

CO-SORPTION OF Cd AND PHOSPHATE ON THE SURFACE OF A SYNTHETIC HYDROXYIRON-MONTMORILLONITE COMPLEX

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Abstract—Hydroxymetal-clay complexes, which contain reactive surface hydroxyl groups, have a strong affinity for both heavy-metal cations and oxyanions and hence can serve as efficient sorbents for ionic contaminants. The co-sorptive behavior of heavy-metal cations and oxyanions on the surface of hydroxymetal-clay complexes is not well understood, however. The objective of the present investigation was to help bridge that gap by determining the feasibility of co-sorbing Cd cations and phosphate from aqueous solution to a hydroxyiron-montmorillonite complex (HyFe-mont). A montmorillonite-rich clay from Inner Mongolia, China, was the starting material. The results showed that Cd and phosphate could be sorbed, simultaneously and synergistically, to HyFe-mont without a change in solution pH. Similarly, when phosphate was sorbed before Cd, the sorption capacities were comparable to those obtained in the simultaneous sorption experiment, and the solution pH did not change. When Cd was pre-sorbed, however, the subsequent sorption of both Cd and phosphate decreased as did solution pH. X-ray photoelectron spectroscopy (XPS) indicated that the binding energies of P_{2p}, Cd_{3/2}, and Cd_{5/2} were of similar magnitude for both the simultaneous sorption system and the phosphate pre-sorbed system. In addition, the single Cd and Cd pre-sorbed systems had similar Cd_{3/2} and Cd_{5/2} binding energies. The combined sorption and XPS results suggested that sorbed phosphate and Cd formed P-bridged ternary complexes on the HyFe-mont surface, contributing to the synergistic uptake of the contaminants in the simultaneous sorption system.

Key Words—Co-sorption, Heavy Metal, Hydroxyiron-montmorillonite, Oxyanion, Ternary Complexes.

INTRODUCTION

Polymeric hydroxymetals and clay minerals are ubiquitous in acid to slightly acid soils where they associate to form hydroxymetal-clay complexes (Hy-clays) (Peak *et al.*, 2006; Janssen *et al.*, 2007). The Hy-clays have a strong affinity for both heavy-metal cations and oxyanions due to abundant surface hydroxyl groups of high reactivity (Harsh and Doner, 1984; Lenoble *et al.*, 2002; Schlegel and Manceau, 2007). As such, Hy-clays can serve as important geosorbents affecting the transport and fate of heavy metals and oxyanions in the environment (Saha and Inoue, 1997, 1998; O'Day and Vlassopoulos, 2010), and have also been used as efficient sorbents for these contaminants in wastewater treatment (Matthes *et al.*, 1999; Yan *et al.*, 2008; Zhou *et al.*, 2010). For these reasons, the interactions of Hy-clay with heavy metals or oxyanions have received a great deal of attention (Bergaoui *et al.*, 1999; Nachtegaal *et al.*, 2005) but separately, whereas the co-sorption of these two types of contaminants on Hy-clay has received much less attention.

For the sorption of heavy-metal cations, hydroxy-aluminum-clay complexes have most often been selected as representative to explore the related sorption mechan-

isms (Lothenbach *et al.*, 1997, 1998, 1999; Janssen *et al.*, 2003, 2007). To a lesser extent, sorption on hydroxyiron-clay complexes (Cooper *et al.*, 2002; Wu *et al.*, 2009; Tomul 2011) and hydroxyzirconium-clay complexes (Comets and Kevan, 1993; Matthes, *et al.*, 1999) have also been explored. According to previous studies, Hy-clay with different hydroxymetals have common mechanisms in terms of the sorption of heavy-metal cations. In general, heavy-metal cations are primarily sorbed as inner-sphere complexes involving the deprotonated surface hydroxyl groups on polymeric hydroxymetals and the edges of clay, especially at low sorption density when sufficient surface hydroxyl groups are available (Comets and Kevan, 1993; Matthes *et al.*, 1999; Saha *et al.*, 2001; Janssen *et al.*, 2003, 2007; Wu *et al.*, 2009). Based on the results from desorption experiments, Lothenbach *et al.* (1998) and Matthes *et al.* (1999) suggested that heavy metals can be adsorbed on Hy-clay through cation exchange, and the exchangeable cations may originate from interlayer metal cations and/or the proton from surface hydroxyl groups. Some heavy metals (*e.g.* Cu²⁺, Zn²⁺, Ni²⁺) may become incorporated into the solid phase of polymeric hydroxymetals (Lothenbach *et al.*, 1997; Nachtegaal *et al.*, 2005). That Ni²⁺ can be incorporated into the gibbsite-like structure in the interlayer space of a hydroxyaluminum-montmorillonite complex was demonstrated by Nachtegaal *et al.* (2005). At high solute concentration and solution pH, heavy

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metals may also form discrete hydroxide precipitates on the surface of Hy-clay, even when their concentration is far below the level at which precipitates are formed in aqueous solution (Matthes *et al.*, 1999; Janssen *et al.*, 2007).

