Phosphorus and Cadmium Sorption by Red Soils and Fe Oxide Concentrates from Thailand

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Abstract

The objectives of this study were to investigate phosphorus (P) and cadmium (Cd) sorption behavior of red soils and of their Fe oxide concentrates. The B horizon of four red soils and their Fe oxide concentrates (prepared by 5M NaOH treatment) from Thailand including Chok Chai (Ci), Ao Luek (Ak) and Yasothon(Yt) soil series and Khao Kho (Kk) soil were used. Phosphorus sorption of red soils in this study was pH independent at ~3.0-7.0 pH range and was in the order of Kk > Ak > Ci > Yt. In contrast, P sorption by Fe oxide concentrates was pH dependent at 3.0-10.0 pH range and was in the order of Ci > Kk > Ak > Yt. Phosphorus sorption by whole soils had positive relationship with soil properties including CEC, Al d, Fe o, SSA, OC, Al p, Fe p, Goe/(Goe+Hem), Alo and %clay, but the P sorption of the Fe oxide concentrates was related only to the IEP. Synthetic goethite had a higher P sorption capacity than did the Fe oxide concentrates except for Ci, specifically at low pH. Cadmium sorption of red soils and their Fe oxide concentrates were highly pH dependent at ~5.0-8.0 pH range and Cd sorption increased with increasing pH. The difference in Cd sorption values among samples were observed at pH ~7.0 for both whole soils and Fe oxide concentrates. Cadmium sorption of these red soils and their Fe oxide concentrates indicated soil pH as the important factor to control the activity of Cd, but it has less effect on their available P.

Keywords: sorption envelopes, batch experiment, Fe oxides, tropical soils

Introduction

Beside aluminosilicates, iron (Fe) oxides are also the main constituent of red soils and they also play important roles on adsorptive properties in these soils as clay sized minerals (Qafoku et al., 2004). Anions adsorbed onto Fe oxides either via specific (inner sphere complexation or ligands exchange) or non specific (ion pair formation and outer sphere complexation) adsorption (Cornell and Schwertmann, 2003). Among anions, phosphorus (P) adsorption has been the most widely studied for Fe oxides and soils (Torrent et al., 1992, 1994; Fontes and Weed, 1996; Wisawapipat et al., 2009). Iron oxides are considered the main controller of P availability in soils. Fontes and Weed (1996) reported that crystalline Fe oxides are the main P adsorbent for Brazilian soil clay. The averages of P adsorption capacity by natural hematite and goethite were 2.35 and 2.62 μmol P m⁻², respectively (Torrent et al., 1992, 1994) and the average P sorption for synthetic goethite was 2.51 μmol P m⁻² (Torrent et al., 1990). For Thai upland soils, there have been some studies on predicting P adsorption by soil properties (Trakoonyingcharoen et al., 2005) and by dithionite- and oxalate-extractable Fe and Al (Wiriyakitnateekul et al., 2005), and on P desorption characteristic (Wisawapipat et al., 2009). However, P adsorption envelope was not studied before for Thai upland soils.
Adsorption of cations on Fe oxides may also be specific or non-specific (Cornell and Schwertmann, 2003). With non-specific adsorption, there is at least one water molecule between the adsorbing species and the surface functional group of the adsorbing mineral. Specific adsorption involves interaction with deprotonated surface hydroxyl groups of the mineral to form mono- and bi-nuclear, inner sphere complexes (Cornell and Schwertmann, 2003). Of the cations, heavy metals, as pollutants, are known to interact with Fe oxides (Wang and Qin, 2007; Ni et al., 2009). Cadmium (Cd) is one of the toxic trace metals, which can be introduced into and accumulated in soils through fertilizer application (Baize, 2009) or derived from soil parent rock (Lund et al., 1981). Iron oxides control the activities and transport of Cd in soils through the adsorption-desorption reactions (He et al., 2005). Recent researches showed the data for Cd adsorption in soils from Brazil (Gomes et al., 2001), Puerto Rico (Appel and Ma, 2002) and China (He et al., 2005). However, adsorption of Cd by red soils and Fe oxides in Thai soils has not been studied. The objectives of this study were to investigate P and Cd sorption behavior of red soils and their Fe oxide concentrates by batch method at 3.0-10.0 pH range.

