Adsorption behavior of condensed phosphate on aluminum hydroxide

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Received 24 April 2006; revised 23 June 2006; accepted 3 July 2006

Abstract
Sodium pyrophosphate (pyro-P, Na2P2O7), sodium tripolyphosphate (tripoly-P, Na5P3O10), and sodium hexametaphosphate (meta-P, (NaPO3)6) were selected as the model compounds of condensed phosphate to investigate the adsorption behavior of condensed phosphate on aluminum hydroxide. The adsorption was found to be endothermic and divisible into two stages: (1) fast adsorption within 1 h; and (2) slow adsorption between 1 and 24 h. The modified Freundlich model simulated the fast adsorption stage well; the slow adsorption stage was described well by the first-order kinetics. The activation energies of pyro-P, tripoly-P, and meta-P adsorption on aluminum hydroxide were determined to be 20.2, 22.8 and 10.9 kJ/mol P adsorbed, respectively, in the fast adsorption stage and to be 66.3, 53.5 and 72.5 kJ/mol P adsorbed, respectively, in the slow adsorption stage. The adsorption increased the negative charge of the aluminum hydroxide surface. Transmission electron microscopy and energy dispersive X-ray analysis analyses provided evidence that the adsorption was not uniform on the surface and that the small crystals contributed more to the fast adsorption than the normal sites did. The results from X-ray fluorescence spectrometry and X-ray photoelectron spectroscopy tests also revealed the uneven adsorption of condensed phosphate as a function of the penetration depth. More condensed phosphates were adsorbed on the outer surface of aluminum hydroxide than in its inner parts.

Key words: activation energy; aluminum hydroxide; condensed phosphate; eutrophication; surface charge

Introduction

Excessive amounts of phosphorous entering into lakes and streams trigger the growth of undesirable algae and other aquatic weeds, which results in the eutrophication problem. Eutrophication has become a common and growing problem in lakes, rivers, estuaries and coastal oceans (Smith, 1998). The phosphorus in surface waters comes from both point and nonpoint sources. The point sources are typically the effluents discharged from industrial and domestic wastewater treatment facilities while the nonpoint sources are mainly associated with polluted runoff from urban areas and farmlands (Carpenter et al., 1998). The nonpoint sources have now become the dominant P pollution sources for most surface waters (USEPA, 1996). Phosphorus fertilizer applications on agricultural lands have been confirmed as a major contributor to the nonpoint sources of phosphorus. The phosphate adsorption capacity of soils affects how the applied P will interact with soils and how much P can remain available for crop uptake or transfer into the runoff or leachate (Hansen et al., 2002). Soils with a low adsorption capacity are less likely to retain P and easily lead to off-site P transport (Novak and Watts, 2004). These processes have therefore been applied in predicting the phosphorus release (Lookmann et al., 1995) and the P transfer (Scheinost and Schwertmann, 1995). Therefore, understanding how phosphates are adsorbed by soils or move through soils is important in evaluating the potential of P loss from soils to water bodies to control phosphorus related contamination problems (Ho and Notodarmojo, 1995; Indiati and Diana, 2004).

Condensed phosphates, especially ammonia polyphosphates, are widely applied as fertilizers to provide P to plants. During the past 30 years, most studies on phosphorus have focused exclusively on orthophosphate, which serves as the most important species of phosphorus in ecological systems (Kotabe, 1987). The important role of condensed phosphates in the phosphorus cycle has been neglected mainly because they are thought to be biologically unavailable without hydrolysis and some are even difficult to measure. However, the development of 31P NMR technology has made researchers recognize the importance of condensed phosphates, especially pyrophosphate and tripolyphosphate (Sundareshwar et al., 2001; Ahlgren et al., 2005). Chung et al. (1999) observed that mono-potassium phosphate and ammonium polyphosphate accounted for the largest quantity of phosphorus in soil leachates, serving as the potential reservoir for the nonpoint phosphorus sources. Sundareshwar et al. (2001) reported that accumulation of pyrophosphate in coastal wetlands exceeded that of soluble orthophosphate. They further demonstrated that pyrophosphate can be readily

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utilized by microbes in coastal wetland sediments in the presence of nitrogen and carbon and it can serve as a reservoir of orthophosphate. The adsorption of condensed phosphates on metal hydroxides in soils or sediments is, therefore, of great interest to soil chemists because their adsorption affects the bioavailability of condensed phosphates in soils (Chapman et al., 1997; Vaz et al., 1992; Liu and Huang, 2000).

