Adsorption of phosphate on hydroxyaluminum- and hydroxyiron-montmorillonite complexes

Mao-Xu Zhu [a],*, Kui-Ying Ding [a], Shao-Hui Xu [b], Xin Jiang [c]

[a] *Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China*
[b] *Department of Environmental Science and Engineering, Qingdao University, Qingdao 266100, China*
[c] *State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, CAS, Nanjing 210008, China*

A B S T R A C T

One hydroxyaluminum-montmorillonite complex (HyAl-Mt), two hydroxyiron-montmorillonite complexes (HyFe-Mts) with different iron contents, and three hydroxyiron/aluminum-montmorillonite complexes (HyFeAl-Mts) with various Fe:Al molar ratios were synthesized. Behavior and kinetics of phosphate (P) sorption on selected Mt-complexes mentioned above were investigated under acidic conditions. The results indicated that the intercalations of polymeric HyFe and/or HyAl ions in interlayers of Na-saturated montmorillonite (Na-Mt) caused significant changes in surface properties of the Na-Mt, such as cation exchange capacity, specific surface area, pH at zero point of charge. In pH range tested (3.0–6.5), P adsorption on the Mt-complexes decreased with increasing pH, whereas the effect became weaker with increasing Fe contents in the Mt-complexes. The adsorption capacities of the HyFeAl-Mts were greater than those of the HyAl-Mt and HyFe-Mt, which could be attributed to decreasing crystallinity of Fe and Al oxides in the HyFeAl-Mts. The equilibrium adsorption of P on the Mt-complexes could be well described using the Langmuir isotherm, and the kinetics of P adsorption could be well described by both the pseudo-second-order and Elovich models. An increase in Fe contents in the Mt-complexes could enhance the initial kinetic rate of P adsorption, as suggested by the Elovich models. It is inferred that a great number of Fe-related active sorption sites have been located on the outer surfaces of the HyFe-Mt, as indicated by extremely high α value in the Elovich model. Previous studies focusing mainly on P sorption on HyAl-Mt complexes might have underestimated the contributions of Mt-complexes to P retention in acidic soils high in Fe contents.

1. Introduction

Phosphate (P) is one of the major nutrients for plant growth and widely distributed in agricultural soils. Phosphate leached from agricultural soils is one of the main sources of P in waters. Excessive supply of P can result in eutrophication of receiving waters, which may cause great adverse consequences on aquatic ecosystem [1]. Phosphate retention in agricultural soils is of immense importance in assessing its fertility and mobility [2]. Adsorption and desorption of P are closely related to soil constituents, among which aluminum (Al) and iron (Fe) (hydro)oxides serve as the most important sinks of P [3,4]. At high P concentrations, Al and Fe oxides may play equally important roles in P retention; at low P concentration, however, P tends to adsorb preferentially on Fe oxides [5].

In acidic soil environments, polymeric hydroxyaluminum (HyAl) cations with various OH/Al ratios form via hydrolysis of Al^{3+} [6]. Polymeric hydroxyiron (HyFe) cations may also form in soils high in Fe content. Some structural models for polymeric HyAl cations have been proposed, for instance single $[Al_6(OH)_{12}{}^{6+}]$ or double $[Al_{10}(OH)_{22}{}^{8+}]$ gibbsite-like rings and much more complex Al_{13} polynuclear species $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}]$ [7]. Due to high surface reactivity and high surface charges, HyAl and HyFe ions tend to adsorb on expandable phyllosilicate clays with high cation exchange capacity (CEC), particularly on montmorillonite (Mt), forming HyAl-Mt, HyFe-Mt, or HyFeAl-Mt complexes depending on solution pH and concentrations of HyAl and HyFe. Evidence has shown that polymeric HyAl and HyFe cations are intercalated in interlayer spaces of clays and also adsorbed on the external planar surfaces and/or at the edges, and that the fixed cations are nonexchangeable. Polymeric HyAl and HyFe cations in the interlayer exhibit much greater surface area than free amorphous Fe and Al hydroxides formed via direct precipitation [8,9]. In acidic to slightly acidic soils, HyAl-Mt, HyFe-Mt or HyFeAl-Mt complexes

* Corresponding author. Tel.: +86 532 66782513; fax: +86 532 66782540.
E-mail address: zhumaoxu@ouc.edu.cn (M.-X. Zhu).

(collectively referred to as Mt-complexes in this study) are ubiquitous [6,10]. Their surface properties and stability have been extensively studied [11–13]. Interactions between polymeric cations and clays may significantly influence surface properties of the pristine clays [11,12,14,15]. Given the high reactivity, large surface areas and high positive charges of HyAl and HyFe cations, Mt-complexes may play a significant role in regulating the mobility of P and some potential anionic pollutants such as arsenate and selenite.

Adsorption/desorption of a wide variety of pollutants on Fe or Al (hydro)oxides, Fe–Al (hydro)oxide co-precipitates, HyAl-Mt or HyFe-Mt complexes have been extensively investigated [15–20]. However, study on P adsorption on Mt-complexes, particularly on HyAlFe-Mt complexes with varying Al:Fe molar ratios is to date very limited. Saha et al. [10] found that P retention on HyAl-Mt complexes was much greater than on pristine Mt, which showed negligible P retention across pH 3–8. The study of Kasama et al. [16] indicated that P sorption on Al-pillared smectite was mostly related to –OH functional groups of HyAl. Violante and Gianfreda [21] investigated competitive adsorption between P and oxalate on HyAl-Mt complexes. To best of our knowledge, only Ramesh et al. [13] most recently reported the adsorption behavior of HyAlFe-Mt complexes as an adsorbent for removal of inorganic and organic arsenic. To date, there is no report on P sorption on HyAlFe-Mt complexes. Considering that *pure* HyAl-Mt, HyFe-Mt and HyFeAl-Mt are not easily obtained from natural soils, laboratory prepared Mt-complexes were used in this study. HyAl-Mt, HyFe-Mt, and HyAlFe-Mt complexes with varying Fe:Al ratio were synthesized and used as model materials for insight into the interactions of naturally occurring HyAlFe-Mt complexes with P in acidic soils high in Fe content, such as red soils widely distributed in southern China [20].