The sorptive characteristics of oxyanion contaminants on Hy-clays have also been studied extensively (Lenoble *et al.*, 2002; Tian *et al.*, 2009; Bergaoui *et al.*, 2010). The primary sorption mechanism is one of ligand exchange, *i.e.* the replacement of surface hydroxyl by the oxyanion, and the resultant release of OH⁻ from the polymeric hydroxymetal leads to an increase in solution pH (Zhu *et al.*, 2009; Yang *et al.*, 2010). The sorbed oxyanions may form a variety of inner-sphere complexes with the dehydroxylated hydroxymetal, depending on such factors as solution pH, density of surface hydroxyls, and sorbed density of oxyanions (Peak *et al.*, 2006). In addition, oxyanions may be immobilized on the surface of Hy-clays by forming coprecipitates with metal cations released from the polymeric hydroxymetal component (Saha and Inoue, 1998; Kasama *et al.*, 2004).

As different contaminants often coexist in the natural environment, their behavior and fate may be influenced significantly by each other. Previous studies have shown that the sorption of heavy-metal cations and oxyanions on metal (oxyhydr)oxide can be either inhibited or promoted when they coexist (Rietra *et al.*, 2001; Waychunas *et al.*, 2002; Grafe *et al.*, 2004; Wang and Xing, 2002, 2004; Swedlund *et al.*, 2009). Decreased sorption may be ascribed to competition for coordination sites at the metal (oxyhydr)oxide surface, or the formation of a stable non-sorbing cation-oxyanion complex in solution (Benjamin *et al.*, 1982; Theis and West, 1986). Promoted sorption may be attributed to the formation of ternary complexes, and/or coprecipitates at the metal (oxyhydr)oxide surface (Li and Stanforth, 2000; Elzinga *et al.*, 2001; Ler and Stanforth *et al.*, 2003; Taylor *et al.*, 2009; Elzinga and Kretzschmar, 2013). Decreased electrostatic repulsion during the co-sorption of oppositely charged contaminants may also enhance sorption (Diaz-Barrientos *et al.*, 1990; Collins *et al.*, 1999). Like metal (oxyhydr)oxides, Hy-clays contain reactive hydroxyl groups on their surfaces, and hence might be expected to have sorptive characteristics which are similar to those of heavy metals and oxyanions.

The objective of the present study was, therefore, to investigate the co-sorptive behavior of heavy-metal cations and oxyanions on the surface of an hydroxymetal-clay complex (HyFe-mont), which was prepared from the combination of polymeric hydroxyiron and montmorillonite. Cd and phosphate were selected as representatives of co-sorbing heavy-metal cations and oxyanions, respectively. The interactions of Cd and phosphate with HyFe-mont under different sorption systems (*e.g.* simultaneous sorption, sequent sorption) were studied, and the microstructure of HyFe-mont after

the sorption of Cd and phosphate was further investigated using XPS to identify the bonding modes of the contaminants.

MATERIALS AND METHODS

Materials

The sample of montmorillonite (purity >95%) with the structural formula $\text{Na}_{0.016}\text{K}_{0.020}\text{Ca}_{0.392}[\text{Al}_{2.518}\text{Fe}_{0.450}\text{Mg}_{1.104}\text{Ti}_{0.360}\text{Mn}_{0.004}][\text{Si}_{7.910}\text{Al}_{0.090}]\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$, was obtained from Inner Mongolia, China. The net charge of the clay mineral was $-0.82 e$ per unit cell, and its cation exchange capacity (CEC) was 108 meq/100 g. FeCl_3 , Na_2CO_3 , KH_2PO_4 , and CdCl_2 of analytical grade (purity >99%) were obtained from Shanghai Chemical Co., China, and used as received.

Preparation of HyFe-mont complex

The HyFe-mont complex was obtained by mixing an FeCl_3 solution (0.05 mol/L, 1 L) with montmorillonite (5 g) under vigorous stirring, and titrating the dispersion of Fe-montmorillonite slowly (for ~3 h) with a Na_2CO_3 solution (0.05 mol/L, 1 L). The amount of Fe^{3+} used to synthesize HyFe-mont was 10 mmol Fe^{3+} /g montmorillonite, and the mole ratio of Na_2CO_3 to FeCl_3 was 1:1. The final pH of the dispersion was ~3.2. After aging for 10 h under ambient conditions, the resultant modified montmorillonite was collected by centrifugation, and washed with distilled water until free of chloride (AgNO_3 test). The washed material was dried at 60°C and ground to pass a 100 mesh sieve.

Sorption experiments

Three different systems were used: (1) sorption of a single contaminant; (2) simultaneous sorption of two contaminants; and (3) sequential sorption of two contaminants. For system #1, the sorption of phosphate only ('P' system) or Cd ('Cd' system) on HyFe-mont was measured using an initial concentration of 30–120 mg/L for both phosphate (calculated using P) and for 50–350 mg/L Cd. For system #2 ('P+Cd'), both phosphate and Cd were sorbed simultaneously on HyFe-mont. The initial concentration of the first contaminant was set the same as in system #1; meanwhile, two concentrations of the coexisting contaminant were considered, *i.e.* 60 mg/L and 100 mg/L. For system #3, one contaminant (*e.g.* phosphate) was first sorbed on HyFe-mont until equilibrium was reached, followed by sorption of the other contaminant (Cd). Thus, in the 'P-Cd' system, phosphate was sorbed before Cd, while the reverse sequence applied to the 'Cd-P' system. The concentration of the first contaminant ranged from 40 to 100 mg/L, and that of the second contaminant was set at 100 mg/L.

