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Adsorption of Phosphate onto Ferrihydrite and Ferrihydrite-Humic Acid Complexes

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ABSTRACT

The adsorption of phosphate onto ferrihydrite (FH) and two FH-humic acid (HA) complexes, obtained by co-precipitating FH with low (FH-HA1) and relatively high amounts of humic acid (FH-HA2), was studied through kinetics and isotherm experiments to determine the differences in phosphate adsorption between FH-HA complexes and FH and to reveal the mechanisms of phosphate adsorption onto two soil compositions. The isoelectric point (IEP) and the specific surface area (SSA) of the mineral decreased as the particle porosity of the mineral increased, which corresponded to an increase in the amount of organic carbon. The adsorption capacity of phosphate was higher on FH than on FH-HA1 and FH-HA2 at the scale of micromoles per kilogram. The initial adsorption rate and adsorption affinity of phosphate decreased with an increase in the amount of HA in the mineral. The sensitivity of phosphate adsorption to the change in the pH was greater for FH than for FH-HA complexes. Ionic strength did not affect the adsorption of phosphate onto FH and FH-HA1 at a lower pH, and the increase in the ionic strength promoted phosphate adsorption at a higher pH. However, for the FH-HA2 complex, the increase in the ionic strength inhibited the adsorption of phosphate onto FH-HA2 at a lower pH and increased the adsorption at a higher pH.

Key Words: adsorption isotherm, adsorption kinetics, co-precipitation, Fe oxides, ionic strength

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Phosphate is not only an essential plant nutrient but also the main element in eutrophication. Therefore, the fate and behavior of phosphate in soil and water environments require attention. Ferrihydrite (FH) is ubiquitous in many near-surface environments and exists as the precursor to hematite as a naturally occurring nanocrystalline iron hydroxide (Michel *et al.*, 2007). Due to its high surface reactivity, FH plays a significant role in controlling the behavior of certain contaminants and nutrients (Michel *et al.*, 2007; Wang *et al.*, 2013). The predominant formation of the inner-sphere bidentate-binuclear complex has been suggested for phosphate adsorption onto FH (Arai and Sparks, 2001; Khare *et al.*, 2007). An increase in ionic strength has no significant effect on the adsorption of phosphate at a low pH but promotes this adsorption at a high pH (Arai and Sparks, 2001; Antelo *et al.*, 2010). The processes of phosphate adsorption include a rapid initial adsorption process followed by a slower process. The two-step adsorption seems to be normal for phosphate adsorption onto FH (Mallet *et al.*, 2013).

Soluble humic substances usually inhibit the adsorption of phosphate (Weng *et al.*, 2008; Shuai and Zinati, 2009). Humic acid (HA), as an important humic substance, is easily adsorbed onto soil particles (Kummert and Stumm, 1980; Saito *et al.*, 2004). HA interacts strongly with various minerals, including FH (Weng *et al.*, 2007), and may inhibit iron oxide crystallization and promote the formation of noncrystalline iron oxides under co-precipitation. The surface properties of iron oxides such as specific surface area and porosity may also change (Singer and Huang, 1990; Violante and Huang, 1992). Thus, these oxides often affect the fate and transport of ions in both aquatic and terrestrial environments (Gerin *et al.*, 2003; Mikutta *et al.*, 2006; Iglesias *et al.*, 2010a, b). Phosphate is not adsorbed directly onto organic matter because both are negatively charged at the pH values normally found in natural environments (Tan, 2003). However, organic matter-metal (Fe or Al)-phosphate complexes can

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form due to the high affinity of both phosphate and organic matter for OH–Fe or Al species (Tan, 2003; Mikutta *et al.*, 2006).