Materials and Methods

Soil, Fe Oxide Concentrate and Synthetic Goethite Samples

The B horizon of four red soils from Thailand including Chok Chai (Ci), Ao Luek (Ak) and Yasothon(Yt) soil series, and Khao Kho (Kk) soil were studied. The soil samples were air dried and passed through a 2 mm sieve before laboratory analysis. The soil samples were treated with H2O2 to remove organic matter before separating the clay fraction by sedimentation method for mineralogical analysis. The Fe oxides in soils were concentrated by boiling the clay fraction with 5M NaOH to remove phyllosilicates and gibbsite (Singh and Gilkes, 1991a). Synthetic goethite used in this study was synthesized from Fe(NO3)3.9H2O in alkaline system (KOH) (Schwertmann and Cornell; 2000). Synthetic goethite had a specific surface area (SSA) by N2-BET method of 32 m² g⁻¹, cation exchange capacity (CEC) by silver thiourea (AgTU⁺) method of 6.5 mmol, kg⁻¹ and the isoelectric point (IEP) via electrophoretic mobility (EM) of 8.0 (pH).

Physicochemical Analysis

The particle size distribution of soil samples was determined by the pipette method after dispersing the sample with sodium hexameta-phosphate (Gee and Bauder, 1986). The SSA of soil and Fe oxide concentrate samples was determined by the N2-BET method (Aylmore et al. 1970). Soil pH was measured in water at 1:1 soil/water ratio (National Soil Survey Center, 1996). Soil organic carbon (OC) was determined by the Walkley and Black method (Nelson and Sommers, 1996). Cation exchange capacity of soil samples and Fe oxide concentrates was determined by the AgTU⁺ method (Gillman et al., 1983). Crystalline, non-crystalline and organic forms of Fe and Al in soils were extracted with dithionite-citrate-bicarbonate solution (DCB) (Fe_d and Al_d), 0.2 M ammonium oxalate solution at pH 3.0 (Fe_o and Al_o), and sodium pyrophosphate (Fe_p and Al_p) (Mehra and Jackson, 1958; McKeague and Day, 1966; McKeague, 1967).

Mineralogical Analysis

Mineralogy of the clay fractions was determined by random powder XRD analysis of clay samples over the range of 4 to 65° 2θ with a step size of 0.02° at 1° min⁻¹ using Cu Kα radiation, λ = 1.5418 Å on a diffractometer (GBC MMA: 35 kV and 28.5 mA). For the identification of phyllosilicates, oriented clays were prepared on ceramic plates and the samples were scanned from 3 to 30° 2θ using a step size of 0.02° at 1° min⁻¹ after various pretreatments (Brown and Brindley, 1980). Random powder XRD analysis of Fe oxide concentrates was done by scanning samples from 3 to 80° 2θ with a step size of 0.02° at 0.2° min⁻¹. The proportion of goethite to hematite (Goe/(Goe+Hem)) in the Fe oxide concentrates was estimated by using the peak area of goethite (110) and hematite (104) reflections in the XRD patterns.
**Isoelectric Point (IEP)**

The IEP was obtained by electrophoretic mobility (EM) measurement as a function of pH. When the EM value was zero, the pH value related to IEP was obtained (Osei and Singh, 1999; Marchi et al., 2006). The EM of colloidal particle determines the velocity of a particle in an electric field (Malvern Instruments, 2004). Briefly, the sample (included clay fractions and Fe oxide concentrates) was placed into a centrifuge tube and washed once by 20 mL of 1M NaCl and three times by 0.01M NaCl. The 0.01M NaCl was used as a supporting electrolyte and the solid concentration was ~0.15 g L⁻¹ (final volume was 20 mL). The suspension was adjusted to required pH (3.0-7.5 with 0.5 unit increments) using either dilute HCl or NaOH, shaking for one hour and then readjusting pH again, and after that shaking overnight. The final pH of suspension was measured and adjusted if it is necessary before EM measurement. The EM of suspensions was measured by a Zetasizer nano series instrument (Malvern Instruments) with a 633 nm He-Ne laser source at 22°C using the DTS1060C-Clear disposable zeta cell.