2. Materials and method

2.1. Montmorillonite samples

Bentonite was collected from Jiashan, Jiangsu Province, China. The $\leq 2.0\,\mu m$ fraction of Mt clay was separated by sedimentation according to the Stokes law after the bentonite was ground to pass through a 100-mesh sieve. Na-saturated Mt (Na-Mt) was obtained by Na^+ exchange using 0.1 mol/L NaCl solution 4 times. The Na-Mt was washed with deionized water until free of Cl^- ions (AgNO₃ examination), then dried under 60 °C for 16 h, and finally gently ground to pass through a 100-mesh sieve for use.

2.2. Preparation of HyFe-Mt, HyAl-Mt and HyFeAl-Mt complexes

A method following Jiang et al. [22,23] and Zhu et al. [24] with some modifications was used for preparation of HyFe-Mt and HyAl-Mt complexes. For the HyAl-Mt and HyFeAl-Mt preparation, NaOH solution of 0.4 mol/L was added slowly into AlCl₃ solution or mixed solution of FeCl₃ and AlCl₃ (Fe:Al molar ratios = 0.1, 0.2, 0.5) at a rate of 1 mL/min under magnetic stirring until the molar ratios of OH^-:Al^{3+} or OH^-:(Al^{3+} + Fe^{3+}) reaching 2.0. After continuous stirring for 2 h, the mixed solutions were aged at 65 °C in a water bath for 24 h, then aged at room temperature for another 48 h and finally filtered (0.20 μm) to remove any solid particles which might have formed. The resulting intercalant solutions were called HyAl and HyFeAl ion solutions, respectively. The preparation of HyFe-Mt was conducted following the procedure of Chen and Zhu [25], but with some modifications. Firstly, Na₂CO₃ solution was added slowly into Fe(NO₃)₃ under magnetic stirring until the molar ratio of Na₂CO₃ to Fe^{3+} reaching 1:1 and the final concentration of Fe^{3+} reaching 0.2 mol/L, then the mixed solution was aged at 65 °C for 24 h followed by aging for another 3 d at room temperature to obtain HyFe ion solution, While vigorous motor stirring, the ion solutions above were slowly added into suspensions containing 4% (wt.) Na-Mt until the ratios of Al^{3+} or (Al^{3+} + Fe^{3+}) to Na-Mt reaching 10 mmol/g for HyAl and HyFeAl, respectively, and the ratios of Fe^{3+}:Mt reaching 2 and 5 mmol/g for HyFe. The total amounts of added metal ions (Al^{3+}, Fe^{3+}) were 3.8–19.8-folds of the CEC of the Na-Mt (Table 1). After continuous stirring for 3 h the slurries were aged at 75 °C in water bath for 24 h, then washed using deionized water, dried at 80 °C and gently ground to pass through a 100-mesh sieve to obtain HyAl-Mt, HyFe-Mt and HyFeAl-Mt complexes. The HyAlFe-Mt complexes with Fe:Al molar ratios of 0.1, 0.2, 0.5 were denoted hereafter as HyFeAl-Mt$_{0.1}$, HyFeAl-Mt$_{0.2}$, HyFeAl-Mt$_{0.5}$, respectively, and the HyFe-Mt complexes with Fe^{3+}:Mt ratios of 2 and 5 mmol/g were denoted as HyFe-Mt$_{\infty 2}$ and HyFe-Mt$_{\infty 5}$, respectively.

2.3. Phosphate adsorption

Phosphate stock solution of 20 mmol/L was prepared by dissolving KH₂PO₄ in deionized water. Phosphate solutions of desired concentrations were obtained by dilution in 0.01 mol/L KCl solution (KCl as background electrolyte), and P solutions of desired pH were obtained by adjustment using dilute NaOH or HCl solutions.

Phosphate adsorption experiments were conducted using a batch technique. Fifty-mg HyAl-Mt, HyFe-Mt or HyAlFe-Mt complexes were weighed into a series of 100-mL conic bottles, to which 25-mL P solutions with varying initial concentrations were added. After capped and vigorously shaken by hand, the conic bottles were put in a water bath of 27 ± 1 °C and gently shaken to predetermined time periods. Then the suspensions were centrifuged ($3.46 \times 10^4\,g$) for 15 min and filtrated (0.45 μm) after transferred to 100-mL centrifuge tubes. Filtrate pH was measured immediately after filtration. The filtrates were then stored at 4 °C until P concentration determination. Equilibrium isotherms and kinetics of P adsorption on selected Mt-complexes were investigated. Also pH effect on P equilibrium adsorption was evaluated.

Table 1
Basic physicochemical properties of Na-Mt and Mt-complexes.

Samples	CEC (cmol/kg)	Specific surface areas (m²/g)	pHs$_{zpc}$	Amounts of loaded Al and Fe (mol/kg Mt)	
				Al	Fe
Na-Mt	51.6	23.08	2.80	–	–
HyAl-Mt	23.5	110.64	4.65	0.89	–
HyFeAl-Mt$_{0.1}$	21.8	97.49	5.60	0.83	0.07
HyFeAl-Mt$_{0.2}$	24.5	102.72	5.65	0.74	0.13
HyFeAl-Mt$_{0.5}$	20.8	131.76	5.80	0.61	0.25
HyFe-Mt$_{\infty 2}$	39.7	n.d.	6.20	–	0.78
HyFe-Mt$_{\infty 5}$	33.3	130.02	6.25	–	0.82

n.d.: not determined.