Inorganic and organic anions, such as phosphate, arsenate, citrate and HA, are strongly adsorbed onto Al and Fe oxides (Tejedor-Tejedor *et al.*, 1992; Fuller *et al.*, 1993; Arai and Sparks, 2001; Grafe *et al.*, 2002; Borggaard *et al.*, 2005; Weng *et al.*, 2007). Because this adsorption likely occurs on the same surface sites of the oxides with the formation of mono- or bidentate surface complexes, these anions may compete for the adsorption sites when present simultaneously. The addition of HA can significantly reduce the amount of phosphate that is adsorbed onto goethite, and the order of the addition of phosphate and HA can also influence the phosphate adsorption (Antelo *et al.*, 2007; Fu *et al.*, 2013). The competition in the adsorption between two or more ligands is not only for the common sites but also changes the electric potential of the mineral surfaces (Violante, 2013). In addition, the mechanisms underlying the competition between phosphate and HA onto variable charged minerals include the dissolution of adsorbents, the creation of new adsorption sites, and the retardation of the crystal growth of poorly ordered Fe or Al oxides (Cornell and Schwertmann, 1979; Singer and Huang, 1990; Borggaard *et al.*, 2005). However, some researchers have demonstrated that HA has a relatively poor influence on the inhibition of phosphate adsorption onto goethite, likely due to the much stronger affinity of phosphate than HA and the inhibition of Fe-oxide crystallization in the presence of HA over the course of the reaction (Gerke, 1993; Borggaard *et al.*, 2005; Violante, 2013).

Although there are many studies on phosphate adsorption onto certain soil components in the presence of HA (Borggaard *et al.*, 2005; Guan *et al.*, 2006; Fu *et al.*, 2013), information on the adsorption of phosphate onto FH-HA complexes is scarce. In this study, we examined phosphate adsorption onto FH-HA complexes compared to that onto pure FH through kinetics and isotherm experiments and the effects of pH and ionic strength on phosphate adsorption. The purposes of this research were to determine the differences in phosphate adsorption between FH-HA complexes and FH and to reveal the mechanisms of phosphate adsorption onto two soil compositions.

MATERIALS AND METHODS

FH synthesis and HA extraction

Two-line FH was synthesized according to Arai and Sparks (2001) in the open atmosphere. Forty grams of ferric nitrate were dissolved in 500 mL of deionized water. The solution was titrated to pH 7.5 by 1.0 mol L^{-1} NaOH and incubated for 45 min. The precipitate was washed with doubly deionized water until the conductivity of the supernatant was less than 10 µS cm^{-1}. The sample was freeze-dried. The specific surface area (SSA) was determined through the Brunauer-Emmett-Teller (BET) method, and the pore diameter was analyzed using a pore size analyzer (Autosorb-IMP-CR Quantachrome Instruments, USA). The isoelectric point (IEP) was determined by electrophoresis using a Zetasizer analyzer (Brookhaven Instruments, Britain). The samples were further characterized by X-ray powder diffraction (XRD) measured at 5°–90° 2θ using Cu $K\alpha$ radiation and by Fourier transform infrared (FTIR) spectra that were collected with an infrared spectrometer (Bruker, Germany) by using the KBr method.

HA was isolated from a soil sample that collected from a mountain meadow (Tibet, China) according to the procedure suggested by Grøn and Raben-Lange (1992). The element composition of HA was: carbon 589.8 g kg^{-1}, nitrogen 30.7 g kg^{-1}, and hydrogen 73.6 g kg^{-1}, as determined using an elemental analyzer (EA3000, EuroVector, Italy).

Preparation of two FH-HA complexes

The preparation method was similar to Singer and Huang (1990), and the content of HA depended on the maximum adsorption of HA onto FH. Two FH-HA complexes, obtained by co-precipitating FH with low (FH-HA1) and relatively high amounts of HA (FH-HA2), were prepared in an open atmosphere. First, 0.35 g (for FH-HA1) and 3.5 g (for FH-HA2) of HA was dissolved in 0.1 mol L^{-1} NaOH, and the pH of the HA solution was adjusted to 7.5 using NaOH or HNO_3. Ferric nitrate (approximately 40.0 g) was dissolved in 500 mL of doubly deionized water, to which HA was added. The solutions were mixed, titrated to pH 7.5 using 1.0 mol L^{-1} NaOH, and incubated for 45 min.

The carbon contents of FH-HA1 and FH-HA2 were 21.6 and 160.3 g kg^{-1}, respectively. The SSA, IEP, XRD, and FTIR analyses of the complexes were performed as described above.

Adsorption kinetics of phosphate

The phosphate adsorption kinetics onto the FH and FH-HA complexes were measured at pH 4.5, 6.5 and 8.5. A stock of FH or FH-HA complex suspension (2.0 g L^{-1}) was prepared by adding 150 mL of 0.001 mol L^{-1} $NaNO_3$ to a glass beaker. The pH of the suspension was then adjusted to the desired value by adding