of Cd(II) with sulfate/phosphate on Fh and to
111 predict the fate of heavy metal cations and oxyanions in the surficial environment.

112 **2. Materials and methods**

113 2.1. Materials and characterization

114 $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, NaOH , HNO_3 , $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, NaH_2PO_4 , and Na_2SO_4 of analytical grade
115 (purity > 99%) were obtained from Guangzhou Chemical Reagent Factory. All reagents were used as
116 received.

117 Fh was synthesized using a modification of the method reported by Schwertmann and Cornell.¹
118 A solution of $\text{Fe}(\text{NO}_3)_3$ (1 M, 50 mL) was added dropwise to a solution of NaOH (6 M, 25 mL) under
119 vigorous magnetic stirring, until the pH of the solution was stable at 7. The resulting suspension was
120 centrifuged at 4000 rpm, and the precipitate was washed using ultra-pure water (>18 M Ω /cm) and
121 freeze-dried. The final product was ground to pass a 200-mesh sieve and stored at 4°C.

122 The X-ray diffraction (XRD) pattern of Fh was recorded using a Bruker D8 ADVANCE X-ray
123 diffractometer (Karlsruhe, Germany), operating at 40 kV and 40 mA using $\text{CuK}\alpha$ radiation. The
124 freeze-dried product showed two broad characteristic peaks of 2-line Fh (Figure S1). The specific
125 surface area was measured to be 309 m²/g using a Surface Area & Pore Size Analyzer from
126 Quantachrome. This value is consistent with previous data.¹¹

127 2.2. Batch adsorption/desorption experiments

128 Co-adsorption of $\text{Cd}(\text{II})$ with sulfate or phosphate was investigated using batch experiments. All
129 batch experiments were carried out by adding 0.05 g of Fh to 20 mL 1 mM NaNO_3 solution (solid
130 concentration was 2.5 g/L) containing different concentrations of $\text{Cd}(\text{II})$ and oxyanions. The reactions
131 occurred in 50 mL polypropylene bottles while they were vigorously shaken in an orbital shaker at
132 150 rpm 25°C. These included adsorption isotherms and pH adsorption edges. Adsorption isotherms
133 were measured using initial concentrations of 0.2–2 mM of $\text{Cd}(\text{II})$ on Fh, in the absence or presence
134 of 0.5, 1, or 2 mM of oxyanions (i.e., sulfate or phosphate) at an initial solution pH 5. The pH
135 adsorption edges were measured with initial concentrations of 0.5, 1, or 2 mM of oxyanions, and 0.2

136 mM of Cd(II); hereafter these systems are referred to as 0.5S/P+Cd, 1S/P+Cd, or 2S/P+Cd,
137 respectively.

138 Desorption of Cd(II) and oxyanions was conducted by removing the supernatant after the
139 adsorption equilibrium was reached, replacing with an equal volume of 0.3 M NaCl solution at pH 5,
140 and stirring the sample for 24 h. Finally, the concentrations of Cd(II) and oxyanions in the supernatant
141 were determined after desorption. Four points were chosen from the adsorption isotherms: 1S+Cd,
142 2S+Cd, 1P+Cd, and 2P+Cd, in which the initial concentrations of oxyanions were 1 or 2 mM, and
143 the concentration of Cd(II) was 2 mM. The molar ratio of Cd/(S or P) can therefore be 2 or 1.

144 After the reactions reached equilibrium, the polypropylene bottles were centrifuged at 4000 rpm
145 for 10 min, and then the upper layer suspension was filtered through 0.45 μm filter membrane to
146 obtain the supernatant for further analysis. The concentration of Cd(II) was determined by atomic
147 absorption spectroscopy (Perkin Elmer AAnalyst 400, USA). The concentration of phosphate was
148 determined by UV-VIS spectrophotometry,³⁸ and the concentration of sulfate was determined using
149 high performance anion exchange chromatography (Dionex ICS 900, USA).

150 Simulation of ion speciation in equilibrium solutions, and the saturation index values of the
151 potential Cd solid phases were calculated using visual MINTEQ (version 3.0, John Gustafsson, KTH,
152 Sweden). The distribution of Cd(II) and ligand species in 1 mM NaNO₃ solution was calculated based
153 on the total soluble Cd(II) and oxyanions concentration, at fixed pH values and CO₂ partial pressure
154 of 0.00038 atm (~38.5 Pa) at 25°C.

155 2.3. *In situ* ATR-FTIR spectroscopy

156 *In situ* ATR-FTIR measurements were conducted using a Bruker Vertex-70 FTIR
157 spectrophotometer, equipped with a multi-bounce horizontal ATR accessory and flow cell (Pike
158 Technologies). A horizontal ZnSe ATR crystal was coated with a film of Fh (2.5 mg) by drying Fh

159 suspension. The solution pH was monitored throughout the experiment and adjusted by adding small
160 amounts of 0.5 M HCl or 0.5 M NaOH. The Fh deposit was allowed to equilibrate with the
161 background solution (1 mM NaCl), after which a spectrum was collected as a background. The
162 adsorption experiments were conducted with different solutions of Cd(II) and oxyanions circulated
163 through a peristaltic pump at a rate of 1 mL/min. The concentrations of anions and Cd(II) were 100
164 and 50 μM , respectively. All of the spectra were collected at 25°C over a range of 400–4000 cm^{-1} ,
165 with a resolution of 4 cm^{-1} and 64 scans. The Fh film was checked at the end of each adsorption
166 experiment, and no erosion of the film was observed. The spectra were baseline corrected before
167 analysis following previously published procedures^{28,37}.

168 2.4. Analysis of ATR-FTIR data

169 Analysis of ATR-FTIR data was based on the symmetry argument,¹³ which assigns molecular
170 symmetry based on the number and position of peaks. A free tetrahedral anion has tetrahedral
171 symmetry and belongs to the point group T_d ; this has only one triply degenerate ν_3 band. Adsorption
172 of tetrahedral oxyanions (e.g., sulfate and phosphate) to minerals' surfaces (e.g., iron (oxyhydr)oxides)
173 leads to symmetry reduction from T_d to C_{3v} , C_{2v} , or C_1 , with the triply degenerate ν_3 band splitting
174 into two, three, or three ν_3 bands. The relationship between the number of active bands and the
175 symmetry of the anions has been successfully applied to interpret the bonding configurations of
176 anions at mineral surfaces.^{13,17} To better examine the changes of the overlapped bands, several spectra
177 at equal time intervals were selected for 2D-COS analysis proposed by Noda,³⁴ using the software
178 "2D Shige" released by Shigeaki Mortia (Kwansei-Gakuin University, Japan). Synchronous and
179 asynchronous spectra can be obtained from this analysis. In the synchronous spectra, auto peaks are
180 responsible for the changes of peak intensity over time, while cross peaks provide the responses of
181 two different bands to a time perturbation. In asynchronous spectra, only cross peaks are present. This

182 indicates the uncorrelated response of two bands, likely originating from different surface complexes.
183 Therefore, the resolution of highly overlapped peaks can be greatly enhanced, and the assignments
184 of peaks belonging to each species can be facilitated by 2D-COS analysis.