In systems #1 and #2, 0.1 g HyFe-mont was combined with 20 mL solutions containing different concentrations of Cd and phosphate in a 25 mL teflon

tube. The tubes were rotated at 150 rpm and 25°C for a specified period of time, and then centrifuged at $1500 \times g$ for 30 min to separate the reaction product. The concentration of Cd in the supernatant was determined by atomic absorption spectrometry, and that of phosphate was measured using the molybdenum method (Ye, 2001). Preliminary experiments indicated that sorption equilibrium was reached within ~6 h. On that basis, 10 h was allowed for the system to reach equilibrium. In order to check the release of H^+ or OH^- , the pH of the HyFe-mont suspension was initially adjusted to ~5.0 using HCl (0.5 mol/L) or NaOH (0.5 mol/L) with no further adjustments being made during the sorption process (the solution pH was measured after sorption equilibrium, as shown in Figures 4 and 5). In system #3, 0.1 g of HyFe-mont was combined with 10 mL of solution containing the first contaminant until sorption equilibrium was reached, and then a 10 mL solution of the second contaminant was added. The final (equilibrium) concentrations of the two contaminants were determined as before. All the sorption experiments were conducted in duplicate.

Control experiments indicated no loss of either of the two contaminants in solution in the sorption process and that no interference occurred between the two contaminants during their analysis. Note that in the sorption process a solution precipitate might form at high solute concentration. The values of $[Cd^{2+}]^3[PO_4^{3-}]^2$ of different experimental samples after sorption equilibrium were calculated, therefore. The results showed that in the simultaneous sorption system with 100 mg/L phosphate as a coexisting solute, the two samples with greatest Cd concentrations (300 and 350 mg/L) might form solution precipitates after sorption equilibrium, *i.e.* with a $[Cd^{2+}]^3[PO_4^{3-}]^2$ value close to the K_{sp} value of $Cd_3(PO_4)_2$ (2.53×10^{-33}) (Street *et al.*, 1977). As such, these two samples were excluded from the sorption results.

Characterization methods

The X-ray diffraction (XRD) patterns of HyFe-mont and the original montmorillonite were recorded using a Bruker D8 ADVANCE X-ray diffractometer (Karlsruhe, German), operating at 40 kV and 40 mA with $CuK\alpha$ radiation. The patterns were recorded over the $1.5-70^\circ 2\theta$ range at a scanning speed of $2^\circ/\text{min}$. Basal spacing values were derived from the corresponding diffraction peaks.

Nitrogen sorption-desorption isotherms at 77 K were determined by means of a NOVA 3000e Surface Area & Pore Size Analyzer from Quantachrome (Boynton Beach, Florida, USA), using samples that were previously degassed under vacuum at 100°C for 12 h. The relative pressure (P/P_0) range from 0.05 to 0.35 was selected for the calculation of BET- N_2 surface areas.

X-ray photoelectron spectroscopy (XPS) analyses were carried out in a Thermo Fisher Scientific

ESCALAB 250 spectrometer using a monochromatic $AlK\alpha$ source (10 mA, 15 kV). The spectra were collected with a pass energy of 1486.8 eV and an analysis area of $500 \mu\text{m}^2$. The instrument work function was calibrated to give a binding energy of 400–420 eV for the Cd_{3d} line and 130–140 eV for the P_{2p} line. The binding energy accuracy was ± 0.05 eV. The samples of HyFe-mont, collected from the sorption systems with 100 mg/L Cd and/or phosphate, were dried in air for 24 h before analysis.

RESULTS AND DISCUSSION

Structural characterization of HyFe-mont

The XRD patterns of the original montmorillonite and HyFe-mont were compared (Figure 1). The appearance of several additional reflections at $11.8, 16.7, 26.7, 34.1, 39.3, 46.5,$ and $55.8^\circ 2\theta$ in the pattern of HyFe-mont is consistent with the formation of polymeric hydroxyiron species, primary akaganeite (Song *et al.*, 2011). Meanwhile, the d spacing (d_{001} value) decreased slightly from 1.52 nm for montmorillonite to 1.46 nm for HyFe-mont, indicating the exchange of Ca^{2+} by hydroxyiron (Yuan *et al.*, 2008). Another reflection at a smaller 2θ value for HyFe-mont corresponded to a d spacing of 3.47 nm. The HyFe-mont synthesized by intercalating hydroxyiron directly into Ca-montmorillonite was shown by Yuan *et al.* (2008) to have two d spacings at 1.47 and 5.59 nm which originated from the intercalated and delaminated parts of HyFe-mont, respectively. The d spacing of 3.47 nm, therefore, may have arisen from the intercalated HyFe-mont or from the delaminated part.

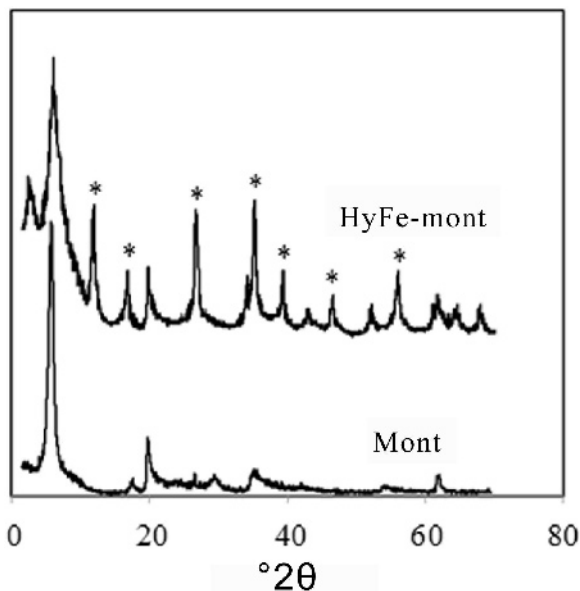


Figure 1. XRD patterns of natural montmorillonite and HyFe-mont. The diffraction peaks labeled * belong to polymeric hydroxyiron (primary akaganeite).