Several studies have been carried out on the adsorption of condensed phosphates on ferrihydrite (Lin and Benjamin, 1992), Fe(OH)$_3$ (Fettig et al., 2000), titania (Gong, 2001) and titanium dioxide (Michelmore et al., 2000). It was reported that ligand exchange occurred and inner-sphere complexes were formed when condensed phosphates were adsorbed on titania and titanium dioxide (Gong, 2001; Michelmore et al., 2000). However, the adsorption of condensed phosphates on aluminum hydroxide, which is an important soil component (Hiemstra and Riemsdijk, 1996), has seldom been reported. Consequently, this study focused on the adsorption behavior of condensed phosphate on aluminum hydroxide. The effects of temperature, pH and concentration on the adsorption kinetics of condensed phosphates were investigated. Sodium pyrophosphate ($\text{pyro-P, Na}_4\text{P}_2\text{O}_7$), sodium tripolyphosphate ($\text{tripy-P, Na}_5\text{P}_3\text{O}_{10}$), and sodium hexametaphosphate ($\text{meta-P, (NaPO}_4)_6$) were selected as the model compounds of condensed phosphate.

1 Methods and materials

1.1 Chemical preparation

Reagent-grade chemicals and double distilled deionized water were used to prepare all solutions used in this study. To minimize the effect of hydrolysis, all phosphate solutions were freshly prepared by dissolving aliquots of pyro-P, tripoly-P, and meta-P (all from Sigma) into the distilled deionized water prior to each test.

The aluminum hydroxide was prepared following the procedure described by Guan et al. (2005). In brief, the pH of a 0.167 mol/L AlCl$_3$ solution was adjusted to 6±0.1 and maintained at this pH level by adding sodium hydroxide. After the pH level of this suspension became stable without any further addition of alkali, it was stirred at room temperature for another 48 h. The suspension was then filtered, re-suspended and centrifuged and the supernatant was decanted. The aluminum hydroxide obtained was freeze-dried and stored at room temperature for another 48 h. The suspension was then maintained at this pH level by adding sodium hydroxide. After the pH level of this suspension became stable without any further addition of alkali, it was stirred at room temperature for another 48 h. The suspension was then filtered, re-suspended and centrifuged and the supernatant was decanted. The aluminum hydroxide obtained was freeze-dried and stored at room temperature. The BET surface area of the aluminum hydroxide powders prepared in our study was measured to be 49.56 m$^2$/g using a surface area and pore size analyzer (Coulter SA 3100).

The XRD analysis using a powder X-ray diffraction system (PW1830) showed that the aluminum hydroxide was amorphous. The surface charge of aluminum hydroxide suspension decreased with increasing pH and its point of zero charge (PZC) was found to be pH 10.

1.2 Experimental procedure

The effects of temperature, initial pH and initial concentration on the adsorption of condensed phosphates on aluminum hydroxide were investigated by carrying out the experiments according to the conditions summarized in Table 1. Prior to each run, 357 mg of the prepared aluminum hydroxide were dissolved in 1000 ml of 0.05 mol/L NaCl solution and shaken for 24 h for dispersion of aggregates and hydration of the surface sites. Seventy milliliters of the hydrated aluminum hydroxide suspension were mixed with 30 ml condensed phosphate solution (1.67 mmol/L or 3.33 mmol/L as P in 0.05 mol/L NaCl solution). Under these conditions, the initial concentration of the aluminum hydroxide in the mixture was 250 mg/L and that of the condensed phosphate was 0.5 mmol/L or 1 mmol/L as P. The initial pH of the aluminum hydroxide suspension and the phosphate solution was adjusted with NaOH and HCl solutions before mixing. The mixed solutions were then shaken at the appropriate temperatures for 2, 5, 10, 20 or 40 min or 1, 2, 4, 8, 12, 16 or 24 h according to the conditions listed in Table 1. One drop of chloroform was added to suppress microbiological activity during the shaking period (Shang, 1989). During the adsorption period, the pH of the mixture was adjusted from time to time and kept constant. Each experiment was repeated at least twice.