2.4. Analytical methods

The amounts of HyAl and HyFe loaded on Na-Mt were determined from the Al and Fe concentrations extracted from the Mt-complexes using NH_4-oxalate [26], which were corrected for by extraction of untreated Na-Mt with the same method. Aluminum and Fe were analyzed using graphite furnace AAS (Thermo Electron Co. USA). Phosphate concentrations were determined using the molybdate blue method. The quantities of P sorbed were determined by differences. X ray diffraction (XRD) patterns of the Na-Mt and Mt-complexes were obtained using a Rigaku D/max-rB diffractometer (Rigaku Corp., Japan) (Cu Ka, 40 kV, 100 mA, $7°$ min^{-1}). The pHs at zero point of charge (pHs_{zpc}) were determined using a simplified method [27]. Specific surface areas and CEC were determined using the BET method and ammonium acetate method [28], respectively.

3. Results and discussion

3.1. Characterization of HyAl-Mt, HyFe-Mt and HyAlFe-Mt complexes

The total amounts of loaded Al and Fe on the Mt-complexes were 1.5–1.7 times higher than the CEC of the Na-Mt (Table 1). The excesses of Al and Fe contents relative to the CEC of the Na-Mt were probably caused by surface precipitation on the Na-Mt. Due to larger ion radius of Fe than that of Al, the excesses of Fe content in HyFe-Mts were slightly smaller than the excess of Al content in HyAl-Mt. The ratios of Fe/Al in HyFeAl-Mt complexes determined by NH_4-oxalate extraction were lower than the original Fe/Al ratios of HyFeAl cation solutions. This result is in agreement with Violante et al. [29], who found that in mixed hydroxy-Al-Fe-Mt complexes formed from the Fe(II) transformations in the presence of Al and Mt, the short-range ordered materials present in the interlayers of Mt even after long aging periods were highly Al-substituted noncrystalline Fe oxides. The XRD patterns of the Na-Mt and Mt-complexes are shown in Fig. 1. Similar to our previous report [24], the intensity of XRD peaks of the HyAl-Mt was much less intense than that of the Na-Mt. The basal spacing of the HyAl-Mt (d_{001} = 17.0 Å) was significantly enlarged compared to that of the Na-Mt (d_{001} = 12.4 Å), indicating that at least some HyAl ions were intercalated the interlayers of the Na-Mt. The (0 0 1) peaks of the HyAlFe-Mt and HyFe-Mt were much less intense as compared to those of the Na-Mt and HyAl-Mt. For the HyFeAl-Mt$_{0.1}$ (Fig. 1g), the peak was almost undetectable. It seems that the (0 0 1) peaks of the Mt-complexes with mixed metals (HyFeAl-Mts) became farther weaker in comparison with the Mt-complexes with single metal (HyFe-Mt or HyAl-Mt). The reduction in diffractogram of the Mt-complexes relative to the Na-Mt was probably due to delamination of Mt layers by HyAl, HyFeAl, or HyFe ions. For the HyFeAl-Mts, the reduction in diffractogram might also be caused by collapsing of the Na-Mt layers due to partial incongruent phase transition of HyFe and HyAl into Fe/Al oxides because of their different ion radii and chemical reactivity, and interactions between HyFe and HyAl ions in interlayers of the Na-Mt during aging and drying, as suggested by Thomas et al. [30]. As a matter of fact, layer collapsing is very common during diagenesis of natural Mt in sediments and soils. The specific surface areas of all the Mt-complexes increased substantially in comparison with that of the Na-Mt (Table 1), which can be attributed to an increase in micropore volume and micropore surface area in the interlayer spaces or on the outer surfaces of the Mt-complexes [13]. For the three HyAlFe-Mts, the specific surface areas increased with an increase in Fe:Al molar ratios. A similar trend was observed for co-precipitated Fe–Al oxides by Potter and Yong [19], which was due to the fact that amorphous Fe oxides exhibit greater specific
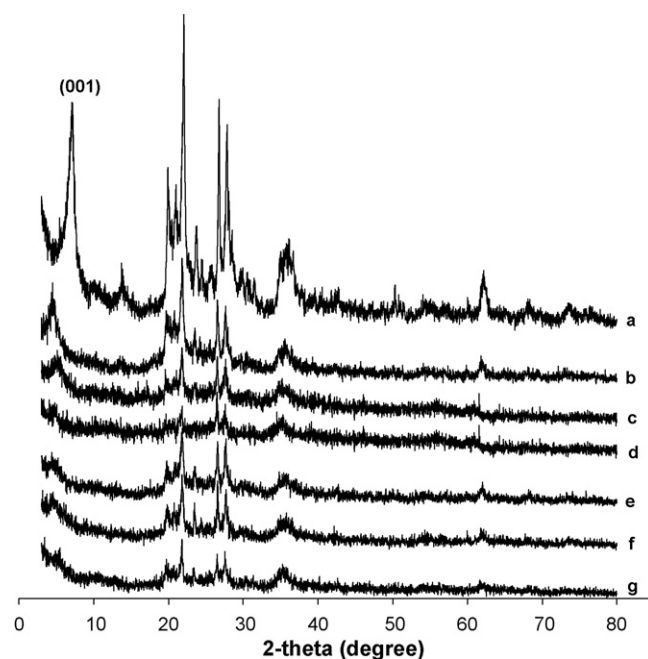

Fig. 1. X-ray diffraction patterns of Na-montmorillonite (Na-Mt) and montmorillonite complexes (Mt-complexes) modified by HyAl or/and HyFe ions. (a) Na-Mt, (b) HyAl-Mt, (c) HyFe-Mt$_{\infty 5}$, (d) HyFe-Mt$_{\infty 2}$, (e) HyFeAl-Mt$_{0.5}$, (f) HyFeAl-Mt$_{0.2}$, (g) HyFeAl-Mt$_{0.1}$.