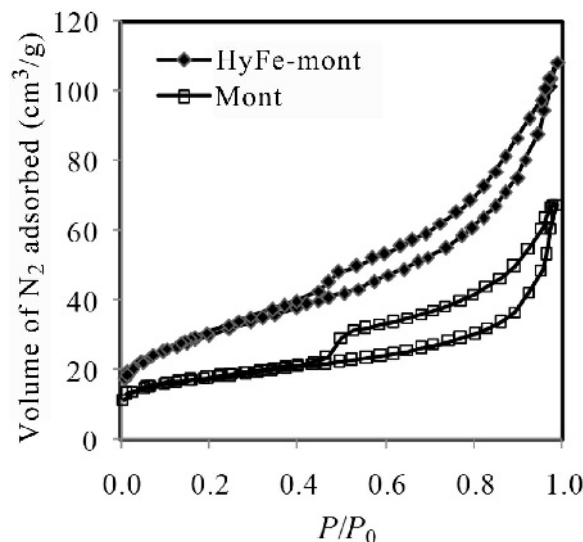


Figure 2. N_2 adsorption-desorption isotherms of natural montmorillonite and HyFe-mont.

The N_2 sorption-desorption isotherms of the original montmorillonite and HyFe-mont (Figure 2) were of the B-type showing hysteresis, indicative of parallel-type pores (Toth, 2001; Wang *et al.*, 2004) in accordance with the layered structure of these materials. The sorption isotherm of HyFe-mont further suggests that the sample contained both micropores and mesopores. The former may be identified with pores between hydroxyiron polymers in the interlayer space, while the mesopores represent spaces between HyFe-mont particles. The BET surface area, calculated from the isotherm, was $55 \text{ m}^2/\text{g}$ for the original montmorillonite and $108 \text{ m}^2/\text{g}$ for HyFe-mont. The relatively large value measured for HyFe-mont was due to intercalation of polymeric hydroxyiron species.

Simultaneous sorption of phosphate and Cd to HyFe-mont

The isotherms for the sorption of phosphate and Cd to HyFe-mont (Figure 3) showed clearly that more of the contaminants were sorbed in the simultaneous sorption system than in the single sorption system, indicating that phosphate and Cd were sorbed synergistically in the 'P+Cd' system. Further, increasing the concentration of one contaminant (*e.g.* phosphate) from 60 to 100 mg/L evidently promoted the sorption of the other contaminant (*e.g.* Cd), which suggests that the sorbed contaminant provided additional sites for the sorption of the other contaminant. Three possible mechanisms have been proposed to account for the synergistic sorption of metal cations and oxyanions to metal (oxyhydr)oxides, namely: the formation of ternary complexes; surface precipitation; and enhanced electrostatic interaction (Venema *et al.*, 1997; Collins *et al.*, 1999; Rietra *et al.*, 2001; Waychunas *et al.*, 2002; Grafe *et al.*, 2004; Swedlund *et al.*, 2009; Elzinga and Kretzschmar, 2013). In common with metal (oxyhydr)oxides, in general, HyFe-mont contains reactive surface hydroxyl groups. As such, the above-mentioned mechanisms would also be operative in the present instance.

The involvement of surface hydroxyl groups in the sorption of oxyanions and heavy-metal cations by hydroxyl-metal-clays has been well documented (Nachtegaal *et al.*, 2005; Janssen *et al.*, 2007; Borgnino *et al.*, 2009; Bergaoui *et al.*, 2010; Yang *et al.*, 2010). The present results demonstrated that in the single-contaminant sorption system, the solution pH decreased after sorption of Cd, and increased after the sorption of phosphate (Figure 4), indicating that sorption of Cd and phosphate leads to the release into solution of H^+ and OH^- , respectively. Similar results were reported for the sorption of heavy-metal cations and oxyanions to

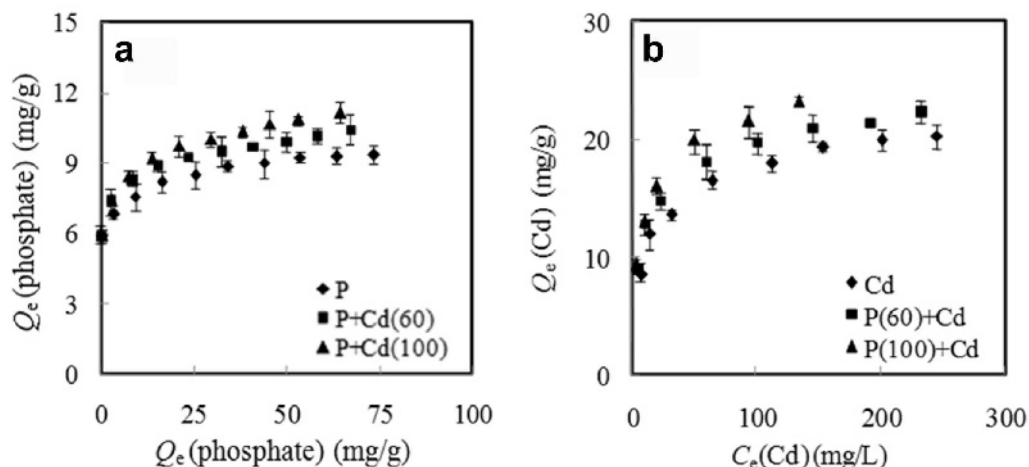


Figure 3. Sorption isotherms of phosphate (a) and Cd (b) on HyFe-mont. Both the single-solute sorption results and two-solutes simultaneous-sorption results are presented. The numbers in parentheses indicate the concentration of coexisting solute.