At the end of the adsorption test, a portion of the mixture was filtered immediately through a 0.45-µm membrane filter made of cellulose acetate (MFS) for analysis of the final condensed phosphate concentration according to the standard method (APHA, 1995). In brief, the concentration of condensed phosphate was obtained by direct colorimetric reading of a spectrophotometer (Spectrometric 3000) at a wavelength of 880 nm after a preliminary acid hydrolysis. The amount of phosphates adsorbed on the aluminum hydroxide was determined from the di-sulfuric acid digestion (Shang, 1989). The solids retained on the filter papers were subjected to a series of physical examinations including X-ray photoelectron spectroscopy (XPS, PHI5600), X-ray fluorescence spectrometry (XRF, JX-3201Z), transmission electron microscopy (TEM, JEM 100CXII), and energy dispersive X-ray analysis (EDAX, JEM 100CXII).

<table>
<thead>
<tr>
<th>Table 1 Experimental conditions</th>
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<tr>
<td><strong>Temperature (°C)</strong></td>
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<tr>
<td><strong>Initial pH</strong></td>
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<tr>
<td><strong>Initial P concentration (mmol/L)</strong></td>
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<tr>
<td>Effect of Temperature</td>
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<tr>
<td>Effect of initial pH</td>
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<tr>
<td>Effect of initial concentration</td>
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</table>
2 Results and discussion

2.1 Adsorption kinetics of condensed phosphate

The kinetic data of condensed phosphate adsorption on aluminium hydroxide at different temperatures and pH levels are shown in Figs. 1 and 2, respectively. The adsorption was improved with decreasing pH and increasing temperature and time. For a particular time span, the amount of phosphate adsorbed increased with increasing temperature, indicating the endothermic nature of the condensed phosphate adsorption process (Balas et al., 1999). The increase in the amount of condensed phosphate adsorbed on aluminium hydroxide at lower pH could be attributable to electrostatic attraction and acid catalysis as illustrated by the following equation (Jordan, 1998; Stumm, 1992):

\[ M-OH + L^- \rightleftharpoons M-L + OH^- \]

The protonation of the leaving group (OH\(^-\)) can weaken the M–O bond and facilitate the OH\(^-\) removal as H\(_2\)O (Masel, 1996). Therefore, the adsorption of condensed phosphate is favored when the amount of aquo sites (M–OH\(_2^+\)) increases with decreasing pH (Rajan et al., 1974). The initial concentrations of condensed phosphates were found to have little effect on the adsorption kinetics on aluminium hydroxide (data not shown).

The condensed phosphate adsorption behaviour was fitted to both empirical models (modified Freundlich (Kuo and Lotse, 1974)) and Elovich kinetics (Chien and Clayton, 1980) and theoretical kinetic models (first-order and second-order equations), as listed in Table 2. The degree of fit of the data to each model was evaluated based on the determination coefficient (\(R^2\)). It was found that none of single model could fit the data well over the entire reaction period. Many researchers have shown that the adsorption of phosphate is rapid at first and then slows down and should thus be divided into several stages (Liu and Huang, 2000; Shang, 1989; Rajan and Fox, 1972; Hingston, 1981; Sparks, 1986). Therefore, in the current study, the condensed phosphate adsorption was divided into the fast adsorption stage, occurring within the first one hour, followed by the slow adsorption stage. The modified Freundlich model was found to be the best equation to describe the fast adsorption, which also agrees with the literature (Chapman et al., 1997; Shariatmadari, 1998). Both the first-order and second-order kinetics equations

### Table 2 Kinetic models examined in this study

<table>
<thead>
<tr>
<th>Model</th>
<th>Linearized equation*</th>
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<tr>
<td>First-order kinetics</td>
<td>( \ln C = \ln C_0 - kt )</td>
</tr>
<tr>
<td>Second-order kinetics</td>
<td>( \frac{1}{C} = \frac{1}{C_0} + kt )</td>
</tr>
<tr>
<td>Modified Freundlich</td>
<td>( \ln q = \ln(KC_0) + \frac{1}{m} \ln t )</td>
</tr>
<tr>
<td>Elovich equation</td>
<td>( q = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t )</td>
</tr>
</tbody>
</table>

\*C is the concentration of adsorbate at time \( t \); \( C_0 \) is the concentration of adsorbate at time \( t_0 \); \( t \) is time; \( q \) is the amount of adsorbate adsorbed; \( K \), \( m \), \( a \) and \( b \) are constants.
were found to describe the slow adsorption well. However, the second-order kinetics was rejected because the derived rate constants did not obey the Arrhenius law in some cases (data not shown). The results of the fitting, including the regression equations and the determination coefficients are shown in Figs. 1 and 2.