185 **3. Results and discussion**

186 **3.1. Batch adsorption/desorption experiments**

187 Adsorption of Cd(II) on Fh in the absence of oxyanions was found to be weak, with an adsorbed
188 amount of 0.04 mmol/g at initial Cd(II) concentration of 2 mM (Figure 1A). The adsorption of Cd(II)
189 resulted in a small decrease of solution pH from ~ 5 to 4.8. In the presence of phosphate and sulfate,
190 the adsorbed Cd(II) increased to ~0.33 mmol/g (0.5 mM oxyanions) and ~0.36 mmol/g (1 mM
191 oxyanions), respectively. As the concentration of oxyanions increased to 2 mM, the differences in co-
192 adsorption of Cd(II) with phosphate or sulfate on Fh became more pronounced, with an adsorbed
193 amounts of Cd(II) of 0.55 and 0.45 mmol/g in the presence of phosphate and sulfate, respectively.

194 Oxyanions were removed from solution completely at concentrations of 0.5 and 1 mM, but not
195 at higher concentration (2 mM). At this high concentration of oxyanions, the adsorbed amounts of
196 phosphate were slightly larger than those of sulfate (Table S1), indicating a different co-adsorption
197 capacity towards Cd(II) on Fh. The adsorption of phosphate and sulfate increased the solution pH
198 (from ~5 to ~6–7.5) at low concentrations of Cd(II), whereas only weak changes of the solution pH
199 (± 0.2) were observed at higher concentrations of Cd(II). The change in solution pH after the
200 adsorption suggests a ligand exchange process.

201 The desorption of Cd(II) and oxyanions at pH 5 in P+Cd and S+Cd systems are different (Figure
202 1B). The desorbed percentages of Cd(II) in P+Cd systems were smaller than those in S+Cd systems.
203 The desorbed Cd(II) decreased with increasing concentration of phosphate, and barely any phosphate
204 ions were detected in the supernatant after the desorption reached equilibrium. As reported in previous

205 studies,³⁹⁻⁴¹ strong ligands such as phosphate and arsenate do not get replaced by electrolytes such as
206 NaCl and NaNO₃. Unlike P+Cd systems, desorbed percentages of both Cd(II) and sulfate increased
207 with increasing concentration of sulfate in S+Cd system. The desorption of Cd(II) was not
208 accompanied by the desorption of phosphate in P+Cd systems, indicating a stronger affinity of Fh
209 surface for phosphate compared to Cd(II). Negligible changes of the solution pH (± 0.1) were
210 observed after the desorption equilibrium. The differences in the desorption of Cd(II) and oxyanions
211 in P+Cd and S+Cd systems indicate different mechanisms of co-adsorption, and reveal the different
212 capacity of phosphate and sulfate ions in the long-term immobilization of Cd(II) on Fh.

213 3.2 pH adsorption edges and thermodynamic calculations

214 As shown in the pH adsorption edges (Figure 2A), the percentage of adsorbed Cd(II) increased
215 with increasing solution pH, from ~0% at pH 3 to ~100% at pH 8. The pH at which 50% of the Cd(II)
216 was adsorbed (pH₅₀) was ~5. In the presence of 0.5 mM oxyanions, the adsorption edge shifted to
217 lower pH with the pH₅₀ decreased by nearly 1 pH unit (from 5 to 4). Little difference was observed
218 between sulfate and phosphate in affecting the adsorption edges of Cd(II) at this concentration. At
219 oxyanion concentrations of 1 mM, adsorption of Cd(II) in the S+Cd system was slightly more
220 pronounced as compared to that in the P+Cd system. As the concentration of oxyanions further
221 increased to 2 mM, the adsorption of Cd(II) in the P+Cd system was more pronounced than it was in
222 the S+Cd system in the pH range of 3–5. The calculated saturation index (Figure S2) of potential Cd
223 solid phases (e.g., Cd(OH)₂ and/or Cd₃(PO₄)₂) was < 0 in the pH range of the experiments (pH 4–8
224 for Cd system and pH 3–6 for Cd+ligands systems). Thus, as precipitation of Cd solid phases in
225 solution can be ruled out, the removal of Cd(II) from solution can be assigned entirely to Fh.

226 Based on the available thermodynamic data, the speciation diagrams of Cd(II) in the presence
227 of phosphate or sulfate were calculated using visual MINTEQ (Figure 2B and C). In S+Cd systems,

228 Cd^{2+} was the predominant species, with a small fraction of $\text{CdSO}_4(\text{aq})$ co-existing at pH from 3 to 8.
229 As the concentration of sulfate increased from 1 to 2 mM, the concentration of Cd^{2+} decreased, while
230 that of $\text{CdSO}_4(\text{aq})$ increased. In contrast, the distribution of species of Cd(II) in P+Cd systems was
231 highly dependent on solution pH. At phosphate concentration of 1 mM, Cd^{2+} and $\text{CdHPO}_4(\text{aq})$ were
232 the dominant species at solution $\text{pH} < 6.8$ and $\text{pH} > 6.8$, respectively; This threshold shifted to pH 6.3
233 at phosphate concentration of 2 mM. It should be noted that at solution $\text{pH} < 4$, the species of Cd(II)
234 in Cd+P systems were unchanged with the change of phosphate concentration; thus, the shift of pH
235 edge from 3.5 to 2.6 with the concentration of phosphate increased from 1 to 2 mM was irrelevant to
236 the soluble metal-ligand complexes, i.e., $\text{CdHPO}_4(\text{aq})$.

