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Impact of crystalline and amorphous iron- and aluminum hydroxides on mechanisms of phosphate adsorption and desorption

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ABSTRACT

Fourier-transform infrared (FT-IR) spectroscopic experiments were carried out during phosphate adsorption on highly crystalline gibbsite, poorly crystalline 2-line-ferrihydrite and amorphous iron–aluminum–hydroxide mixtures in the molar ratio 1:0, 10:1, 5:1, 1:1, 1:5, 1:10 and 0:1. The OH stretching vibrational bands were utilized to analyze changes in structural and surface OH groups during adsorption, because the position of characteristic P–O vibrational bands can shift depending on reaction conditions, pH or adsorbed phosphate content. Adsorption and desorption kinetics were studied at pH 6 and different initial phosphate concentrations to achieve varying phosphate coverage on the mineral surfaces. For gibbsite the formation of $AlHPO_4$ and Al_2HPO_4 can be assumed, while for ferrihydrite, a $FeHPO_4$ or Fe_2PO_4 complex and the precipitation of $FePO_4$ with longer equilibration time were proposed. Fe_2HPO_4 or a Fe_2PO_4 surface complex was deduced for Fe-hydroxides, an AlH_2PO_4 surface complex was identified for Al-hydroxide, and both displayed either hydrogen bonds to neighboring hydroxyl groups or hydrogen bonds to outer-sphere complexes. Fe:Al-hydroxide mixtures with high Al ratios showed a low phosphate desorption rate, while ferrihydrite and the Fe:Al-hydroxide mixtures with high Fe ratios had almost negligible desorption rates. It was concluded that within the weakly associated amorphous FeO(OH) materials, $FePO_4$ precipitated, which was bound by outer-sphere hydrogen bonds. With high Al ratios, desorption increased, which indicated weaker phosphate binding of both inner-sphere and outer-sphere complexes and hence, either no or minor quantities of precipitate. Ferrihydrite showed a more rigid structure and a lower extent of precipitation compared to amorphous Fe-hydroxide.

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Introduction

Sorption of phosphorus by soil minerals such as iron and aluminum-(hydr)oxides is of interest because of its critical role in terms of limitation as a nutrient for plant uptake, but also due to leaching effects and surface runoff into water bodies caused by excess fertilization, leading to eutrophication (Sims and Pierzynski, 2005). Notably, the formation of these iron and

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aluminum-hydroxides is characteristic during soil alteration and strongly affects phosphorus transport and bioavailability by adsorption and desorption processes. Due to the important role of phosphate in the environmental nutrient cycle, the reactions of phosphate with pedogenic iron and aluminum-hydroxides have been thoroughly studied (Arai and Sparks, 2001, 2007; Barrow, 1983; Hinsinger, 2001; Krumina et al., 2016; Torrent et al., 1992). A major aspect is the kinetics of adsorption and desorption on soil iron and aluminum-particles, showing a biphasic behavior including a very fast initial adsorption process during the first 2 hr, followed by a slow reaction phase (Luengo et al., 2006; McLaughlin et al., 1977; Reddy et al., 1999; Shang et al., 1992; Strauss et al., 1997; Torrent et al., 1992; Willett et al., 1988). Adsorption experiments with synthetic iron and aluminum-(hydr)oxides showed the occurrence of ligand exchange and the formation of stable inner-sphere surface complexes with metal ions (Goldberg and Sposito, 2008; Parfitt, 1979). Torrent (1997) summarized theories explaining the slower process step with the formation of initial mononuclear complexes and transformation to binuclear complexes, competition with anions on the surface or surface precipitation processes, respectively. This can also be attributed to the diffusion of phosphate into the inner particle pores of hydroxides (Chitrakar et al., 2006). It was reported that the phosphate uptake increased with increasing initial phosphate concentration in the same ratio (Talebi Atouei et al., 2016), while the degree of crystallinity or porosity of hydroxides affects the extent of phosphate adsorption (Parfitt, 1989). Mineral crystallinity is an important aspect in phosphate sorption processes, since soils contain amorphous, poorly crystalline and well-crystallized hydroxides during pedogenesis, offering varying properties such as specific reactive surface area (Scheffer et al., 2010). Also, hydroxides occur as multi-component solids in soil systems, and affect phosphate adsorption behavior (Anderson and Benjamin, 1990).

