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Effects of Al³⁺ doping on the structure and properties of goethite and its adsorption behavior towards phosphate

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ABSTRACT

Al substitution in goethite is common in soils, and has strong influence on the structure and physicochemical properties of goethite. In this research, a series of Al-doped goethites were synthesized, and characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR) and extended X-ray absorption fine structure (EXAFS) spectroscopy. The adsorption behavior of these samples towards PO₄³⁻ was also investigated. Characterization results demonstrated that increasing Al content in goethite led to a reduction in crystallinity, increase in specific surface area (SSA), and morphology change from needle-like to granular. Rietveld structure refinement revealed that the lattice parameter *a* remained almost constant and *b* slightly decreased, but *c* was significantly reduced, and the calculated crystal density increased. EXAFS analysis demonstrated that the Fe(Al)–O distance in the structure of the doped goethites was almost the same, but the Fe–Fe(Al) distance decreased with increasing Al content. Surface analysis showed that, with increasing Al content, the content of OH groups on the mineral surface increased. The adsorption of phosphate per unit mass of Al-doped goethite increased, while adsorption per unit area decreased owing to the decrease of the relative proportion of (110) facets in the total surface area of the minerals. The results of this research facilitate better understanding of the effect of Al substitution on the structure and properties of goethite and the cycling of phosphate in the environment.

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Introduction

Iron (hydr)oxides are ubiquitous earth minerals that are found in 16 iron (hydr)oxide forms, with high adsorption capacities for toxic elements and degradation ability towards organic

contaminants. Among them, goethite is the most ubiquitous and abundant iron oxide mineral (Liu et al., 1995, 1999; Yapp, 2001; Cornell and Schwertmann, 2003).

Cation substitution often occurs in the formation and transformation processes of goethite in soils, and Al

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substitution is the most common phenomenon (Cornell and Schwertmann, 2003; Bazilevskaya et al., 2011). The substitution of Al in natural goethite can reach 33 mol% (Norris and Taylor, 2006; Fitzpatrick and Schwertmann, 1982; Schwertmann and Carlson, 1994; Carlson, 1995; Cornell and Schwertmann, 2003). Due to the differences in properties between Al^{3+} and Fe^{3+} , such as ionic radius (Shannon, 1976) and electronegativity (Portier et al., 1994), Al substitution causes changes in the structure and physicochemical properties of goethite. Because the ionic radius of Al^{3+} ($r = 0.535 \text{ \AA}$) is smaller than that of Fe^{3+} ($r = 0.645 \text{ \AA}$) (Shannon, 1976), the incorporation of Al reduces the lattice parameters of goethite, as proven by previous studies (Thiel, 1963; Schwertmann et al., 1985; Krehula and Musić, 2010). Increasing Al incorporation into goethite leads to the formation of more structural defects (Gonzalez et al., 2002; Cornell and Schwertmann, 2003) and crystal surface active sites, such as OH groups (Wolska and Schwertmann, 1993). Meanwhile, the existence of Al restrains the crystal growth of goethite (Cornell and Schwertmann, 2003; Bazilevskaya et al., 2012), and promotes the transformation from polycrystallinity to monocrystallinity, the diminution of particles and the decrease of crystal length–width ratio (Schulze and Schwertmann, 1987; Maurice et al., 2000; Liu et al., 2012; Wang et al., 2014; Ma et al., 2015). In virtue of its higher ionic potential (Lide and Haynes, 2010), Al^{3+} is stronger than Fe^{3+} in terms of binding force to other ions, such as OH^- . This results in a higher dehydroxylation temperature in Al-doped goethite than in the pure material (Schulze and Schwertmann, 1984; Cambier, 1986; Ruan and Gilkes, 1995). Compared to pure goethite, Al-doped goethite has better chemical stability, as evidenced by the decrease in the dissolution rate in strong acids or strong reductants (Schwertmann, 1984; Cornell and Schindler, 1987; Torrent et al., 1987). The bioreductivity of Al-doped goethite is rather confusing, because the increase of Al substitution may lead to a decrease (Bousserrhine et al., 1999; Liu et al., 2001), increase (Maurice et al., 2000) or unchanged bioreductivity (Kukkadapu et al., 2001) for goethite under different conditions. Additionally, Al incorporation can also affect the magnetic properties of goethite (Fleisch et al., 1980; Murad and Schwertmann, 1983; Bazilevskaya et al., 2011).