237 3.3. Infrared spectroscopy results

238 3.3.1 Sulfate/Fh spectra in the absence or presence of Cd(II)

239 Adsorbed sulfate on Fh displayed asymmetric bands in the IR spectrum (Figure 3A), unlike
240 sulfate in solution that showed symmetric bands centered at $\sim 1100 \text{ cm}^{-1}$ (Figure S3). The synchronous
241 contour plots (Figure 3B) exhibit only one prominent auto peak on the diagonal at $\sim 1100 \text{ cm}^{-1}$,
242 indicating a strong change in the intensity of the peak. The asynchronous spectra show four peaks at
243 1155, 1140, 1100, and 1048 cm^{-1} , and the peak at $\sim 1100 \text{ cm}^{-1}$ has asynchronous signal with the other
244 three peaks. Thus, two sets of peaks for sulfate spectra at pH 7 and 5 can be distinguished. The
245 adsorption of sulfate at pH 9 was too weak to obtain a 2D contour plot. Details of 2D data analysis
246 are summarized in Table S2. The peak at 1100 cm^{-1} represents the outer-sphere complexes of sulfate.
247 Another species with two distinctive peaks at 1048 and 1140 cm^{-1} and a shoulder at 1155 cm^{-1} can be
248 considered as bidentate inner-sphere sulfate complexes, similar to the species proposed by Zhang et
249 al.³¹ As the adsorption of sulfate increased with decreasing pH, the ν_1 band became more prominent,
250 although sulfate ions were adsorbed as both outer and inner-sphere complexes at pH 7. The curve-

251 fitting results (Figure S4) suggest that the proportion of inner-sphere surface complexes increased
252 from ~33% to 40% (estimated from the area of the peaks) as the solution pH decreased from 7 to 5.
253 It is worth noting that sulfate is adsorbed only as inner-sphere surface complexes on hematite (Hm),⁴²⁻
254 ⁴³ while it forms a mixture of outer and inner-sphere complexes on Gt at $\text{pH} \leq 6$.²⁸ while on Fh, a
255 mixture of the two complexes can form at $\text{pH} \leq 7$. This adsorption behavior of sulfate on Fh is similar
256 to Gt where a mixture of outer and inner-sphere surface complexes is found at pH values up to 7. This
257 result indicates the different adsorption reactivity of the three iron (oxyhydr)oxides towards sulfate.

258 With the co-existence of Cd(II), the IR spectra of sulfate became broader (Figure 3C),
259 particularly at higher solution pH (7 and 9), indicating a more complicated split of IR active bands.
260 The multiple signals exhibited in the 2D asynchronous spectra (Figure 3D) further verify the
261 complicated split. Thus, Cd(II) not only promoted sulfate adsorption, but also generated a more
262 diverse co-adsorption environment with three species co-existed on the surfaces of Fh (Table 1 and
263 details in Table S3). At pH 9, large amounts of sulfate (~51%) were adsorbed as outer-sphere
264 complexes, with the presence of both C_{2v} or C_1 inner-sphere complexes, in addition to the inner-
265 sphere complexes with bands at 1085 and 1020 cm^{-1} . As the pH decreased (to pH 7 and 5), the same
266 three complexes co-existed on Fh with the proportion of outer-sphere complexes decreasing (40%
267 and 36%, respectively) and that of the inner-sphere complexes increasing, similar to the results of
268 sulfate adsorption. The proportions of C_{2v} inner-sphere complexes in the co-adsorption systems (~38%
269 at pH 7 and 41% at pH 5) were larger than those in the single systems (~31% at pH 7 and 35% at pH
270 5).

271 The increase of proportion of inner-sphere complexes can correspond to two scenarios. In the
272 first scenario, the inner-sphere complexes are adsorbed on Fh; while the negative sulfate anions can
273 reduce the surface charge of Fh thus enhancing the attraction between the surface and Cd(II), the

274 adsorbed Cd(II) can increase the proportion of inner-sphere sulfate complexes in a similar way. In the
275 second scenario, a part of sulfate is adsorbed directly to Cd(II). Sulfate and Cd(II) can be adsorbed
276 synergistically, but they can still compete for Fh surface sites. Hence, the proportion of outer-sphere
277 complexes would decrease, and sulfate would interact with the adsorbed Cd(II) forming ternary
278 complexes with a C_{2v} symmetry. As Cd(II) ions are multi-coordinated in an aqueous environment,
279 this could also involve sulfate. However, if the sulfate was directly bound to Cd(II), the change of
280 bonding environment should cause an evident shift of the bands, which was not detected in this study.
281 Therefore, the increased formation of inner-sphere complexes could be primarily due to the surface
282 charge modification induced by Cd(II) on Fh, hence the first scenario.

283 The additional surface complexes seen in S+Cd systems (as compared with single adsorption
284 systems) showed two bands at 1085 and $\sim 1030\text{ cm}^{-1}$. In the co-adsorption study of Cd(II) and sulfate
285 on Gt,³¹ complexes with bands at 1115 and 1080 cm^{-1} were identified as ternary complexes with
286 monodentate-like symmetry (C_{3v}). A shoulder at 1025 cm^{-1} was also distinguished in their difference
287 spectra, although this was not taken into account. These results are quite similar to the bands observed
288 in our study on Fh. Therefore, the band at 1130 cm^{-1} , which had no asynchronous signal with the
289 bands at 1085 and 1020 cm^{-1} , could be a shared band between two species; this will also explain the
290 relative high intensity of the band at 1130 cm^{-1} in the S+Cd system. Besides, the overestimation to
291 the peak area of the complexes with C_{2v} symmetry should be considered, but overrating to a single
292 band cannot cause an increase to $\sim 6\%$ of the corresponding complexes. As the shoulder band at 1020
293 cm^{-1} was extremely weak, the surface complexes could be assigned as monodentate-like complexes
294 with C_{3v} symmetry.³¹ It is possible that the peak at 1020 cm^{-1} could be the result of a hydrogen bond
295 between an oxygen atom of a monodentate complexes and an adjacent surface site. Two possible
296 configurations can be proposed based on this argument (Figure 4). Cd(II) can be coordinated in a

297 bidentate binuclear fashion to Fe-OH or S-OH, as suggested by the EXAFS results in previous
298 studies.⁴⁴ In configuration A (Figure 4A), monodentate inner-sphere sulfate surface complexes have
299 an additional hydrogen bond to the adjacent adsorbed Cd(II). In configuration B (Figure 4B), sulfate
300 coordinates to adsorbed Cd(II) with an additional hydrogen bond to the adjacent water molecules,
301 forming cation-bridged ternary complexes.