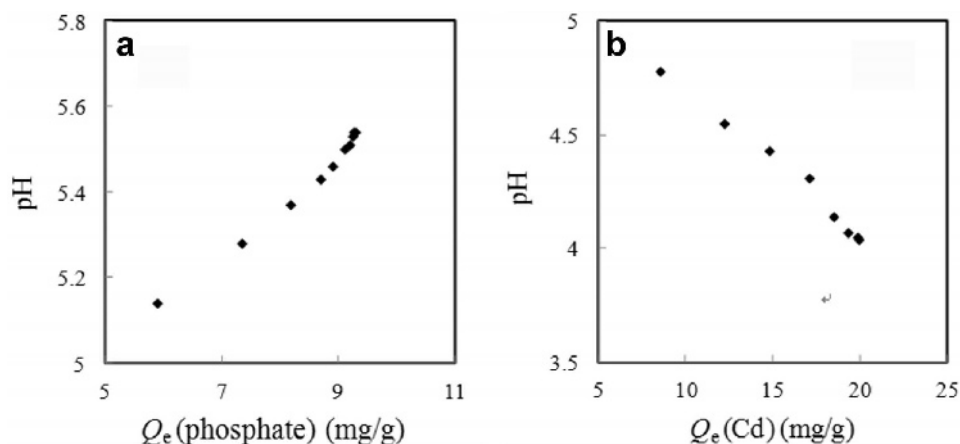


Figure 4. Correlations between amount of solutes sorbed and the equilibrium pH in the single-solute sorption system: (a) correlation between phosphate and pH; and (b) correlation between Cd and pH.

metal (oxyhydr)oxides and Hy-clays (Miyazaki *et al.*, 1996; Kasama *et al.*, 2004; Zhu *et al.*, 2009). For the 'P+Cd' system, on the other hand, the final solution pH changed only slightly (<0.2 pH unit) and no obvious correlation was observed between the amount of contaminants sorbed and solution pH (Figure 5). The OH^- and H^+ ions released during the sorption process would be expected to neutralize each other.

Sequential sorption of phosphate and Cd to HyFe-mont

The results of the sequential sorption of Cd and phosphate to HyFe-mont were compared with those obtained for the simultaneous sorption system (Figure 6). In the phosphate pre-sorbed ('P-Cd') system, the two contaminants were sorbed to a similar extent as in the 'P+Cd' system. In both sorption systems, the sorption capacity of Cd was apparently enhanced by sorbed phosphate, as the enhancement was proportional to the amount of phosphate sorbed (Figure 6b). This

observation implies that the pre-sorbed phosphate provides additional sorption sites for Cd. The enhanced sorption of metal cations on mineral surfaces due to the presence of pre-sorbed oxyanions has been ascribed to increased electrostatic interactions (Wang and Xing, 2004) or to the formation of surface precipitates (Taylor *et al.*, 2009).

Less phosphate was sorbed in the Cd pre-sorbed ('Cd-P') system than in the 'P+Cd' system (Figure 6c). When the amount of Cd sorbed increased, phosphate sorption increased in the 'P+Cd' system but decreased in the sequential sorption system. The amount of phosphate sorbed in the 'P' system was 9.2 mg/g, which was larger than that in the 'Cd-P' system. These observations indicated that in the 'Cd-P' system, the pre-sorbed Cd occupied some of the phosphate sorption sites on the HyFe-mont surface. Furthermore, slightly less Cd was sorbed in the 'Cd-P' system than in the 'P+Cd' system in the high-Cd sorption density range (Figure 6d), where

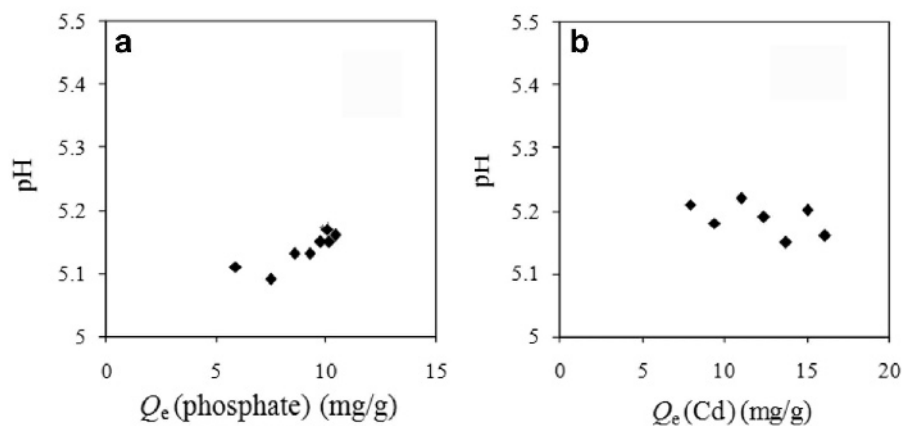


Figure 5. Correlations between the amount of solutes sorbed and the equilibrium pH in the simultaneous-sorption system: (a) correlation between phosphate and pH; and (b) correlation between Cd and pH. The initial concentrations of Cd in (a) and phosphate in (b) were both set to 100 mg/L.