surface areas than amorphous Al oxides [31,32], and Fe oxides are more resistant to crystallize than Al oxides during aging, particularly when Al oxides are present [26]. Similar to Fe and Al oxides, the relationship may also hold true for the HyFe and HyAl. However, the specific surface areas of two HyFeAl-Mts (HyFeAl-Mt$_{0.1}$ and HyFeAl-Mt$_{0.2}$) with low Fe contents were lower than that of the HyAl-Mt, which might be caused by layer collapsing of the Na-Mt mentioned above. The specific surface area of the HyFeAl-Mt$_{0.5}$ is similar to that of the HyFe-Mt, probably because Fe content of the HyFeAl-Mt$_{0.5}$ was beyond a critical level, above which the HyFeAl-Mt$_{0.5}$ and the HyFe-Mt were not differentiable with respect to their specific surface areas. The coverage of permanent negative charge sites on the surfaces of the Na-Mt by the HyAl and HyFe, altogether with high pH-dependent charges (variable surface charges) of the HyAl and HyFe themselves, rendered a decrease in CEC of all the Mt-complexes (Table 1) relative to the Na-Mt. Though the pHs_{zpc} of the HyAl and HyFe are unknown, we believe that they are not significantly different than those of amorphous Al and Fe oxides, respectively, because their surficial functional groups (i.e., $\equiv Al-OH/OH_2$, $\equiv Fe-OH/OH_2$) are similar in nature. Therefore, an increase in pHs_{zpc} of the Mt-complexes as compared to that of the Na-Mt is understandable in that the pHs_{zpc} of both Fe oxides (pHs_{zpc} 7–8) and Al oxides (pHs_{zpc} 9–9.5) are much higher than that of the Na-Mt (Table 1). The pHs_{zpc} of the Mt-complexes increased with an increase in Fe contents, which is inconsistent with Anderson and Benjamin [31] and Potter and Yong [19], who found that the pHs_{zpc} of co-precipitated Al-Fe hydroxides decreased with increasing Fe contents, and attributed the decrease to lower pHs_{zpc} of Fe (hydro)oxides than those of Al (hydro)oxides. In the case of the Mt-complexes, the pHs_{zpc} may be closely related to the coverage of external planar surfaces of the Mt and blockage of the interlayer spaces by the HyAl and HyFe polymers. Much higher pHs_{zpc} of two HyFe-Mts than those of the HyAl-Mt might imply that the HyFe polymers were mainly fixed on the external planar surfaces due to large molecular size, whereas more HyAl polymers were fixed in interlayer spaces of the Mt and some of them were buried
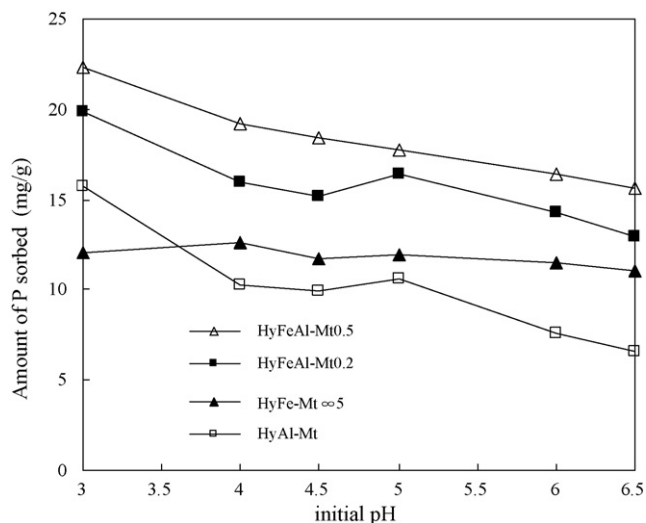
Fig. 2. Effect of pH on phosphate adsorption on various montmorillonite complexes (Mt-complexes) at initial phosphate concentration of 1.6 mmol/L.

in the interlayer spaces during layer collapsing. Therefore, HyFe played a dominant role in determining the overall pHs$_{zpc}$ of the two HyFe-Mts, which is seemingly confirmed by their only slightly lower pHs$_{zpc}$ than those of amorphous Fe oxides (pHs$_{zpc}$ 7–8). The pH$_{zpc}$ of the HyAl-Mt, however, was determined by the pHs$_{zpc}$ of both HyAl and the Na-Mt. Similarly, HyFe in the HyFeAl-Mts played a progressively increasing role in determining the overall pHs$_{zpc}$ with the increase in Fe contents. No peaks of crystalline Fe and Al oxide minerals were detected in the Mt-complexes as shown in Fig. 1. Thus it can be inferred that only amorphous or poorly crystalline Fe and Al (hydro)oxide phases were formed during phase transition of HyAl and HFe.

3.2. pH-dependency of P adsorption

Generally, pH exerts significant impact on ion adsorption on surface of solid phases, particularly on solid phases with variable charge surfaces, such as Al and Fe oxides. It has long been established that P sorbs on Fe/Al oxides and clay minerals mainly via ligand-exchange with reactive surficial functional groups ≡Al–OH/OH$_2$ or ≡Fe–OH/OH$_2$, forming strong inner-sphere complexes [15,33]. Three possible P inner-sphere complexes may be formed: monodentate, bidentate, and binuclear, depending on reactivity and density of surficial functional groups and P concentrations. This mechanism was indirectly confirmed by the increases in pHs of the equilibrium solutions relative to their initial pHs, with pH increments from 0.4 to 2.5. It is unlikely, however, to directly identify the specific surface complexes of P on the Mt-complexes using the present macroscopic experiments. Molecular-level techniques such as X-ray adsorption near-edge structure spectrum, nuclear magnetic resonance spectrum, and zeta potential measurements are needed for further confirmation.