302 To further evaluate the co-adsorption mechanism of sulfate and Cd(II), the quantity of Fh surface
303 sites was calculated using a Gran plot (Figure S5) to be ~ 2.78 sites/nm², and the available adsorption
304 sites were $\sim 6.04 \times 10^{20}$ sites/g. The concentrations of Cd(II) and sulfate were also monitored before
305 and after the *in situ* adsorption experiment, and the estimated total adsorbed amounts of Cd(II) and
306 sulfate were no less than 8.00×10^{20} ions/g in all systems. Considering the potential steric hindrance
307 of the adsorbed species and the occupation of surface sites by bidentate species, the surface sites were
308 insufficient for monolayer adsorption of the ions in S+Cd systems. Hence, surface precipitation and/or
309 ternary complexes (configuration B) should be included in the analysis. However, as the IR spectrum
310 of CdSO₄(s)³¹ has sharp peaks at 1111, 1095 cm⁻¹ and a weak peak at 978 cm⁻¹, which were not seen
311 in our IR spectra, surface precipitation can be excluded. The synergistic adsorption of sulfate and
312 Cd(II) could be attributed to the change in Fh surface charge, as proved by the increase of inner-
313 sphere C_{2v} sulfate complexes in the presence of Cd(II), and to the adsorbed Cd(II) that can bond
314 sulfate forming ternary complexes. Moreover, we have observed a high desorption rate of sulfate in
315 macroscopic studies, which suggests that the presence of monodentate sulfate as part of ternary inner-
316 sphere complexes is relatively unstable. This instability has also been proposed for chromate surface
317 complexes on Fh.⁴⁵

318 3.3.2 Phosphate/Fh spectra in the absence or presence of Cd(II)

319 Multiple bands of the adsorbed phosphate are seen in both synchronous and asynchronous

320 contour plots (Figure 5B), indicating that there is a more complicated correlation between the peaks
321 and thus there could be a variety of phosphate surface complexes. In the phosphate adsorption
322 systems, three bands at 1075, 1025, and 950 cm^{-1} are seen in the asynchronous spectra at pH 9,
323 which can be identified as bidentate non-protonated inner-sphere complexes; this was also seen
324 previously on Gt⁴⁶⁻⁴⁷ and Fh.²⁹ At pH 7 (details in table S4), two sets of bands are identified. Whereas
325 the fraction of bidentate non-protonated inner-sphere complexes decreased (~69%), outer-sphere
326 surface complexes with C_{3v} symmetry (1100 and 970 cm^{-1}) were observed. As these bands are close
327 to those of $\text{HPO}_4^{2-}(\text{aq})$ (Figure S6), this indicates the formation of outer-sphere surface complexes
328 of HPO_4^{2-} via electrostatic attraction and/or hydrogen-bonding complexes. At solution pH 5, the
329 proportion of the bidentate non-protonated inner-sphere complexes further decreased (~57%), and
330 complexes with C_{2v} symmetry were detected.

331 The synchronous spectra of phosphate in the presence of Cd(II) are similar to those in the
332 absence of Cd(II), but asynchronous contour plots show evident differences. At lower solution pH (5
333 and 7), at least three phosphate complexes co-existed on the surfaces of Fh (Table 2). This will be
334 discussed in details in the next section. At pH 9, two sets of bands can be identified (Figure 5D):
335 complexes with peaks at 1090, 1033, and 936 cm^{-1} , and complexes with peaks at 1118, 1070, and 975
336 cm^{-1} . The former set is attributed to bidentate non-protonated inner-sphere complexes as in the single
337 adsorption system at pH 9. The band at 1118 cm^{-1} of the latter set is consistent with the $\nu(\text{P}=\text{O})$
338 vibration, which is found only at lower pH when bidentate mono-protonated phosphate complexes
339 are formed, as reported in previous studies.^{30, 46} This band suggested the formation of two different
340 complexes (Figure 6). In configuration A, P-bridged ternary complexes are formed, whereas in
341 configuration B, protonated monodentate phosphate complexes are adsorbed on the surface of Fh,
342 with additional bonding to the adjacent adsorbed Cd(II). To determine the most likely configuration,

343 the concentrations of Cd(II) and phosphate before and after the adsorption were measured. The total
344 adsorbed amounts of Cd(II) and phosphate ($\geq 8.02 \times 10^{20}$ ions/g) were greater than the available
345 surface sites as reported in section 3.3.1, suggesting the formation of ternary complexes and/or surface
346 precipitation. However, surface precipitation can be excluded, since the adsorption isotherms are
347 quite different from the model of surface precipitation proposed by Farley et al.,⁴⁸ besides, the
348 difference spectra (spectra of co-adsorption systems minus those of single adsorption systems)
349 (Figure S8) show a significant difference compared to the reference spectra of Cd-PO₄ precipitates
350 ¹⁰. Thus, we propose that Fe-P-Cd ternary complexes (configuration A) should be the most likely
351 complexes that form as the newly generated species in the co-adsorption systems.

352 3.4 Discussion and comparison with previous work

353 Many studies have demonstrated that sulfate and phosphate could be adsorbed synergistically
354 with heavy metal cations by iron (oxyhydr)oxides.^{20, 39, 49-51} Most of the studies on co-adsorption of
355 sulfate and Cd(II) on Gt and Fh reported a shift of pH₅₀ between 0.4–0.8 of the Cd(II) adsorption
356 edge (Table 3),^{20, 49, 51} whereas a shift of 1-2 was found in this study. This discrepancy is related to
357 the properties and dosages of adsorbents, the ionic strength, and the concentrations of sulfate and
358 Cd(II). As shown in Table 3, systems with lower ionic strength show a more significant shift of the
359 Cd(II) adsorption edge. This dependence is consistent with the formation of Cd-bridged ternary
360 complexes. As pointed out by Hoins et al.⁵¹ in model calculation studies on Gt, co-adsorption of
361 anions and cations accompanied by the formation of cation-bridged ternary complexes can be
362 inhibited by high ionic strength due to charge repulsion. In contrast to the results in S+Cd systems,
363 the pH₅₀ of Cd(II) shifted to lower pH by 1.2–2 units in the presence of phosphate as reported in
364 previous^{39, 50} and the present studies, although at different ionic strengths. Comparison with previous
365 literature suggests that the co-adsorption of sulfate and Cd(II) decreases in solutions with higher ionic

366 strength, whereas the co-adsorption of phosphate and Cd(II) is much less sensitive to ionic strength.^{20,}
367 ^{39, 49-51} Therefore, comparative experiments carried out under the same conditions are essential in
368 verifying the differences between Cd+S and Cd+P co-adsorption systems.