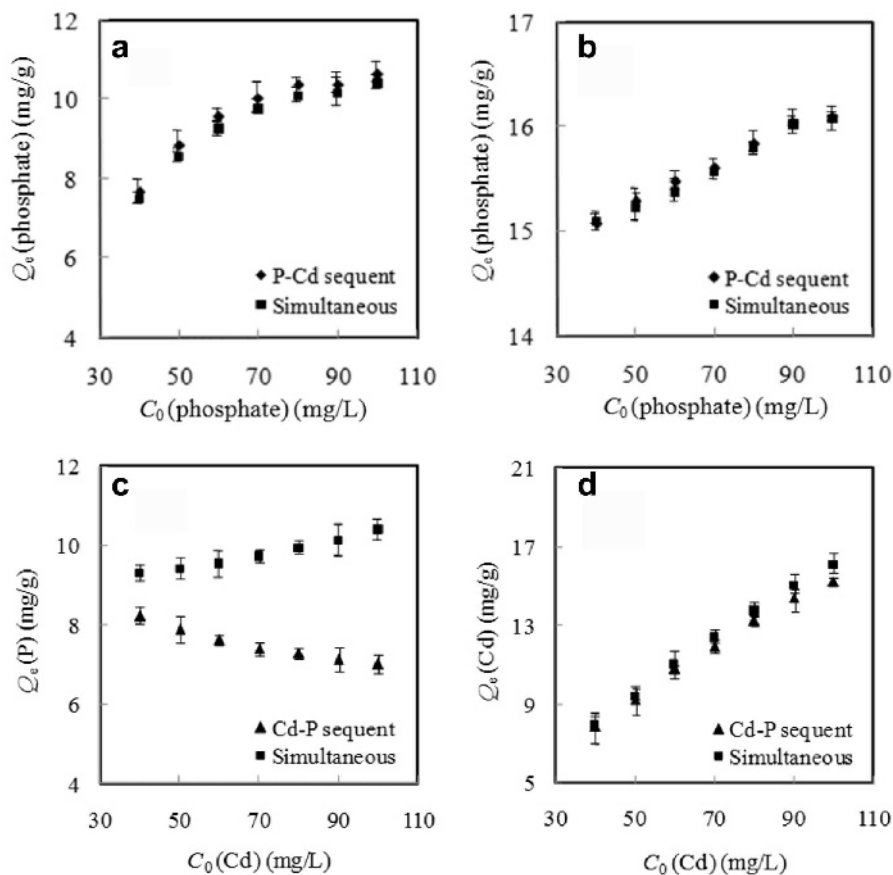


Figure 6. Sequential sorption results of the phosphate and Cd on HyFe-mont: (a) phosphate sorption in the 'P-Cd' system (*i.e.* first phosphate and then Cd); (b) Cd sorption in the 'P-Cd' system; (c) phosphate sorption in the 'Cd-P' system (*i.e.* first Cd and then phosphate); and (d) Cd sorption in the 'Cd-P' system. For comparison purposes, the sorption results in the simultaneous sorption are also presented. The concentrations of the coexisting solute (*i.e.* Cd in the 'P-Cd' system and phosphate in the 'Cd-P' system) were both set at 100 mg/L.

the difference in phosphate sorption between the two systems was more evident. Reduced sorption of Cd in the 'Cd-P' system may, therefore, be attributed to a decrease in Cd sorption sites provided by the sorption of P. In a fully reversible and equilibrated sorption system, the sorption sequence should not lead to a notable difference in the sorption capacity of the sorbates. The different sorption behavior of the 'Cd-P' system (compared to those of the 'Cd+P' and 'P-Cd' systems), therefore, should be attributed to the different sorption kinetics and/or sorption irreversibility of the two contaminants.

The presence of Cd did not appear to influence the sorption of phosphate on goethite in both the simultaneous sorption and Cd pre-sorbed systems, according to Wang and Xing (2004), possibly because the amount of Cd sorbed was very small. On the other hand, the amount of Cd sorbed on HyFe-mont was more than an order of magnitude greater than that on goethite. Measurements in the present study also showed that in low-Cd concentration range, the difference in the amount of phosphate sorbed between the 'P+Cd' system and the

'Cd-P' system decreased (Figure 6c), similar to that found in the 'P' system (9.2 mg/g).

The relationship between the final solution pH and the amount of contaminants sorbed in the sequential sorption systems were examined (Figure 7). In the 'P-Cd' system (Figure 7a), the change of solution pH was quite small (<0.2 pH unit), similar to that observed for the 'P+Cd' system. The sorption of Cd apparently releases H^+ into the solution, neutralizing the OH^- liberated during the sorption of P. The similarity in sorption capacity and solution pH between the 'P-Cd' and the 'P+Cd' systems also suggests that the contaminants were attached in a similar manner to the HyFe-mont surface, *i.e.* directly bound to the HyFe-mont surface in both systems.