Further investigations are needed in the area of connecting the detailed characteristics of adsorbed surface complexes with the change of binding motifs over time and their impact on desorption behavior. Gibbsite and ferrihydrite are the most common aluminum and iron hydroxides in soils, and their surface properties are well characterized; hence, they are good model minerals for investigation of phosphate surface reactions (Antelo et al., 2010; Arai and Sparks, 2001; Arlidge et al., 1963; Johnson et al., 2002; Khare et al., 2007; Krumina et al., 2016; Laiti et al., 1996; Li et al., 2013; Lijklema, 1980; Persson et al., 1996; Zheng et al., 2012). The objective of this work was to detect changes in phosphate binding motifs on gibbsite, ferrihydrite and binary iron and aluminum hydroxide surfaces with varying degrees of crystallinity during short- and long-term equilibration times with varying phosphate concentration, by using Diffuse reflection (DRIFT) Fourier-transform infrared (FT-IR) spectroscopy. On the basis of these investigations, amorphous iron and aluminum hydroxide mixtures were used to compare phosphate adsorption mechanisms. Besides the symmetric and asymmetric P–O stretching vibrations, which have been widely used for phosphate species symmetry analyses (Arai and Sparks, 2001; Krumina et al., 2016; Tejedor-Tejedor and Anderson, 1990), the OH stretching bands and their changes during adsorption were included for speciation of the adsorbed phosphate surface complexes. Adsorption and desorption experiments were used to identify the different binding mechanisms and phosphate binding forms, which were detected after adsorption and contributed primarily to desorption. Furthermore, the sorption mechanism of phosphate on soil mineral particles is highly pH dependent and the phosphate binding motifs change with pH, as shown by several studies (Antelo et al., 2005; Laiti et al., 1998; Rahnemaie et al., 2007; Weng et al., 2011). With the background that eutrophication of rivers and lakes caused by over-enrichment with phosphorus is still a widespread problem, for which non-point-sources from agricultural soils are the main polluters (Carpenter et al., 1998), this study focused on the pH conditions of agricultural soils, which range most frequently between pH 5.0 and 6.8 (Scheffer et al., 2010), where phosphate shows its optimal availability due to the high solubility of Fe- and Al-phosphates (Johnson et al., 2002; Scheffer et al., 2010). Due to this reason, the pH for the adsorption and desorption experiments was set to a value of 6.

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1. Materials and methods

1.1. Adsorbents

The commercially available synthetic adsorbent used in this study was gibbsite (analytical grade, Merck Millipore, Merck KGaA, Darmstadt, Germany). 2-line-ferrihydrite was prepared according to Schwertmann and Cornell (2008), for which 350 mL of 1 mol/L KOH was added to 500 mL of a 0.2 mol/L Fe(NO$_3$)$_3$·9 H$_2$O-solution, until a pH of 7.5 was reached. The developed precipitate was centrifuged and washed for 5 min at 12134 ×g (Avanti J-25 Centrifuge, Beckman Coulter, Brea, USA), subsequently frozen, freeze-dried, and stored in a desiccator. The mixed iron-aluminum-hydroxides (Fe:Al-hydroxide) were prepared as described by Sujana et al. (2009), for which 0.1 mol/L Fe(NO$_3$)$_3$·9 H$_2$O and 0,1 mol/L Al(NO$_3$)$_3$·9 H$_2$O were mixed in molar ratios Fe to Al of 1:0, 10:1, 5:1. 1:1, 1:5, 1:10 and 0:1, adjusted to a pH of 6 with 5 M KOH, equilibrated for 1 hr, and centrifuged for 5 min at 12134 ×g. The washed precipitate was dried at 60°C and ground into a powder. All chemicals used for preparation of adsorbents were of analytical grade, and the solutions were prepared with ultrapure water. The elemental composition of the adsorbents was verified by using SEM–EDX, scanning electron microscopy (DSM 962, Zeiss, Oberkochen, Germany) with energy dispersive X-ray spectroscopy (X-Max 50 mm^2 with INCA, Oxford Instruments, Abingdon, Great Britain). The formation of pure Al(OH)$_3$ and FeO(OH) for the amorphous hydroxides was revealed. Determination of the adsorbent crystallization as well as amorphous structures was carried out by X-ray diffraction (XRD) using a PANalytical Empyrean powder diffractometer (Almelo, Netherlands) from GFZ Potsdam, with a theta–theta-goniometer, Cu-Kα radiation (λ = 0.15418 nm), automatic divergent and anti-scatter slits and a PIXcel3D detector. Diffraction data were recorded from 4.6° to 84.9° 2Θ with a step-size of 0.0131 and a step time of 58.4 sec. The generator settings were 40 kV and 40 mA. Specific surface areas of all adsorbents used as well as the coated silica sand were determined with an Autosorb-1 (Quantachrome, Odelzhausen, Germany) using a five-point BET-measurement (Brunauer–Emmett–Teller) and nitrogen as the adsorptive

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