**Phosphorus (P) Sorption**

Phosphorus sorption envelopes of soil and Fe oxide concentrate samples were determined by batch experiment using 0.01M NaCl as the supporting electrolyte. Soil sample weight used in this experiment was 0.5 g and the initial P concentrations were 10, 10, 15 and 5 µmol P g⁻¹ sample for Ci, Ak, Kk and Yt, respectively. For the Fe oxide concentrate samples, sample weight was 0.01 g and the initial P concentration was 100 µmol P g⁻¹ sample. The accurately-weighed amounts of oven-dry sample were placed in 8 centrifuge tubes and then 0.01M NaCl was added, dispersing for one minute by using an ultrasonic probe. The suspensions were adjusted to have pH 3.0 to 10.0 by dilute HCl and NaOH. After the first pH adjustment, some amount of 0.01M NaH₂PO₄·2H₂O was added to obtain the required P concentration for each sample and the pH of the suspension was then adjusted again. The pH of suspension were readjusted again after shaking for two hrs and four hrs, and then suspension were shaken overnight at ambient temperature (22±1°C) to complete 24 hrs. The suspensions were centrifuged at 3000 rpm for 15 minutes and the final pH were then measured. The supernatant was filtered through a Millipore membrane (0.22 µm GSWP). Then, P concentration of the supernatant was measured by ascorbic acid method (Murphy and Riley, 1962; Kuo, 1996) using an UV mini 1240, UV-VIS spectrophotometer. The P sorbed was calculated from the difference between the initial P and final P concentrations of the solution.

**Cadmium (Cd) Sorption**

Cadmium sorption envelopes by batch experiment were also carried out. The procedures of the experiment were similar to P sorption experiment. Sample weights were 0.5 g for the soil, and 0.01 g for the Fe oxide concentrates. The initial Cd concentration was 180 µmol Cd g⁻¹ sample for both soil and Fe oxide concentrate samples. A 0.01M Ca(NO₃)₂ solution was used as supporting electrolyte using dilute HNO₃ and Ca(OH)₂ for adjustment of pH and 0.01M Cd(NO₃)₂ was used as source of Cd. Cadmium concentration was determined by a SpectrAA 220FS, atomic absorption spectrometer (AAS). The Cd sorbed was also calculated from the difference between the initial Cd and final Cd concentrations of the solution likewise P sorbed calculation.

**Results and Discussion**

**Soil Properties**

Ci and Ak (Oxisols), and Yt and Kk (Ultisols) derived from various parent materials including basalt, limestone, old local alluvium and rhyolitic tuff respectively. Samples of the B horizons of these soils were used in this study. Most samples had high clay content (clayey texture) except for Yt that had sandy clay loam texture due to the effect of parent materials. The SSA of these soils ranged from 7 to 47 m² g⁻¹ where Yt had the lowest the SSA corresponding to their clay content (Table 1). Soil pH varied from extremely to moderately acid. Most soils had low OC content and CEC, especially Yt soil due to its low clay content. Moreover, they had very low available P. Most soils had low OC content and CEC, especially Yt soil due to its low clay content. Most samples had similar amount of Al₄, Al₃, and Al₅ in soils. However Kk
soil contained higher amount of Al$_p$ than did other soils, presumably due to its higher OC content (Table 2).

**Mineralogy and Properties of Clay Fractions, Fe Oxide Concentrates and Synthetic Goethite**

Clay fraction of red soils in this study consisted mainly of kaolinite. Hematite was the minor mineral for Ci and Ak, and quartz was the minor mineral for Kk and Yt. Accessory amounts of goethite, maghemite, quartz, anatase, rutile, vermiculite, hydroxyl-Al interlayered vermiculite (HIV) and smectite were also present in these clay fractions. The IEP of Ci and Yt clay samples were at pH lower than 3.0, and those of Ak and Kk were at pH 3.9 and 3.0, respectively (Table 3). The IEP of these clays were influenced by their mineralogy (Osei and Singh, 1999).

Hematite and goethite were the main Fe oxide minerals of Fe oxide concentrates in this study. Hematite always was the dominant mineral (Goe/(Goe+Hem) ratio<0.5) except for Kk that goethite was the major mineral. However, maghemite, anatase and rutile were also present in these Fe oxide concentrate samples. The CEC of the Fe oxide concentrate samples were higher than

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**Table 1** Classification, parent material, horizon, depth and some physical properties of the soil samples used for the study.