In the 'Cd-P' system (Figure 7b), on the other hand, solution pH decreased markedly as the amount of Cd sorbed increased and phosphate sorption decreased. This observation is quite different from that in the 'P+Cd' system but similar to that in the single Cd-sorption system, implying that in the 'Cd-P' system most of the sorbed Cd was bound directly to the HyFe-mont surface,

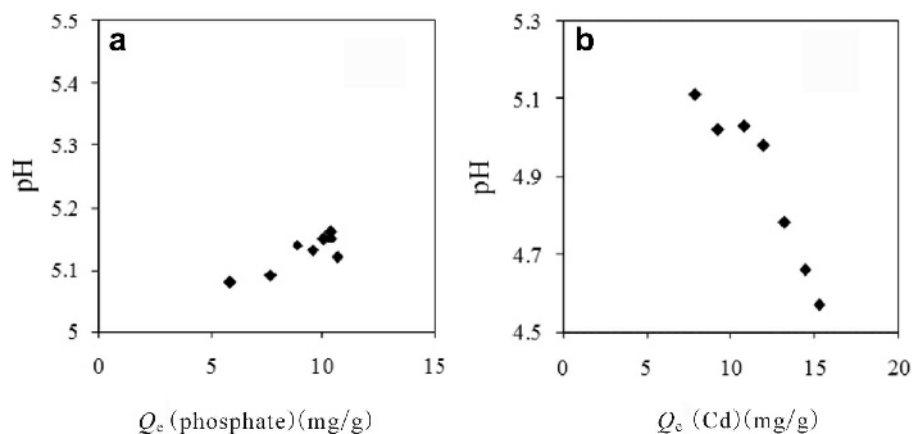


Figure 7. Correlations between the amount of solutes sorbed and the equilibrium pH in the sequential sorption system: (a) correlation between phosphate and pH in the 'P-Cd' system; and (b) correlation between Cd and pH in the 'Cd-P' system. The initial concentrations of Cd in (a) and phosphate in (b) were both 100 mg/L.

causing the release of H^+ from the surface as was the case in the single-Cd sorption system. This finding suggests strongly that Cd was bound to the sorbed phosphate in the 'P+Cd' system, in agreement with the hypothesis above that in this system, phosphate binds directly to the HyFe-mont surface. As phosphate sorption leads to the release of OH^- , while H^+ is liberated during Cd sorption, the decreased sorption of phosphate in the 'Cd-P' system and the lack of phosphate sorption in the Cd system are responsible for the decrease in solution pH.

Bonding mode of phosphate and Cd on HyFe-mont

In the present study, the change in solution pH during sorption is indicative of strong interactions (*i.e.* more than just electrostatic) between phosphate and Cd in the 'P+Cd' system. In other words, phosphate and Cd might form surface precipitates and/or ternary complexes on the HyFe-mont surface. Both surface precipitation and ternary-complex formation involved multilayer complex formation according to Ler and Stanforth (2003), and those authors considered these two mechanisms to be similar. Thus, the same treatment was applied in the present study and both are referred to as 'ternary-complex formation.'

Previous studies showed that the formation of ternary complexes on metal (oxyhydr)oxide surfaces is mediated by either oxyanion bridging (Ler and Stanforth 2003; Elzinga and Kretzschmar, 2013) or cation bridging (Elzinga *et al.*, 2001; Swedlund *et al.*, 2009; Elzinga and Kretzschmar, 2013), depending on the cation-anion pair and the physicochemical characteristics of the surface. The present authors suggest that in the 'P+Cd' system (as well as in the 'P-Cd' system), the HyFe-mont surface is primarily occupied by sorbed P, while most of the sorbed Cd is attached to the sorbed P, rather than directly to the HyFe-mont surface. In order to obtain supporting evidence for this hypothesis the HyFe-mont

samples containing sorbed contaminants were examined by XPS. Although the XPS characterization method is only applicable for dried samples (*i.e.* *ex situ* characterization) and may not fully explore the interactions in an aqueous system, XPS has been used many times to assess the interactions of inorganic ions with solid surfaces (Dideriksen and Stipp, 2003; Daou *et al.*, 2007; Seyama *et al.*, 2006; Li and Zhang, 2007).

High-resolution XPS patterns were obtained of the HyFe-mont samples after sorption of the contaminants (Figure 8). The P_{2p} binding energy of sorbed phosphate in the different systems increased gradually in the order 'Cd-P' < 'P+Cd' < 'P-Cd' < 'P' (Table 1). In the 'P' system, the sorbed phosphate was bound directly to the HyFe-mont surface as an inner-sphere complex, giving rise to the large P binding energy. As the amount of phosphate that is directly bound to the HyFe-mont surface should decrease in the order 'P-Cd' > 'P+Cd' > 'Cd-P', so does the P binding energy. The P_{2p} binding energy suggests that the chemical environment for phosphate in the 'P-Cd' system was similar to that in the 'P+Cd' system, in accord with the sorption results.

The binding energies of the sorbed Cd were different in different sorption systems (Table 1). Thus, the Cd $3d_{3/2}$

Table 1. The binding energies (eV) of P_{2p} , $Cd_{3/2}$, and $Cd_{5/2}$ on different HyFe-mont samples after the sorption of the contaminants.

Samples	P_{2p}	$Cd_{3/2}$	$Cd_{5/2}$
P	133.83	—	—
Cd	—	407.03	413.78
P+Cd	133.78	405.78	412.53
P-Cd	133.79	405.98	412.88
Cd-P	133.74	406.93	413.63

Note: these samples are as indicated in Figure 6.