369 Although a large number of studies deal with ATR-FTIR characterization of sulfate and
370 phosphate complexes forming at iron (oxyhydr)oxide surfaces, the results and assignments are varied.
371 One general standpoint is that sulfate is only adsorbed as inner-sphere complexes on Hm, and as a
372 mixture of outer and inner-sphere complexes on Gt and Fh when the pH is below the point of zero
373 charge. This difference can be attributed to the differences in surface physicochemical properties of
374 the minerals (i.e., surface charge). In addition, the density and topology of surface functional groups
375 can also contribute to different adsorption behavior as discussed by Peak et al.²⁸ When inner-sphere
376 complexes are assigned to IR active bands, the results are not always consistent. Hug et al.⁴³ proposed
377 that when sulfate was adsorbed on Hm, it was predominantly adsorbed as monodentate complexes
378 with two ν_3 bands (1128 and 1059 cm^{-1}). The weak shoulder band at 1185 cm^{-1} in the IR spectra was
379 attributed to hydrogen-bonding interactions between sulfate and adjacent water molecules of the iron
380 hydration shell. Peak et al.²⁸ and Wijnja et al.⁵² suggested that there was a combination of outer-
381 sphere and inner-sphere sulfate complexes on Gt based on their assignment of the peaks of inner-
382 sphere complexes at 1043, 1121, and 1175 cm^{-1} and that of outer-sphere complexes at 1105 cm^{-1} .
383 Peak et al.²⁸ further proved that the inner-sphere complexes were either monodentate bisulfate surface
384 complexes or monodentate sulfate surface complexes with hydrogen bonding to an adjacent surface
385 site by using D₂O as a solvent. In contrast, Lefevre and Fédoroff⁵³ proposed the possibility that there
386 was a mixture of monodentate and bidentate complexes, with the calculations of Paul et al.⁵⁴
387 supporting this standpoint. Recent studies of Zhu et al.⁵⁵ and Gu et al.⁵⁶ confirmed the formation of
388 bidentate binuclear inner-sphere and outer-sphere complexes on Fh surfaces, based on the three ν_3

389 bands (1043, 1121, and 1175 cm^{-1}) of ATR-FTIR spectra, in combination with the results of EXAFS
390 and quantum mechanical calculations.

391 The different interpretation of the ATR-FTIR data in these studies could be due to the differences
392 in the FTIR techniques (most notably the use of *in situ* versus *ex-situ* conditions during data
393 collection), reaction conditions (e.g., anions/adsorbent ratios), quantity and reactivity of sites on the
394 minerals, and the complexity of surface species (i.e., multiple complexes may exist simultaneously).
395 The two complexes assigned respectively by Peak et al.²⁸ and Zhu et al.⁵⁵ to the species with bands
396 at 1043, 1121, and 1175 cm^{-1} could form on the minerals simultaneously, but their relative amounts
397 can vary due to the differences of site densities and reactivity on Gt and Fh. The results of our *in situ*
398 ATR-FTIR study in single adsorption systems were consistent with that of Zhu et al.;⁵⁵ thus we can
399 state that bidentate binuclear complexes are the dominant inner-sphere sulfate complexes on Fh,
400 accompanied by the outer-sphere complexes.

401 In the presence of divalent cations, Swedlund et al.^{20,49} proposed the formation of $\equiv\text{FeOHMeSO}_4$
402 ternary complexes with heavy metal cations (Co(II), Pb(II), and Cd(II)) directly bonding to Fh, based
403 on the diffuse layer modeling results. Zhang et al.³¹ concluded that the additional sulfate complexes
404 in the co-adsorption systems with bands at 1115 and 1080 cm^{-1} were ternary complexes with
405 monodentate-like symmetry (C_{3v}) on Gt. They also suggested that a portion of the initially adsorbed
406 inner-sphere complexes were converted into Cd-SO₄ ternary complexes with the addition of Cd(II).
407 In contrast, an increased proportion of the initial inner-sphere complexes was observed in this study.
408 As discussed above, the electrostatic attraction combined with the formation of cation-bridged ternary
409 complexes, contributed to the synergistic adsorption, which is also in agreement with the batch
410 adsorption and desorption experiment and spectroscopic results. This difference is a consequence of
411 the higher surface area and more abundant functional groups on Fh compared to Gt. Considering the

412 amorphous structure of Fh and the diversity of its surface sites, topology, and reactivity, it is likely
413 that different mechanisms contributed to the synergistic adsorption of oxyanions and Cd(II).

414 Elzinga and Sparks³⁰ discussed the adsorption of phosphate on iron (oxyhydr)oxides, with focus
415 on three complexes. The first complexes are preferentially formed on Hm at low pH and high surface
416 coverage in the pH range 3.5–7.5, and show IR bands at 1117, 1007, and 964 cm^{-1} . The second
417 complexes have three bands at 1086, 1034 and 966 cm^{-1} and are assigned as a bridging non-
418 protonated surface complexes. The third complexes forming at pH values above 6, have two bands at
419 1057 and 966, or 1075 and 990 cm^{-1} depending on the adsorbent, and they are assigned as
420 monodentate mononuclear non-protonated surface complexes. The phosphate adsorption on different
421 iron (oxyhydr)oxides produced different results; as mentioned above, this should be due to the surface
422 properties of the minerals. For example, phosphate complexes at Fh surfaces at high pH (e.g., 7.5)
423 are non-protonated, whereas protonated phosphate complexes form at Hm surface under similar
424 condition.

425 In this study, C_{2v} complexes formed at Fh surfaces in all the adsorption systems are consistent
426 with bridging non-protonated surface complex. The C_{3v} complexes formed at pH 7 with two peaks at
427 ~ 1100 and 970 cm^{-1} , are likely to be outer-sphere or hydrogen-bonded surface complexes, as
428 explained above. We also detected C_{2v} complexes at pH 5, which are generally found at $\text{pH} < 7.5$ in
429 previous studies.²⁹⁻³⁰ As their bands (1105, 1050, and 995 cm^{-1}) are fairly similar to that of the
430 monodentate mononuclear Fe–P (aq) complexes reported by Arai et al.,²⁹ we are able to assign them
431 as protonated monodentate complexes. As the loading of phosphate was comparatively high at low
432 pH, it is likely that this will form monodentate complexes due to the lack of surface sites and steric
433 hindrance.

434 In the co-adsorption systems, slight differences in the band positions between the C_{2v} complexes

435 formed at high pH (with bands at 1090, 1033, and 936 cm^{-1}) and those formed at low pH (with bands
436 at 1080, 1045, 935 cm^{-1}) were observed. Similar results were reported by Elzinga and Kretzschmar¹⁰
437 in the co-adsorption of phosphate and Cd(II) onto Hm. They proposed that Cd-bridged complexes
438 should be the dominant species at high pH, and phosphate-bridged complexes became dominant at
439 low pH. However, they also suggested that their IR data could not rule out the possibility of
440 differences in the phosphate protonation state. The C_{3v} complexes at pH 7 can be assigned to
441 monodentate mononuclear non-protonated complex as was also proposed by Persson.⁴⁷ The C_{3v}
442 complexes at pH 5, however, should be outer-sphere surface complexes of HPO_4^{2-} formed via
443 electrostatic attraction and/or hydrogen-bonding complexes. In comparison with the spectra of
444 phosphate at pH 5 in the single adsorption system, the extra C_{3v} complexes suggest that electrostatic
445 interactions could also have contributed to the synergistic adsorption of phosphate and Cd(II). Still,
446 the species with a band of $\nu(\text{P}=\text{O})$ could be detected in all the co-adsorption systems, indicating the
447 presence of species with similar symmetry.