<table>
<thead>
<tr>
<th>Soil profile/series</th>
<th>Classification</th>
<th>Parent Material</th>
<th>Horizon</th>
<th>Depth (cm)</th>
<th>Clay (%)</th>
<th>SSA (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chok Chai (Ci)</td>
<td>Rhodic Kandiustox</td>
<td>Basalt</td>
<td>Bto1</td>
<td>30-51</td>
<td>86.8</td>
<td>35</td>
</tr>
<tr>
<td>Ao Luek (Ak)</td>
<td>Typic Kandiuadox</td>
<td>Limestone</td>
<td>Bto1</td>
<td>17-42</td>
<td>85.2</td>
<td>40</td>
</tr>
<tr>
<td>Yasothon (Yt)</td>
<td>Typic Paleustult</td>
<td>Old local alluvium</td>
<td>Bt3</td>
<td>50-80</td>
<td>20.0</td>
<td>7</td>
</tr>
<tr>
<td>Khao Kho Soil (Kk)</td>
<td>Typic Paleudult</td>
<td>Rhyolitic tuff</td>
<td>Bt1</td>
<td>40-61</td>
<td>62.9</td>
<td>47</td>
</tr>
</tbody>
</table>

**Table 2** Chemical properties of the soil samples used in the study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH (1:1 H$_2$O)</th>
<th>OC (%)</th>
<th>CEC (mmol c kg$^{-1}$)</th>
<th>Available P (mg kg$^{-1}$)</th>
<th>Fe$_d$</th>
<th>Fe$_o$</th>
<th>Fe$_p$</th>
<th>Al$_d$</th>
<th>Al$_o$</th>
<th>Al$_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ci</td>
<td>4.5</td>
<td>0.87</td>
<td>41.4</td>
<td>4.24</td>
<td>121.61</td>
<td>2.48</td>
<td>0.28</td>
<td>5.10</td>
<td>3.81</td>
<td>2.70</td>
</tr>
<tr>
<td>Ak</td>
<td>5.7</td>
<td>0.57</td>
<td>54.9</td>
<td>2.74</td>
<td>55.91</td>
<td>2.70</td>
<td>0.27</td>
<td>5.29</td>
<td>5.42</td>
<td>2.14</td>
</tr>
<tr>
<td>Yt</td>
<td>4.35</td>
<td>0.15</td>
<td>14.2</td>
<td>0.19</td>
<td>10.07</td>
<td>0.63</td>
<td>0.17</td>
<td>2.93</td>
<td>3.30</td>
<td>1.56</td>
</tr>
<tr>
<td>Kk</td>
<td>5.3</td>
<td>1.07</td>
<td>76.2</td>
<td>0.75</td>
<td>55.14</td>
<td>7.71</td>
<td>13.28</td>
<td>9.48</td>
<td>4.48</td>
<td>17.66</td>
</tr>
</tbody>
</table>

**Table 3** The mineral composition and the isoelectric point (IEP) of the clay fractions, and mineral composition, the Goe/(Goe+Hem) ratios, CEC and IEP of the Fe oxide concentrates from soils.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Clay fraction</th>
<th>IEP (pH)</th>
<th>Fe oxide concentrate</th>
<th>Mineral composition</th>
<th>Goe/(Goe+Hem)</th>
<th>CEC (mmol c kg$^{-1}$)</th>
<th>IEP (pH)</th>
<th>SSA (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ci</td>
<td>Kao &gt;&gt; Hem &gt; Ant, Goe, Qtz, Rut, Mhm</td>
<td>&lt;3.0</td>
<td>Kao &gt;&gt; Hem &gt; Ant, Goe, Rut, Mhm</td>
<td>0.12</td>
<td>59.4</td>
<td>6.5</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>Ak</td>
<td>Kao &gt;&gt; Hem &gt; Goe, Qtz, Ant, HIV, Mhm, Rut</td>
<td>3.9</td>
<td>Hem &gt;&gt; Goe &gt; Rut, Ant, Mhm</td>
<td>0.36</td>
<td>58.4</td>
<td>4.1</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>Yt</td>
<td>Kao &gt;&gt; Qtz &gt; Hem, Goe, Sme, Ant, Rut</td>
<td>&lt;3.0</td>
<td>Hem &gt;&gt; Goe &gt; Rut, Mhm, Ant</td>
<td>0.31</td>
<td>58.5</td>
<td>&lt;3.0</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>Kk</td>
<td>Kao &gt;&gt; Qtz &gt; Goe, Hem, Ver, HIV, Rut</td>
<td>3.0</td>
<td>Goe &gt;&gt; Hem, Mhm</td>
<td>0.74</td>
<td>50.0</td>
<td>4.9</td>
<td>128</td>
<td></td>
</tr>
</tbody>
</table>