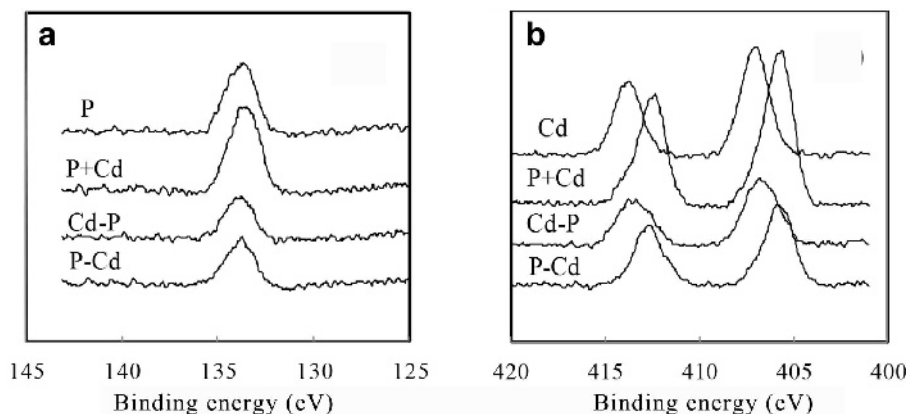


Figure 8. XPS patterns of montmorillonite samples after sorption of the contaminants. The binding energies of P_{2p} and Cd_{3d} are shown in (a) and (b), respectively. The meaning of the symbols is the same as shown in previous figure captions.

and Cd $3d_{5/2}$ binding energies in the ‘Cd’ system were slightly larger than those in the ‘Cd-P’ system but were much larger than the values measured in the ‘P+Cd’ and ‘P-Cd’ systems. This finding indicates that the sorbed Cd was in a similar chemical environment in both the ‘Cd’ system and ‘Cd-P’ system where most of the sorbed Cd was bound directly to the HyFe-mont surface. On the other hand, the chemical environment for Cd in the ‘P+Cd’ and ‘P-Cd’ systems was rather different from that in the ‘Cd’ and ‘Cd-P’ systems. As such, one would expect that in the ‘P+Cd’ and ‘P-Cd’ systems, the Cd sorbed was bound to phosphate rather than directly to the surface of HyFe-mont.

The strong interactions between sorbed phosphate and Cd in the ‘P+Cd’ system would indicate that electrostatic attraction was not the predominant mechanism underlying the synergistic sorption of phosphate and Cd in the ‘P+Cd’ system, although its contribution could not be ruled out. Rather, the formation of ternary complexes/surface precipitates was primarily responsible for the synergistic sorption of phosphate and Cd to HyFe-mont.

On the basis of the sorption and XPS results, the following model for the binding of phosphate and Cd to HyFe-mont in the ‘P+Cd’ system was proposed. First, phosphate binds directly to surface Fe-OH groups *via* a ligand-exchange mechanism, forming a $\equiv Fe-P$ inner-sphere complex. The resultant release of OH^- leads to an increase in solution pH. Second, Cd binds to the sorbed phosphate to form a $\equiv Fe-P-Cd$ ternary complex. As no significant change occurs in solution pH, the second process appears to liberate H^+ from phosphate ($H_2PO_4^-$ or HPO_4^{2-}), neutralizing the released OH^- . Third, the bound Cd may further sorb phosphate, forming a $\equiv Fe-P-Cd-P$ complex. Thus, more phosphate is sorbed in the ‘P+Cd’ system than in the ‘P’ system. A similar bonding mode was proposed by Li and Stanforth (2002) and Ler and Stanforth (2003) for the sorption of phosphate and Fe by goethite where Fe, spiked into the solution, or directly dissolved from goethite, was the source of iron (Ler and Stanforth 2003).

The possibility that other sorption models are applicable to the interactions of phosphate and Cd with HyFe-mont cannot be ruled out. For example, seven sorption models for the formation of ternary P/Cd complexes on hematite were proposed by Elzinga and Kretzschmar (2013), namely: two lateral interaction complexes; two metal-bridged complexes; and three P-bridged complexes. These and other possible models for a ternary sorption system are subject to influence by such factors as solution pH, physicochemical properties of the minerals, and sorption densities of the contaminants (Collins *et al.*, 1999; Grafe *et al.*, 2004; Swedlund *et al.*, 2009; Elzinga and Kretzschmar, 2013). Systematic studies using spectroscopic methods and quantum mechanical calculations are necessary to clarify the binding of metal cations and oxyanions to, and the formation of ternary complexes on, HyFe-mont surfaces.

CONCLUSIONS

The co-sorption of phosphate and Cd to hydroxyiron-montmorillonite (HyFe-mont) was investigated by comparing sorption capacities and equilibrium solution pH values of different sorption systems. Phosphate and Cd could be sorbed synergistically in both the simultaneous sorption and phosphate pre-sorbed systems without affecting solution pH values. On the other hand, in the Cd pre-sorbed system, the sorption capacity for both Cd and phosphate decreased as did solution pH. Using XPS, the binding energies of P_{2p} , $Cd_{3/2}$, and $Cd_{5/2}$ were shown to depend heavily on the sorption systems. Similar binding energies were measured for the simultaneous sorption and phosphate pre-sorbed systems, consistent with their having similar sorptive characteristics toward phosphate and Cd. Similar $Cd_{3/2}$ and $Cd_{5/2}$ binding energies were also found for the single Cd sorption and the Cd pre-sorbed systems. In the simultaneous sorption system, the sorbed phosphate and Cd are suggested here to have formed phosphate-bridged ternary complexes ($\equiv Fe-P-Cd-P$) on the HyFe-mont surface, contributing

to the synergistic sorption of the contaminants. This investigation sheds new light on the sequestration of heavy-metal cations and oxyanions by hydroxymetal-clay complexes.

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