448 Antelo et al.¹⁶ found that $\text{Fh-PO}_4\text{-Ca}$ ternary complexes could be adequately described by the
449 CD model based on the experiment data. However, Tiberg et al.³⁹ identified a $\text{Cd}\cdots\text{P}$ distance at
450 approximately 3.4 Å by EXAFS analysis, indicating the formation of ternary complexes, and then
451 proposed the formation of Fe-Cd-P ternary complexes on Fh based on the obtained distances of Cd-
452 O, $\text{Cd}\cdots\text{Fe}$, $\text{Cd}\cdots\text{P}$ and SCM results. Contrary to Tiberg's interpretation, we propose the presence of
453 Fe-P-Cd ternary complexes based on the appearance of the $\nu(\text{P}=\text{O})$ band in the co-adsorption
454 systems, similar to that reported by Hinkle et al.⁵⁷ in their studies on co-adsorption of Fe(II) and
455 phosphate on Gt and Hm. As EXAFS provides only average structural information over a short-range
456 near 5 Å, and the distance of $\text{Fe}\cdots\text{Cd}$ could be larger than 6.5 Å in the Fe-P-Cd ternary complexes,
457 the evidence of Fe-P-Cd ternary complexes could be overlooked by EXAFS analysis. Singh et al.⁵⁸

458 also suggested in their co-adsorption study of uranium and phosphate on Gt that while their EXAFS
459 data could be explained by U-bridging ternary surface complexes, it was impossible to statistically
460 distinguish this scenario from that of P-bridged complexes. Hence, we propose that phosphate-
461 bridged ternary complexes can also form in the co-adsorption of phosphate and Cd(II) on Fh; the
462 electrostatic interaction should have made a contribution at the same time.

463 **Conclusions**

464 This study confirms that Cd(II) was adsorbed synergistically with sulfate and phosphate on Fh.
465 Sulfate and phosphate at low concentrations (0.5 or 1 mM) showed a similar synergistic adsorption
466 capacity to Cd(II). However, it is striking that the efficiency of phosphate was enhanced at high anion
467 concentrations (2 mM) with a greater uptake of Cd(II). In addition, the percentages of desorbed Cd(II)
468 and oxyanions in P+Cd systems were smaller than those in S+Cd systems, indicating a stronger long-
469 term immobilization of phosphate and Cd(II) when they are co-existed. The results of ATR-FTIR
470 spectroscopy indicated that the synergistic adsorption of sulfate and Cd(II) was due to electrostatic
471 interaction and the formation of cation-bridged ternary complexes. In contrast, phosphate form anion-
472 bridged ternary complexes with Cd(II) in most of the co-adsorption systems, in addition to the
473 electrostatic interaction. Thus, this study provides additional insights for understanding the
474 geochemical processes involving heavy metal cations and naturally occurring ligands.

475

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- 612 58. Singh, A.; Catalano, J. G.; Ulrich, K. U.; Giammar, D. E. Molecular-Scale Structure of Uranium (VI)
613 Immobilized with Goethite and Phosphate. *Environmental Science & Technology*, **2012**, 46, 6594–6603.
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617 Table 1. Summary of the sulfate IR bands in the ATR-IR experiments.

System	Species	ν_3 bands position (cm ⁻¹)		
S-pH 7	OS	1100		
	C _{2v}	1155	1140	1048
S-pH 5	OS	1100		
	C _{2v}	1150	1130	1047
S+Cd-pH 9	OS	1105		
	C _{2v}	1155	1130	1050
	C _{3v}	1130	1075	(1030)
S+Cd-pH 7	OS	1105		
	C _{2v}	1155	1130	1060
	C _{3v}	1130	1085	(1030)
S+Cd-pH 5	OS	1105		
	C _{2v}	1160	1130	1060
	C _{3v}	1130	1085	(1020)

618 OS represents the outer-sphere complexes; C_{2v} and C_{3v} denote the complexes with symmetry of C_{2v} and C_{3v},
619 respectively.

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621 Table 2. Summary of the phosphate IR bands in the ATR-IR experiments.

System	Species	ν_3 bands position (cm⁻¹)		
P-pH 9	C _{2v}	1075	1025	950
P-pH 7	C _{2v}	1075	1035	945
	C _{3v}	1100	970	
P-pH 5	C _{2v}	1075	1025	945
	C _{2v}	1105	1050	995
P+Cd-pH 9	C _{2v}	1118	1070	975
	C _{2v}	1090	1033	936
P+Cd-pH 7	C _{2v}	1125	1000	945
	C _{2v}	1075	1025	975
	C _{3v}	1075	1010	
P+Cd-pH 5	C _{2v}	1128	1062	995
	C _{2v}	1080	1045	935
	C _{3v}	1100	970	

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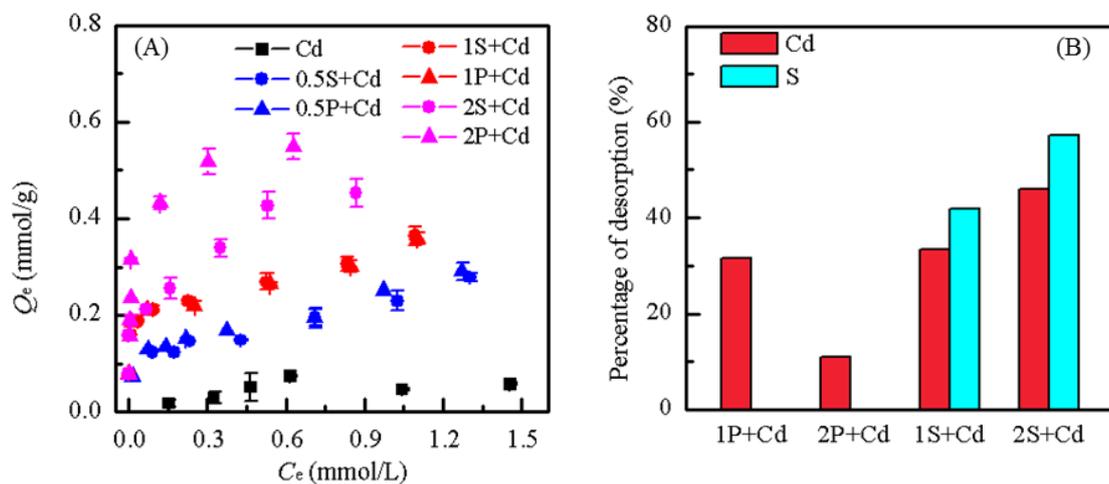
624 Table 3. The offset values of pH_{50} (the difference of pH values at which 50% of the Cd(II) was adsorbed in the
 625 absence and presence of ligands) in pH adsorption edges in the co-adsorption studies of Cd(II) and ligands (sulfate
 626 or phosphate).