Kao=kaolinite; Ver=vermiculite; HIV= hydroxyl-Al interlayered vermiculite; Sme=smectite; Qtz=quartz; Hem=hematite; Goe=goethite; Mhm=maghemite; Ant=anatase; Rut=rutile.
that of synthetic goethite (6.5 mmol\textsubscript{c} kg\textsuperscript{-1}) with values ranging from 50.0 to 59.4 mmol\textsubscript{c} kg\textsuperscript{-1}. The IEP of Fe oxide concentrates were at pH 6.5, 4.1, <3 and 4.9 for Ci, Ak, Yt and Kk, respectively, which were lower than that of the synthetic goethite (IEP was at pH 8.0). These results might be a result of the presence of amorphous phase from the preparation process by 5M NaOH treatment or by anions from clay mineral dissolution re-adsorbed onto the Fe oxide surfaces. The SSA of the Fe oxide concentrates were very high ranging from 88 to 128 m\textsuperscript{2} g\textsuperscript{-1} (Table 3).

**Phosphorus Sorption Envelopes of Red Soils, Fe Oxide Concentrates and Synthetic Goethite**

Phosphorus sorption envelopes of four red soils in this study were in the order Kk > Ak > Ci > Yt (Figure 1a). Kk soil showed the highest P sorption in 3.0-10.0 pH range. Yt soil had the lowest P sorption in the pH range due to its low clay content. In the 3.0-7.0 pH range, P sorption was largely pH independent (plateau) and showed the sorption maximum value, and P sorption decreased with increasing at pH higher than pH 7.0 for every sample. Similarly, P sorption characteristic of an Inceptisol from Japan was pH independent in 4.0-7.0 pH range and the P sorption ranged between ~10 and 15 µmol P g\textsuperscript{-1} soil (Hiradate and Uchida, 2004) which was similar to that of Kk sample. However, Wang et al. (2009) reported that P sorption of two Oxisols from China in their study was pH dependent in ~3.0-7.0 pH range and having P sorption capacity of >30 µmol P g\textsuperscript{-1} soil at pH 7.0. This P sorption capacity values was higher than that of the two Oxisols and two Ultisols in this study. Phosphorus sorption had highly significant relationship with soil properties including CEC, Al\textsubscript{p}, Fe\textsubscript{o}, SSA, OC, Al\textsubscript{p}, Fe\textsubscript{o} and Goe/(Goe+Hem) at P<0.001 and had relationship with Al\textsubscript{p} and clay content (P<0.05) (Table 4). The results for four examples are shown in Figures 2a, b, c and d. These results were consistent with previously published data by Singh and Gilkes (1991b) for Australian soils, B"orling et al. (2001) for Swedish soils, Agbenin (2003) for Nigerian soils, and data reported by Trakoonyingcharoen et al. (2005), Wiriyakitnateekul et al. (2005) and Wisawapipat et al. (2009) for Thai soils. The P sorption of red soils in this study showed no relationship with Fe\textsubscript{ox}. This might be due to effects of other soil properties on P sorption that masked the influence of Fe\textsubscript{ox}.