Besides ligand-exchange mechanism, phosphate may also partly be adsorbed by electrostatic force mechanism forming outer-sphere complexes, which subsequently transform slowly into inner-sphere ones. The ligand-exchange mechanism is much less dependent on pH than the electrostatic one. As shown in Fig. 2, P adsorption on the Mt-complexes at initial P concentration of 1.6 mmol/L decreased to different extents with increasing pH. This could be attributed to the following two pH-dependent factors: (i) a decrease in the extent of protonation or an enhancement in the extent of deprotonation (depending on the pHs$_{zpc}$ of the Mt-complexes) on the Mt-complex surfaces with increasing pH increased the density of negative surface charge sites, and thus the electrostatic repulsion between P and the surfaces; (ii) equilibrium shift towards the right side of the following reaction with an increase in pH caused an increase in the fraction of HPO$_4^{2-}$, a more negatively charged species, which is unfavorable for P retention via electrostatic mechanism.

$$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$$
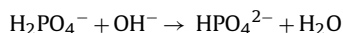
For the HyAlFe-Mt, pH exerted progressively less effect on P retention with an increase in Fe:Al molar ratios. In the extreme case, i.e., Al:Fe = 0 for HyFe-Mt, the effect of pH on P retention was slight in experimental pH range (3.0–6.5). An increase in Fe contents in the HyFeAl-Mt implies an increase in density of active sites available for P sorption via ligand-exchange, particularly at high pH due to an increase in the fraction of HPO$_4^{2-}$ species, and consequently progressively less pH-dependent of P sorption, because ligand-exchange is the dominant mechanism of P sorption and is less pH-dependent in comparison with electrostatic mechanism.

3.3. Isotherms for P sorption on Mt-complexes

The Langmuir (Eq. (1)) and Freundlich (Eq. (2)) equations are commonly used to describe P equilibrium sorption on soils, phyllosilicate minerals and metal oxides, and can be expressed mathematically as follows:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L \cdot Q_m} \tag{1}$$

$$\ln Q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \tag{2}$$

where Q_e (mg/g) is the amount of P sorbed at equilibrium, Q_m (mg/g) the theoretical maximum monolayer sorption capacity, C_e (mg/L) the equilibrium concentration of P in solution. K_L, n and K_F are empirical constants. K_L measures the affinity of the sorbent for the solute. A high value of K_L means a high sorption level at low solution concentration. The value of n measures the extent of impact on sorption of a change in solution concentration from unity [34]. A high value of n implies a relatively large change in sorbed P when the solution concentration deviates from unity. The isotherm data for P sorption on the Mt-complexes were fitted to the Langmuir and Freundlich equations, and the calculated parameters are given in Table 2. As evidenced by the correction coefficient R^2, P equilibrium sorption on the Mt-complexes could

Table 2
Langmuir and Freundlich isotherm parameters for phosphate sorption on selected Mt-complexes.

	Langmuir			Freundlich		
	K_L (L/mg)	Q_m (mg/g)	R^2	n	K_F (L/g)	R^2
HyAl-Mt	0.47	10.06	0.982	0.18	9.23	0.817
HyFe-Mt$_{\infty5}$	0.48	13.12	0.983	0.12	11.96	0.880
HyFeAl-Mt$_{0.2}$	0.90	15.97	0.993	0.14	15.43	0.881
HyFeAl-Mt$_{0.5}$	2.16	20.45	0.995	0.11	20.48	0.938

R^2: correction coefficient.

Fig. 3. Langmuir isotherm modeling of phosphate adsorption on various montmorillonite complexes (Mt-complexes).
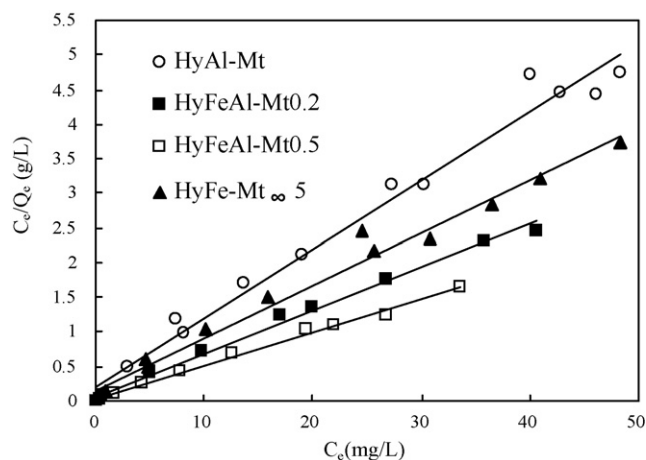

Fig. 4. Variations of phosphate adsorption on various montmorillonite complexes (Mt-complexes) with time.

be much better described using the Langmuir model than using the Freundlich one. A linear plot of the Langmuir fitting is given in Fig. 3. Based on the values of Q_m and K_L (Table 2), the order of maximum sorption capacities and affinities of the Mt-complexes for P is: HyAl-Mt < HyFe-Mt$_{\infty5}$ < HyFeAl-Mt$_{0.2}$ < HyFeAl-Mt$_{0.5}$. Understandable is the smaller sorption capacity and weaker affinity of the HyAl-Mt than those of the HyFe-Mt$_{\infty5}$, respectively, because the affinity of amorphous Fe oxides for P is much stronger than that of amorphous Al oxides [5]. However, it is interesting to note that the sorption capacity of the HyFe-Mt$_{\infty5}$ was lower than those of the two HyFeAl-Mts even though the facts that the HyFe-Mt$_{\infty5}$ exhibited similar specific surface area to that of the HyFeAl-Mt$_{0.5}$, and the Fe content in the HyFe-Mt$_{\infty5}$ was higher than in the two HyFeAl-Mts (Table 1). A probable explanation is that the presence of HyAl on the interlayers of the Na-Mt interfered with the crystallization of HyFe while aging and drying, resulting in higher reactivity of surficial functional groups and thus higher sorption capacities of the two HyAlFe-Mts. The increase in Q_m and K_L with increasing Fe contents in the Mt-complexes (except the HyFe-Mt) further confirmed the important role Fe played in the enhancement of P sorption.

It may be concluded that the presence of a large amount of HyAlFe-Mt complexes in acidic soils high in Fe contents could enhance substantially P retention on soil solid phases, and therefore reduce P mobility. It should be pointed out that, although the sorption of P and other ions on pristine Mt and HyAl-Mt complexes has been extensively studied in recent years, the existences of pristine Mt, *simple* HyAl- or HyFe-Mt complexes in a large amount are not common in acidic soils high in Fe contents, instead, HyAlFe-Mts are probably the main Mt-complexes. If this assumption holds true, previous studies focusing mainly on P sorption on HyAl-Mt complexes [10,16,21] may have underestimated the contributions of Mt-complexes to P retention in acidic soils high in Fe contents, which should be considered in assessing P mobility and bioavailability.