Offset of pH_{50}	C_{Cd} (mM)	C_{S} (mM)	I (mM)	D_{Fh} (g/L)	D_{Gt} (g/L)	Q_{Cd} ($\mu\text{mol/g}$)	Reference
0.6	0.07	10	100		1.4	25	49
0.5	0.07	2	100		1.4	25	49
0.8	0.03	2	10		12.5	1.2	51
0.4	0.01	10	100	1		5	20
0.4	0.1	10	100	1		50	20
1	0.2	0.5	1	2.5		40	this study
1.4	0.2	1	1	2.5		40	this study
2	0.2	2	1	2.5		40	this study
Offset of pH_{50}	C_{Cd} (mM)	C_{P} (mM)	I (mM)	D_{Fh} (g/L)	D_{Gt} (g/L)	Q_{Cd} ($\mu\text{mol/g}$)	Reference
1.2	0.03	0.6	10	0.3		50	39
2	0.01	1	10		10	0.5	50
1	0.2	0.5	1	2.5		40	this study
1.3	0.2	1	1	2.5		40	this study
2	0.2	2	1	2.5		40	this study

627 D_{Fh} and D_{Gt} represent the dosages of Fh and goethite, respectively; C_{cd} , C_{P} , and C_{S} denote the concentrations
 628 of Cd(II), phosphate and sulfate, respectively; I represents the ionic strength; Q_{Cd} (the adsorbed amount of Cd(II))
 629 was estimated from data in the given reference.

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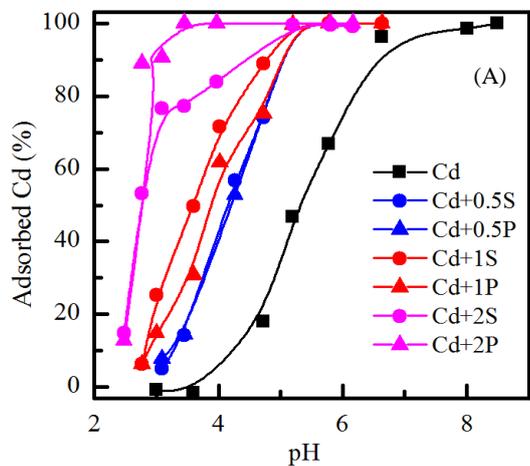
631 Figure 1. Adsorption isotherms (A) of Cd(II) in the absence or presence of sulfate (S) or phosphate
632 (P) (Numbers in the legend denote that the initial concentrations of S or P were of 0.5, 1, or 2 mM;
633 the concentrations of Cd(II) were of 0.2–2 mM in the adsorption isotherms and 0.2 mM in the pH
634 adsorption edges); the percentages of desorbed Cd(II), S, and P by equilibrating with 0.3 M NaCl (B).
635 (No phosphate was desorbed in the desorption experiment)



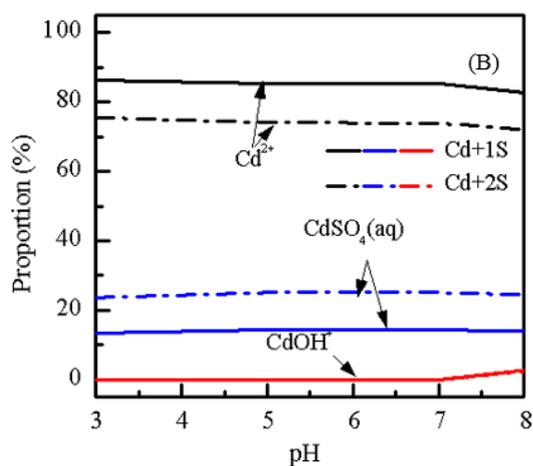
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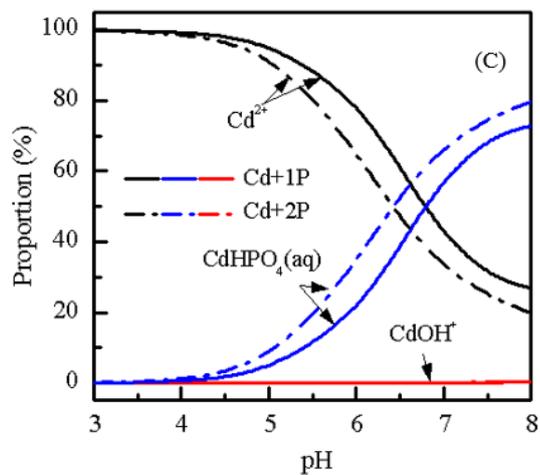
638 Figure 2. The adsorption of Cd(II) at varied pH in the absence or presence of S or P (A); the Cd(II)
 639 speciation in the presence of 1 or 2 mM S (B) or P (C) (denoted as “Cd+1S or P” or “Cd+2S or P”
 640 system) calculated using visual MINTEQ (the concentrations of Cd(II) and oxyanions were set the
 641 same as those in the pH adsorption edges).