Phosphorus sorption envelopes of Fe oxide concentrates from the Thai red soils were in the order of Ci > Kk > Ak > Yt (Figure 1b). Unlike the case of soil samples, P sorption for the Fe oxide concentrates was pH dependent over 3.0-10.0 pH range with P sorption decreasing with increasing pH. Similarly, P sorption of synthetic goethite was also pH dependent. The Fe oxide concentrates showed the maximum P sorption value at pH 3.0, except for Ci, of which maximum sorption occurred at pH 4.0. The indifferent P sorption for Ci was influenced by the effect of an amorphous phase present in Fe oxide concentrates or higher anatase content in the sample. Anatase had P adsorption capacity similar to hematite (Torrent et al., 1994). Synthetic goethite had a higher P sorption than did Kk, Ak and Yt at all pH ranges, and had P sorption

![Figure 1](image-url) Phosphorus sorption envelopes of the four red soils (a), and the Fe oxide concentrates of the soils (b). Data for a synthetic goethite are also plotted along with Fe oxide concentrates for comparison. 0.01M NaCl was used as a supporting electrolyte in the sorption experiments.
The representative of highly significant relationships (***P < 0.001) between soil properties including SSA (a), CEC (b), Feo (c) and Al_d (d) and phosphorus sorption by four Thai red soils.

Table 4 The R² for the linear relationships between soil properties and P sorption of four Thai red soils, and properties of Fe oxide concentrates and P sorption of four Fe oxide concentrates from soils.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Whole soil</th>
<th>Fe oxide concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Clay</td>
<td>0.20**</td>
<td>-</td>
</tr>
<tr>
<td>SSA</td>
<td>0.69***</td>
<td>0.01</td>
</tr>
<tr>
<td>OC</td>
<td>0.67***</td>
<td>-</td>
</tr>
<tr>
<td>CEC</td>
<td>0.82***</td>
<td>0.07</td>
</tr>
<tr>
<td>Avai. P</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Fe_d</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>Fe_o</td>
<td>0.81***</td>
<td>-</td>
</tr>
<tr>
<td>Fe_p</td>
<td>0.62***</td>
<td>-</td>
</tr>
<tr>
<td>Al_d</td>
<td>0.83***</td>
<td>-</td>
</tr>
<tr>
<td>Al_p</td>
<td>0.26*</td>
<td>-</td>
</tr>
<tr>
<td>Al_o</td>
<td>0.65***</td>
<td>-</td>
</tr>
<tr>
<td>Goe/(Goe+Hem)</td>
<td>0.49***</td>
<td>0</td>
</tr>
<tr>
<td>IEP</td>
<td>-</td>
<td>0.26*</td>
</tr>
</tbody>
</table>

* = P < 0.05 and *** = P < 0.001.

less than did Ci at low pH (~pH 3.0-6.0), and synthetic goethite had lower SSA than did other samples in the study. Moreover, the P sorption maximum value of Fe oxide concentrates (at pH 3.0) in this study was lower than the average P sorption capacity of natural hematites (\(\bar{x} = 2.35\) \(\mu\)mol P m\(^{-2}\)) (Torrent et al., 1994), natural goethites (\(\bar{x} = 2.62\) \(\mu\)mol P m\(^{-2}\)) (Torrent et al., 1992) and Fe oxide concentrates of Brazilian Oxisols (\(\bar{x} = 2.15\) \(\mu\)mol P m\(^{-2}\)) (Fontes and Weed, 1996). These results might be due to the difference of methodology used to study the P sorption, and the Fe oxide concentrates in this study might contain amorphous phase or their surface were modified (Singh and Gilkes, 1991a). Phosphorus sorption of Fe oxide concentrates had poor relationship with the IEP (R\(^2 = 0.26, P<0.05\) and had no relationship with Goe/(Goe+Hem), CEC and SSA (Table 4). The IEP was the only one major factor affecting P sorption by Fe oxide concentrates for this study. However, Strauss et al. (1997) indicated that SSA had some effect on P sorption by Fe oxides.

Phosphorus sorptions of soils in comparison to their Fe oxide concentrates were very low and had lower pH dependency. Kaolinite was the major clay mineral of soils in this study which had low
phosphorus sorption capacity and low pH independency for P sorption (Ioannou and Dimirkou, 1997). Nevertheless, soil organic matter could decrease the pH dependency of P sorption in soils (Hiradate and Uchida, 2004), which might be the case for the studied samples. These results indicated that soil pH management might not affect the P sorption for red soils.