Further work is needed to determine both the lower and upper limits of Fe contents in the HyFeAl-Mt, respectively, below and above which the HyFeAl-Mt and the HyAl-Mt, and HyFeAl-Mt and the HyFe-Mt, respectively, are undifferentiable with respect to their adsorption capacities.

3.4. Phosphate sorption kinetics

Given the great differences in sorption capacities among the Mt-complexes studied, a low initial P concentration (0.8 mmol/L) was chosen for kinetic studies in the HyAl-Mt and HyFe-Mt systems, and a high initial P concentration (1.2 mmol/L) was chosen
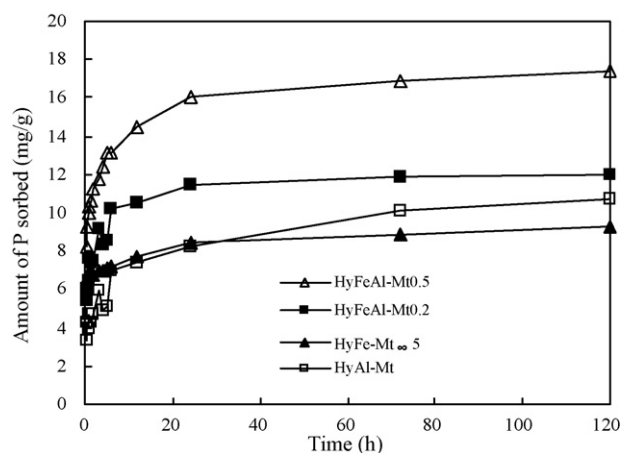
in the HyAlFe-Mt system. As shown in Fig. 4, there is a rapid step followed by a slow one in P kinetic sorption for all the Mt-complexes. In the rapid step, P sorption increased rapidly within 12 h, then increased gradually for more than 20 h in the slow step. The rapid step could be attributed to direct ligand-exchange process together with electrostatic sorption on the outer surfaces and at the wide pore entrances of the Mt-complexes. Phosphate also
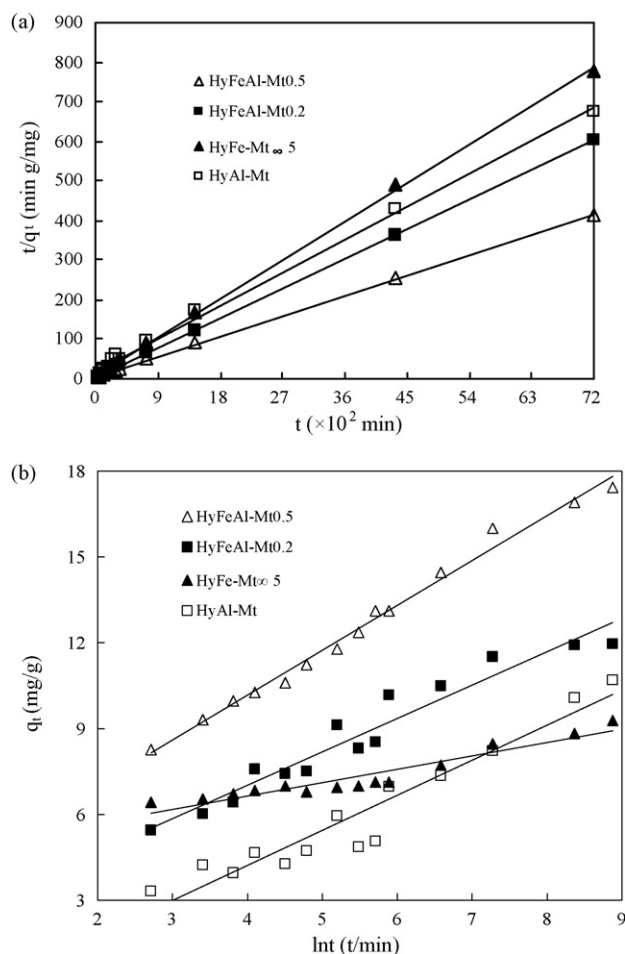

Fig. 5. Kinetics modeling of phosphate adsorption on montmorillonite complexes (Mt-complexes) using pseudo-second-order (a) and Elovich (b) models.

Table 3
Kinetic parameters for phosphate adsorption on selected Mt-complexes.

	Pseudo-second-order model			Elovich model		
	K [g/(mg s)]	q_e (mg/g)	R^2	α	β	R^2
HyAl-Mt	6.66	10.78	0.9960	0.702	0.82	0.923
HyFeAl-Mt$_{0.2}$	27.14	12.08	0.9998	8.91	0.86	0.940
HyFeAl-Mt$_{0.5}$	68.4	18.98	0.9995	19.08	0.64	0.990
HyFe-Mt$_{\infty5}$	12.42	9.23	0.9991	1.34×10^4	2.14	0.906

R^2: correction coefficient.

diffuses into solid-phase matrix through meso- and micropores, and then adsorbs on the inner surfaces of deep pores [35]. In the present study, pore size distribution and porosity of the samples were not determined. However, the average pore sizes of the Mt-complexes were estimated to be at the range of 5.5–12.5 nm based on the reports of Ramesh et al. [13] and Shin and Han [15]. Diffusion rate of ion in pores is closely dependent on pore geometry such as pore size and pore connectivity. Generally, ion diffusion in pores is a slow process, particularly with increasing pore depth and decreasing pore size (less than 2 nm). Thus the slow step could be attributed to P (0.22 nm in radius) diffusion into pores.

Several commonly used rate models including the pseudo-first-order equation (Eq. (3)), pseudo-second-order equation (Eq. (4)), power function equation (Eq. (5)), Elovich equation (Eq. (6)), and intraparticle diffusion model (Eq. (7)) are tested to describe P sorption kinetics.