Furthermore, Al substitution can also change the adsorption properties of goethite towards various nutrients, heavy metal(loid) cations and organic pollutants. The adsorption of phosphate is initially rapid, but then slows, ascribed to the diffusion into micropores or grooves (Barrow et al., 1981; Pena and Torrent, 1990; Nilsson et al., 1992; Strauss et al., 1997; Luengo et al., 2006). Previous studies showed that, in acidic or neutral mediums, each phosphate ion replaces two singly coordinated surface OH groups to form a bridging binuclear surface complex (Parfitt et al., 1975; Nanzyo, 1986; Torrent et al., 1990). For synthetic and natural goethites with a wide range of morphologies, the phosphate sorption capacity is essentially the same per unit area, due to the dominance of (110) facets in all the goethites (Cornell and Schwertmann, 2003). Compared with pure goethite, Al-doped goethite has larger specific surface area but lower adsorption rate for PO_4^{3-} , probably due to the steric hindrance effect of Al^{3+} cations (Ainsworth et al., 1985; Ainsworth et al., 1985). The introduction of Al in goethite enhances the adsorption of As(V), and inhibits the release of As from the mineral surface, owing to bioreductive

dissolution (Silva et al., 2010). Al-doped goethite also shows good adsorption properties towards organic pollutants, such as the azo dye Eriochrome Black T (Wang et al., 2014). It also has high affinity and adsorption capacity for heavy metals in water or soils. For example, Ma et al. (2015) reported that the surface active site densities, adsorption capacity and affinity of Al-doped goethite are higher than those of pure goethite, and the desorption rate of Ni^{2+} on Al-doped goethite is much lower. Simply put, Al-doped goethite not only can change the bioavailability of phosphorus, but also has the capability to remediate heavy metals in contaminated water or soils.

Most previous studies about Al-doped goethite have mainly focused on the effects of Al doping on the structure of the resulting minerals (Schulze, 1984; Fazey et al., 1991; Schwertmann and Carlson, 1994; Pinney and Morgan, 2013a, 2013b; Wang et al., 2014). But the relationships between the changes of structural features and mineral properties remain poorly understood, e.g., whether there is any modification in the crystal morphology and the content of surface hydroxyl groups with increasing Al substitution, and whether and how these modifications would affect the adsorption of phosphorus on the mineral surfaces. Therefore in this study, to elucidate the underlying relationships between the adsorption behaviors of PO_4^{3-} and the properties of Al-doped goethite, a series of Al-doped goethite samples were synthesized based on previous reports, and characterized by several modern techniques, e.g., X-ray diffraction (XRD), Rietveld structure refinement, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and extended X-ray absorption fine structure (EXAFS) spectroscopy. Investigation into the characteristics of Al-doped goethite from the aspects of crystal habits and surface groups can provide further insights into the mineralogy and geochemical behaviors of iron oxides, as well as the transfer and fates of soil nutrients and environmental pollutants.

1. Materials and methods

1.1. Al-doped goethite synthesis

Pre-determined amounts of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ($\text{Al}/(\text{Al} + \text{Fe}) = 0\text{--}32\%$) were dissolved in 1 L deionized water bubbled with N_2 for 30 min to eliminate dissolved O_2 . After that, 180 mL NaHCO_3 solution was added dropwise at a rate of 30–40 mL/min. The mixture was stirred in air for 48 hr until the slurry color was ochre. To remove the amorphous component, 30 mL ammonium oxalate solution ($\text{pH} = 3.2$) was added into the slurry. The mixture was shaken in the dark for 4 hr, and the amounts of Al and Fe in the amorphous component were measured. Then NH_4HCO_3 solution was used to remove the remaining ammonium oxalate, and the suspension was washed several times in deionized water. The obtained samples were dried at 40°C . Finally, the samples were ground carefully in an agate mortar, passed through a 100 mesh screen, and kept in polyethylene plastic tubes at room temperature. The obtained samples were labeled as Goe, AlG4, AlG8, AlG12, AlG16, AlG20, AlG24, AlG28 and AlG32, respectively.

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