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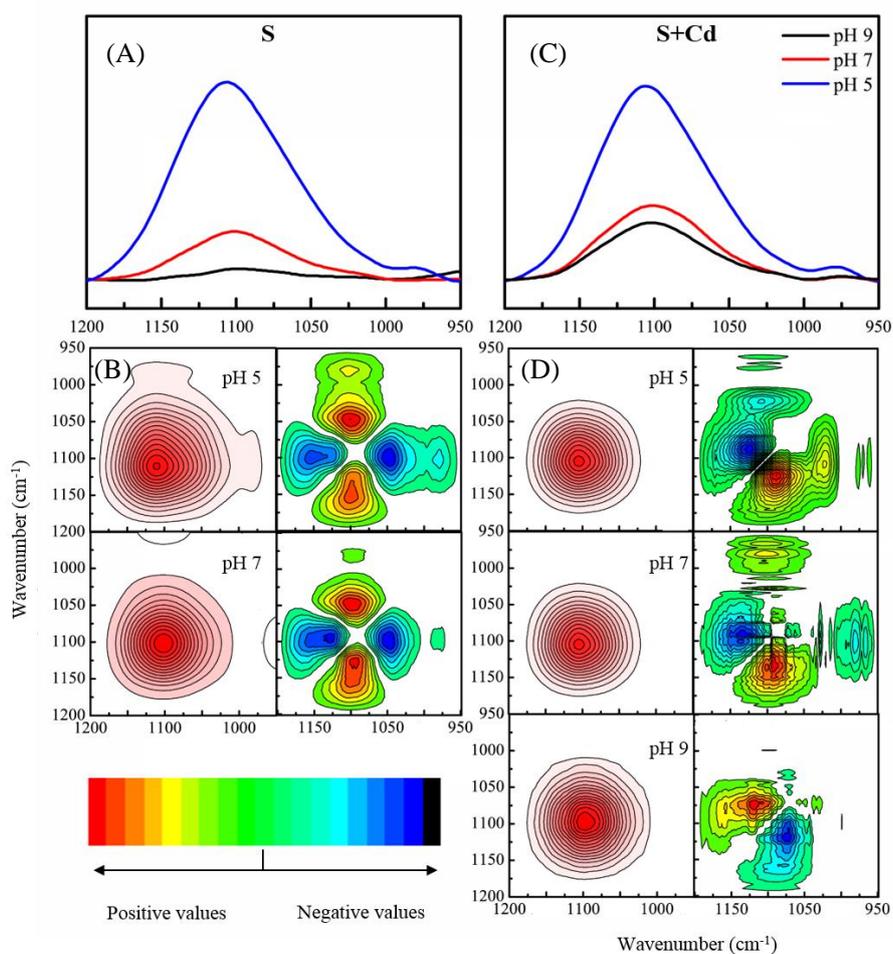
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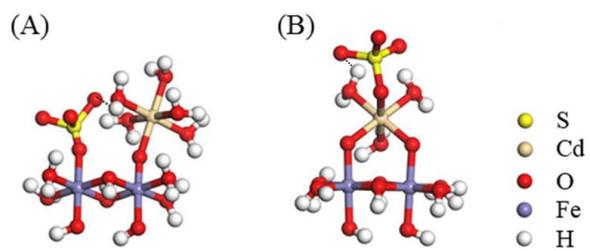
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646 Figure 3. Infrared spectra of sulfate at the water-Fh interface at pH 5–9 in S systems (A) and S+Cd
 647 systems (C); synchronous (red images) and asynchronous (colored images) contour plots obtained
 648 from the 2D-COS analysis of the infrared spectra of sulfate adsorbed on Fh at pH 9, pH 7 and pH 5
 649 in S systems (B) and S+Cd systems (D). (In the colored images: from green to red, the values of z are
 650 positive, while from green to blue, the values are negative). Since the adsorbed amount of sulfate at
 651 pH 9 was too small to obtain a series of spectra as a function of time, the 2D contour plots of the S-
 652 pH 9 system could not be obtained.



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656 Figure 4. Proposed configurations of the sulfate–Cd complexes (A and B). Cd surface complexes are
657 in octahedral coordination with O ligands according to previous studies.⁴⁴

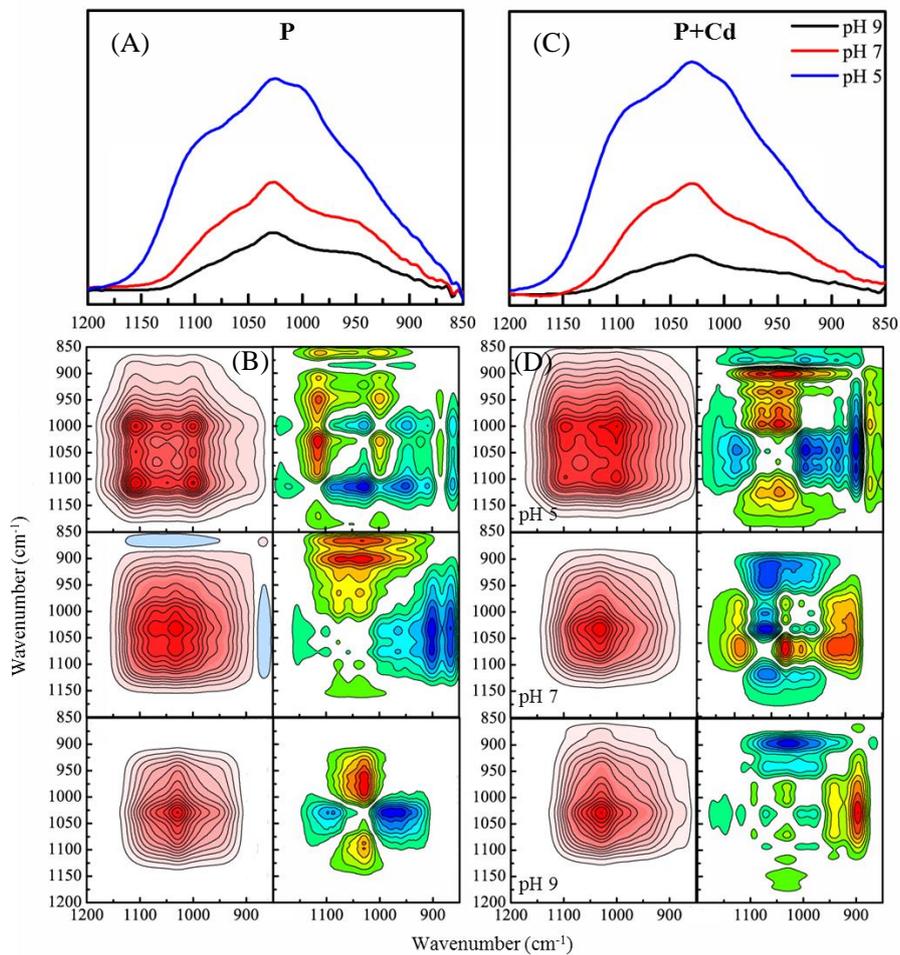


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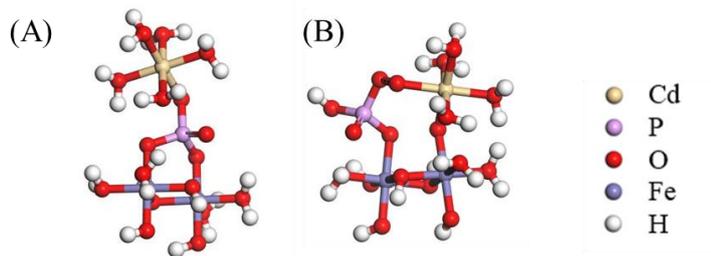
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661 Figure 5. Infrared spectra of phosphate at the water-Fh interface at pH 5–9 in P systems (A) and P+Cd
662 systems (C); synchronous and asynchronous contour plots obtained from the 2D-COS analysis of the
663 infrared spectra of phosphate adsorbed on Fh at pH 9, pH 7, and pH 5 in P systems (B) and P+Cd
664 systems (D).



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668 Figure 6. Proposed configurations of the phosphate–Cd (A and B) complexes in the co-adsorption
669 systems.



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