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303}t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{4}$$

$$\ln q_t = \ln(Kq_e) + \frac{1}{m}\ln t \tag{5}$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{6}$$

$$q_t = k_d t^{1/2} + C \tag{7}$$

where q_t (mg/g) and q_e (mg/g) are the amounts of P adsorbed at time t (min) and at equilibrium, respectively; k is sorption rate constant; k_d is diffusion coefficient; α is the initial adsorption rate and β is related to surface coverage and activation energy of chemisorption [36]; K, m, and C are constants of respective models. Among the above kinetic models tested, P sorption kinetics could be well described using both the pseudo-second-order (Eq. (4)) and Elovich (Eq. (6)) models with the correlation coefficients, R^2, above 0.90. The linear plots of P sorption kinetics to the two models and the calculated kinetic parameters are given in Fig. 5 and Table 3, respectively. As mentioned above, parameter α is the initial kinetic rate in the Elovich model, and thus could be roughly regarded as the kinetic rate in the rapid step. It can be seen that the initial rates, α, increased with an increase in Fe content in the Mt-complexes (Table 3), indicating the important role Fe played in regulating P adsorption kinetics in the rapid step. For the HyFe-Mt (Al = 0), the value of α is 1.34×10^4 mg/(g min), 2–4 orders of magnitude larger than those for the HyAl-Mt and HyAlFe-Mt. This might imply that much higher Fe-related active adsorption sites were located on the outer surfaces of the HyFe-Mt for direct ligand-exchange sorption in comparison with the case of the HyAlFe-Mts. This conclusion is in accordance with the results of surface characterization of the HyFe-Mt (Section 3.1). It is worth pointing out that, even though P diffusion in pores was the main kinetic process over the later period of time as discussed above, the kinetic data could not be satisfactorily described by the intraparticle diffusion model (Eq. (7)).

This is probably because of only minor contribution of the diffusion process to the whole kinetic processes.

4. Concluding remarks

The intercalations of HyFe and/or HyAl polymeric ions in interlayer spaces of Mt caused significant changes in chemical and physical properties of the Na-Mt. The presence of Fe at low contents in the HyFeAl-Mt$_{0.1}$ and HyFeAl-Mt$_{0.2}$ diminished the specific surface areas of the two Fe-bearing Mt-complexes in comparison with that of the HyAl-Mt; however, when Fe content was high enough in the HyFeAl-Mt$_{0.5}$, the specific surface area was similar to that of the HyFe-Mt. The pHs$_{zpc}$ of the Mt-complexes increased with an increase in Fe contents in the complexes probably because HyFe polymers were mainly fixed on external planar surfaces of the Mt. In pH range tested (3.0–6.5), P adsorption on the Mt-complexes decreased with increasing pH. However, the effect of pH on P adsorption became weaker when Fe contents in the Mt-complexes increased due probably to increasing fraction of ligand-exchange. The adsorption capacities of the HyFeAl-Mts were greater than those of the HyAl-Mt and HyFe-Mt, which could be attributed to decreasing crystallinity of Fe and Al oxides in the HyFeAl-Mts during aging and drying. The equilibrium adsorption of P on the Mt-complexes could be well described using the Langmuir isotherm. The kinetics of P adsorption on the Mt-complexes could be well described using both the pseudo-second-order and Elovich models. An increase in Fe contents in the Mt-complexes could enhance the initial kinetic rate of P adsorption, as suggested by the Elovich models. For the HyFe-Mt, an extremely high α value calculated based on the Elovich model might imply that a great number of Fe-related active sorption sites have been located on the outer surfaces. Previous studies focusing mainly on P sorption on HyAl-Mt complexes might have underestimated the contributions of Mt-complexes to P retention in acidic soils high in Fe contents, and thus P mobility and bioavailability should be evaluated within the context of the present results.

References

[1] D.L. Correll, The role of phosphorus in the eutrophication of receiving waters: a review, J. Environ. Qual. 27 (1998) 261–266.
[2] T. Peretyazhko, G. Sposito, Iron(III) reduction and phosphorous solubilization in humid tropical forest soils, Geochim. Cosmochim. Acta 69 (2005) 3643–3652.
[3] G.R. Reiner, T. Andersson, L. Lövgren, P. Persson, Phosphate sorption in aluminum- and iron-rich humus soils, Soil Sci. Soc. Am. J. 69 (2005) 77–86.
[4] F.E. Rhoton, J.M. Bigham, Phosphate adsorption by ferrihydrite-amended Soils, J. Environ. Qual. 34 (2005) 890–896.

[5] N. Khare, D. Hesterberg, S. Beauchemin, S.-L. Wang, XANES determination of adsorbed phosphate distribution between ferrihydrite and boehmite in mixtures, Soil Sci. Soc. Am. J. 68 (2004) 460–469.

[6] K. Inoue, M. Yoshida, Composition and behavior of aluminum ions and colloidal aluminosilicates in acidified terrestrial waters, Soil Sci. Plant Nutr. 36 (1990) 461–468.

[7] P.M. Bertsch, D.D. Parker, Aqueous polynuclear aluminum species, in: G. Sposito (Ed.), The Environmental Chemistry of Aluminum, Lewis Publisher, Michigan, 1996, pp. 117–167.

[8] J.B. Harsh, H.B. Doner, Specific adsorption of copper on a hydroxy-aluminum-montmorillonite complex, Soil Sci. Soc. Am. J. 48 (1984) 1034–1039.

[9] R.P.T. Janssen, M.G.M. Bruggenwert, G. van Dijk, W.H. van Riemsdijk, Lead ion adsorption on montmorillonite-Al hydroxide polymer systems, Eur. J. Soil Sci. 58 (2007) 1136–1144.

[10] U.K. Saha, S. Hiradate, K. Inoue, Retention of phosphate by hydroxyalumino-silicate- and hydroxyaluminum-montmorillonite complexes, Soil Sci. Soc. Am. J. 62 (1998) 922–929.