The Arrhenius equation (Vaz et al., 1992), as shown below, has been widely used to calculate the activation energy ($E_a$) of an adsorption reaction to evaluate whether the adsorption is diffusion controlled or chemically controlled (El-Batouti et al., 2003).

$$K = A \cdot e^{-E_a/RT}$$

The Arrhenius plots for the adsorption of condensed phosphates are shown in Fig. 3. The linearity of the Arrhenius plots indicates that the kinetics of the condensed phosphate adsorption obeys the Arrhenius law. The activation energy of the fast adsorption and slow adsorption is calculated from the slope of these linear plots. The activation energies of the fast adsorption of pyro-P, tripoly-P, and meta-P on aluminum hydroxide were 20.2, 22.8 and 10.9 kJ/mol P adsorbed, respectively. This range of activation energy indicated that film diffusion was the rate-limiting step in the fast adsorption of condensed phosphate (Sparks, 1986). On the other hand, the activation energies of the slow adsorption of pyro-P, tripoly-P, and meta-P were found to be 66.3, 53.5, and 72.5 kJ/mol P adsorbed, respectively, indicating that the slow adsorption was chemically controlled (Sparks, 1986).

There are several possibilities that can lead to the changes in the activation energy in the process of the adsorption reaction. Firstly, the fast adsorption can be attributed to the coordinately unsaturated defect sites such as step edges, open tips and corners on the aluminum hydroxide surface (Masel, 1996). Secondly, the build-up of negative surface charges increases the repulsive force between the adsorbate and the adsorbent, resulting in an increase in the energy barrier of the adsorption reaction and a decrease in adsorption rate (Vaz et al., 1992). Finally, the availability of total surface sites also plays a role in controlling the adsorption rate of condensed phosphates on aluminum hydroxide (Lin and Benjamin, 1992; Shang, 1989).

2.2 Contribution of small crystals on the adsorbent surface to the fast adsorption of condensed phosphate

Some small crystals were observed on the surface of the aluminum hydroxide particles through TEM in the current study. Fig. 4a shows a panoramic image of an aluminum hydroxide particle and Fig. 4b presents an amplificatory image of one part of this particle. In Fig. 4, the dark area in the pictures is the aluminum hydroxide particle and the small crystals are circled to facilitate identification. The P:Al ratios of these small crystals and the regular sites after 10 min or 24 h adsorption of meta-P were analyzed with EDAX and are summarized in Table 3 (each P:Al ratio is the mean of the values obtained from 6–8 similar sites on the surface). It was found that the P:Al ratios of the small crystals were much larger than those of the normal sites, indicating that the small crystals could adsorb more phosphate than could the surrounding regular sites. This may be due to the fact that the surface functional
groups of the small crystals are different from those in the bulk or that the small crystals serve as adsorption conduits from which phosphate ions diffuse to the rest of the surface. The EDAX analysis also revealed that the P:Al ratio for the small crystals increased by 26.3% from 10 min to 24 h while that for the normal sites increased by 59.4%, suggesting that the small crystals were preferentially occupied by adsorbed condensed phosphate in the fast adsorption stage. In summary, the TEM and EDAX analyses demonstrated that the small crystals on the surface of aluminum hydroxide contributed to the fast adsorption of condensed phosphate and that the adsorption did not occur uniformly across the aluminum hydroxide surface.

<table>
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<tr>
<th>Adsorption time</th>
<th>Adsorption sites</th>
<th>P:Al ratio</th>
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<tbody>
<tr>
<td>10 min</td>
<td>Small crystals</td>
<td>0.19</td>
</tr>
<tr>
<td>10 min</td>
<td>Regular sites at the edge</td>
<td>0.069</td>
</tr>
<tr>
<td>24 h</td>
<td>Small crystals</td>
<td>0.24</td>
</tr>
<tr>
<td>24 h</td>
<td>Regular sites at the edge</td>
<td>0.11</td>
</tr>
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2.3 Change in the aluminum hydroxide surface charge with adsorption of condensed phosphate