Cadmium Sorption Envelopes of Red Soils, Fe Oxide Concentrates and Synthetic Goethite

Cadmium sorption behaviour of the four red soils was pH dependent (sigmoid curve) (Figure 3a). This behaviour was similar to Cd sorption of clay fraction in two acid soils from Greece (Spathariotis and Kallianou, 2001). Cadmium sorption increased with increasing pH in pH 3.0-10.0 range and reached maximum (nearly 100%) at pH ~9.0. Between pH 7.0 and 8.0, Cd sorption values of soils were in the order of Kk > Ci > Ak > Yt. The Kk soil had the highest Cd sorption value and the Yt soil had the lowest Cd sorption value reflecting the effect of the SSA of the soils (Spathariotis and Kallianou, 2001). Angove et al. (1997) reported that the difference in Cd sorption of two kaolinites at the plateau region (5.0-7.0 pH range) reflected the different surface areas. Gomes et al. (2001) reported that Cd sorption of Brazilian soils was affected by CEC of soils. Cadmium sorption capacity of Ci (~32.5 μmol g⁻¹) and Kk (~36 μmol g⁻¹) at pH ~6.0 were closely similar to that of Oxisol (~32 μmol g⁻¹), Ultisol (~34 μmol g⁻¹) and Mollisol (~32 μmol g⁻¹) from Puerto Rico reported by Appel and Ma (2002). However, Cd sorptions of Ak (~13 μmol g⁻¹) and Yt (~9 μmol g⁻¹) were lower.

Cadmium sorption behavior of the four Fe oxide concentrates was similar to the Cd sorption of the whole soils (Figure 3b). However, sorption maximum was reached earlier (at pH 8.0) for the Fe oxide concentrates. The sorption edge range was relatively smaller (pH 6.0-8.0) for Fe oxide concentrates than for the whole soils (pH 6.0-9.0). They were highly pH dependent at ~5.0-8.0 pH range and consistent with that of synthetic goethite. These results were consistent with those of Wang and Xing (2002) which showed that Cd sorption by goethite was highly pH dependent at ~5.0-7.0 pH range. Similar to the case of whole soils, the difference of Cd sorption values by the four Fe oxide concentrates and a synthetic goethite were observed at pH ~7.0 (Ak > Kk, Yt > Ci > synthetic goethite). However, over the pH range the differences in Cd sorption of the four Fe oxide concentrates were minimal. The Cd sorption of Fe oxide concentrates was not related to their CEC, IEP, Goe/(Goe+Hem) or SSA.

Cadmium sorption values of whole soils and their Fe oxide concentrates were similar, which may be due to the similar Cd sorption capacity of clay minerals, organic matter and Fe oxides (Angove et al., 1997; Wang and Xing, 2002; Gou et al., 2006). Moreover, the low IEP of Fe oxide concentrates might partly enhance Cd sorption. However, Yt soil sample had lower value of Cd sorption than its Fe oxide concentrate due to the lower clay content of the soil. The results confirmed that soil pH management is an important key to control activity of heavy metals for these red soils.

![Figure 3](image-url) Cadmium sorption envelopes of the four red soils (a), and the Fe oxide concentrates of the soils (b). Data for a synthetic goethite are also plotted along with Fe oxide concentrates for comparison. 0.01M Ca(NO₃)₂ was used as a supporting electrolyte in the sorption experiments.
Conclusions

Phosphorus sorption of four red soils in this study was pH independent in ~3.0-7.0 pH range and was in the order of Kk > Ak > Ci > Yt. Phosphorus sorption had positive relationship with soil properties including CEC, Al_d, Fe_o, SSA, OC, Al_p, Fe_p, Goe/(Goe+Hem), Al_o and %clay. Most of Fe oxide concentrates from soils could sorb P more than the whole soils and they showed pH dependent behavior in the pH range 3.0-10.0, reflected by P sorption decreased with increasing pH. Phosphorus sorption by Fe oxide concentrates was related to their IEP. The average of P sorption capacity of Fe oxide concentrates in this study were lower than those in other studies due to the presence of some amorphous phase or their surface modification. Cadmium sorption of the red soils and their Fe oxide concentrates were highly pH dependent in ~5.0-8.0 pH range as Cd sorption increased with increasing pH. Both material types showed the difference in Cd sorption of samples at pH ~7.0. The results clearly revealed that Cd sorption of soils and Fe oxide concentrates indicated soil pH as the important factor to control activity and transport of Cd, but having less effect on available P.

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