[11] K. Inoue, C. Satoh, Electric charge and surface characteristics of hydroxy-aluminosilicate- and hydroxyaluminumvermiculite complexes, Clays Clay Miner. 40 (1992) 311–318.

[12] K. Inoue, C. Satoh, Surface charge characteristics of hydroxyaluminosilicate- and hydroxyaluminum-montmorillonite complexes, Soil Sci. Soc. Am. J. 57 (1993) 545–555.

[13] A. Ramesh, H. Hasegawa, T. Maki, K. Ueda, Adsorption of inorganic and organic arsenic from aqueous solutions by polymeric Al/Fe modified montmorillonite, Sep. Purif. Technol. 56 (2007) 90–100.

[14] R.P.T. Janssen, M.G.M. Bruggenwert, W.H. van Riemsdijk, Effect of Al hydroxide polymers on cation exchange of montmorillonite, Eur. J. Soil Sci. 54 (2003) 335–345.

[15] E.W. Shin, J.S. Han, Phosphate adsorption on aluminum-impregnated meso-porous silicates: surface structure and behavior of adsorbents, Environ. Sci. Technol. 38 (2004) 912–917.

[16] T. Kasama, Y. Watanabe, H. Yamada, T. Murakami, Sorption of phosphates on Al-pillared smectites and mica at acidic to neutral pH, Appl. Clay Sci. 25 (2004) 167–177.

[17] Y. Masue, R.H. Loeppert, T.A. Kramer, Arsenate and arsenite adsorption and desorption behavior on coprecipitated aluminium:iron hydroxides, Environ. Sci. Technol. 41 (2007) 837–842.

[18] D. Nguyen-Thanh, K. Block, T.J. Bandosz, Adsorption of hydrogen sulfide on montmorillonites modified with iron, Chemosphere 59 (2005) 343–353.

[19] H.A.B. Potter, R.N. Yong, Influence of iron/aluminium ratio on the retention of lead and copper by amorphous iron–aluminium oxides, Appl. Clay Sci. 14 (1999) 1–26.

[20] M.-X. Zhu, K.-Y. Ding, X. Jiang, H.-H. Wang, Investigation on co-sorption and desorption of fluoride and phosphate in a red soil of china, Air Water Soil Pollut. 183 (2007) 455–465.

[21] A. Violante, L. Gianfreda, Competition in adsorption between phosphate and oxalate on an aluminum hydroxide montmorillonite complex, Soil Sci. Soc. Am. J. 57 (1993) 1235–1241.

[22] J.Q. Jiang, N.J.D. Graham, Enhanced coagulation using Al/Fe(III) coagulants: effect of coagulant chemistry on the removal of colour-causing NOM, Environ. Technol. 17 (1996) 937–950.

[23] J.Q. Jiang, C. Cooper, S. Ouki, Comparison of modified montmorillonite adsorbents Part I: preparation, characterization and phenol adsorption, Chemosphere 47 (2002) 711–716.

[24] M.-X. Zhu, M. Xie, X. Jiang, Interaction of fluoride with hydroxyaluminum-montmorillonite complexes and implications for fluoride-contaminated acidic soils, Appl. Geochem. 21 (2006) 675–683.

[25] J. Chen, L. Zhu, Catalytic degradation of Orange II by UV-Fenton with hydroxyl-Fe-pillared bentonite in water, Chemosphere 65 (2006) 1249–1255.

[26] A. Violante, M. Ricciardella, M. Pigna, Adsorption of heavy metals on mixed Fe–Al oxides in the absence or presence of organic ligands, Water, Air, Soil Pollu. 145 (2003) 289–306.

[27] Y. Wang, E.J. Reardon, Activation and regeneration of a soil sorbent for defluo-ridation of drinking water, Appl. Geochem. 16 (2001) 531–539.

[28] M. Zhu, X. Jiang, G. Ji, Experimental investigation on aluminum release from Haplic Acrisols in southeastern China, Appl. Geochem. 19 (2004) 981–990.

[29] A. Violante, G.S.R. Krishnamurti, P.M. Huang, Formation and stability of hydroxy aluminum-iron-montmorillonite complexes: influence of ferrous iron, Soil Sci. Soc. Am. J. 62 (1998) 1448–1454.

[30] S.M. Thomas, J.A. Bertrand, M.L. Occelli, F. Huggins, S.A. Gould, Micro-porous montmorillonites expanded with alumina clusters and M $[(\mu\text{-}OH)Cu(\mu\text{-}OCH_2CH_2NEt_2)]_6(ClO_4)_3$, (M = Al, Ga, and Fe), or Cr $[(\mu\text{-}OCH_3)(\mu\text{-}OCH_2CH_2NEt_2)CuCl]_3$, Inorg. Chem. 38 (1999) 2098–2105.

[31] P.R. Anderson, M.M. Benjamin, Surface and bulk characteristics of binary oxide suspensions, Environ. Sci. Technol. 24 (1990) 692–698.

[32] P.R. Anderson, M.M. Benjamin, Modeling adsorption in aluminium–iron binary oxide suspensions, Environ. Sci. Technol. 24 (1990) 1586–1592.

[33] S.M. Kraemer, V.Q. Chiu, J.G. Hering, Influence of pH and competitive adsorption on the kinetics of ligand-promoted dissolution of aluminum oxide, Environ. Sci. Technol. 32 (1998) 2876–2882.

[34] K.C. Cheung, T.H. Venkitachalam, Improving phosphate removal of sand infil-tration system using alkaline fly ash, Chemosphere 41 (2000) 243–249.

[35] K. Wang, B. Xing, Adsorption and desorption of cadmium by goethite pretreated with phosphate, Chemosphere 48 (2002) 665–670.

[36] M. Özacar, Contact time optimization of two-stage batch adsorber design using second-order kinetic model for the adsorption of phosphate onto alunite, J. Hazard. Mater. B137 (2006) 218–225.