The adsorption of condensed phosphates on aluminum hydroxide brings negative charges to the surface. Fig. 5 shows that the zeta potentials of the aluminum hydroxide decreased from 20–40 mV to approximately –12 to –30 mV after the adsorption of tripoly-P at various pH after adsorption of tripoly-P (the changes of the zeta potentials of the aluminum hydroxide after adsorption of pyro-P and meta-P were similar and are not shown). Once the condensed phosphates came in contact with the aluminum hydroxide, the surface charge of the aluminum hydroxide shifted from positive to negative in the first 2 min and then the charge stayed almost constant. The most negative zeta potential observed in the adsorption process was about –30 mV, regardless of the phosphate species, the final phosphate concentrations and the solution pH. This phenomenon was also observed by Lin and Benjamin (1992). It indicates that aluminum hydroxide may have a critical negative surface charge value in the process of phosphate adsorption, which may be attributed to the co-adsorption of counter-ions accompanying the adsorption of anions as well as the different adsorption reactions occurring at different adsorption stages (Shang, 1989).

We found that condensed phosphates were heavily adsorbed on the aluminum hydroxide in the first two minutes and the decrease in the surface charge of the adsorbent primarily occurred in the same period. We inferred that the build-up of negative surface charges on the aluminum hydroxide played a role in limiting the adsorption speed of condensed phosphates (Lin and Benjamin, 1992). This phenomenon is possibly related to the nature of chemical adsorption because a covalent bond, which is a short-distance force, is formed when chemical adsorption occurs. The merging of electron clouds is necessary in forming a covalent bond (Ognalaga et al., 1994). However, the accumulation of a negative surface charge leads to an increase in the negative potential of the surface. Consequently, the merging of electron clouds becomes difficult and ligand adsorption deteriorates.

2.4 Distribution of adsorbed condensed phosphates in aluminum hydroxide particles

For the first time, XRF analysis with a 10-µm penetration depth and X-ray photoelectron spectroscopy (XPS) analysis with a 5-nm penetration depth were employed together to investigate the distribution of adsorbed condensed phosphate perpendicular to the surface of aluminum hydroxide particles. The P:Al ratios obtained from the XPS analysis represent those on the aluminum hydroxide surface while the P:Al ratios obtained from the XRF analysis are the average P:Al ratios of the entire aluminum hydroxide particle. The average P:Al ratios measured at different penetration depths at given sampling times at pH 6 are illustrated in Fig. 6. The substantial differences in the P:Al ratios obtained from the XPS and XRF tests revealed the uneven distribution of adsorbed phosphate on aluminum hydroxide particles perpendicular to the surface. The outer part of the aluminum hydroxide particles adsorbed more condensed phosphates than did the inner parts, because the surface of aluminum hydroxide likely has a lower degree of metal coordination of the O/ OH ions and a lower degree of neutralization (Hiemstra and Riemsdijk, 1996). The spatial difference can also be
attributable to the limitation in the diffusion of condensed phosphates within the capillary pores of the aluminum hydroxide particles or the lack of active sites in the inner parts of the adsorbent particles (Sposito, 1994).

3 Conclusions

The adsorption of condensed phosphates on aluminum hydroxide is divisible into two stages: (1) fast adsorption (0 to 1 h); and (2) slow adsorption (1 to 24 h). The fast adsorption fits the modified Freundlich equation well while the slow adsorption follows the first-order kinetics behavior. The activation energies of the fast adsorption of pyro-P, tripoly-P, and meta-P on aluminum hydroxide were 20.2, 22.8 and 10.9 kJ/mol P adsorbed, respectively, indicating that the fast adsorption of condensed phosphates is film-diffusion controlled. On the other hand, the activation energies of the slow adsorption of pyro-P, tripoly-P, and meta-P were 66.3, 53.5, 72.5 kJ/mol P adsorbed, respectively, suggesting that the slow adsorption of condensed phosphates is chemically controlled.

TEM and EDAX measurements revealed that the small crystals on the surface of aluminum hydroxide particles contributed to the fast adsorption of the condensed phosphates and the adsorbed condensed phosphates were found to be unevenly distributed on the surface of the aluminum hydroxide. The substantial difference in the P:Al ratios obtained from XPS and XRF analyses revealed the uneven distribution of adsorbed phosphate in aluminum hydroxide particles perpendicular to the surface. The surface of aluminum hydroxide contributed more to the adsorption of condensed phosphate than the bulk solid did.

References


Shang C, 1989. Interaction of organic and inorganic phosphates...
with short-range ordered aluminum and iron precipitates[D]. Ph.D Dissertation. University of Saskatchewan, Saskatoon, Sask.


