



Review

An overview of the role of goethite surfaces in the environment

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HIGHLIGHTS

- Overview the structure and physicochemical properties of goethite.
- Overview the role of goethite in adsorption of anions, cations, organic matter, etc.
- Overview the adsorption mechanism of goethite.
- Proposal of the possible applications of goethite.

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ABSTRACT

Goethite, one of the most thermodynamically stable iron oxides, has been extensively researched especially the structure (including surface structure), the adsorption capacity to anions, organic/organic acid (especially for the soil organic carbon) and cations in the natural environment and its potential application in environmental protection. For example, the adsorption of heavy metals by goethite can decrease the concentration of heavy metals in aqueous solution and immobilize; the adsorption to soil organic carbon can decrease the release of carbon and fix carbon. In this present overview, the possible physicochemical properties of the goethite surface contributing to the strong affinity of goethite to nutrients and contaminants in natural environment are reported. Moreover, these chemicals adsorbed by goethite were also summarized and the suggested adsorption mechanism for these adsorbates was elucidated, which will help us understand the role of goethite in natural environment and provide some information about goethite as an adsorbent. In addition, the feasibility of goethite used as catalyst carrier and the precursor of NZVI was proposed for removal of environmental pollution.

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Contents

1. Introduction	1
2. Surface properties of goethite	2
3. Adsorbent	3
3.1. For anions	3
3.2. For organic compounds and organic acids	4
3.3. For cations	4
3.4. For gases	6
4. Catalysts	6
5. Effect of Al substitution	7
6. Conclusions and summary	7
References	7

1. Introduction

Goethite (α -FeOOH) is a widespread soil mineral and a major component of many ores, sediments and soils and it is one of the most thermodynamically stable iron oxide (Cornell and Schwertmann,

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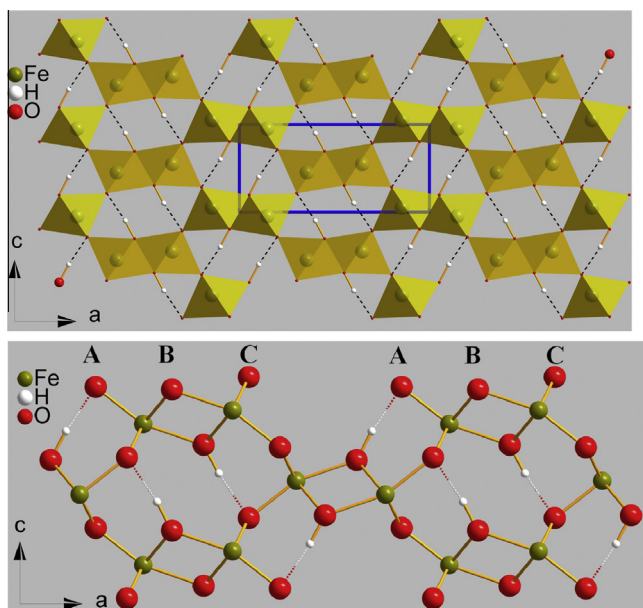
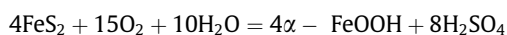
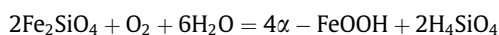


Fig. 1. (010) plane of goethite (top) polyhedral framework and (bottom) ball and stick model (Blue line represents unit cell and the dash line denotes the hydrogen bonding). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2003). Goethite can be found in both humid and semiarid regions and also appears as the weathering product of various iron-containing rocks (Kemp, 1985). The orthorhombic structure of goethite has been confirmed as hexagonally close-packed array of O^{2-} and OH^- anions with Fe^{3+} in the center of the octahedral (Cornell and Schwertmann, 2003). The two octahedrons compose double chains of octahedra formed by edge sharing, running parallel to the [001] direction. Fig. 1 shows these chains are linked to adjacent double chains by corner-sharing with one chain and the OH groups are linked to another O atom in a chain diagonally opposite.

Generally, goethite can be found in pedosphere, hydrosphere and biosphere, resulting from rock weathering. In terms of goethite, it can derive from olivine or pyrite due to complicated processes including physical, chemical and biological. As is written in the book (Schwertmann and Cornell, 2000), the general formation process can be described as followed.



The newly formed goethite has a low solubility and it is the most stable iron oxyhydroxide in nature. Generally, goethite formed from weathering is often poorly crystalline and rich in defects and impurities, which makes goethite has much good surface activity. Moreover, goethite displays nanometer sized particles in width and several microns in length for both naturally formed and the laboratory synthesized analog. Such sizes make goethite with a high specific surface area, varying from 10 to $132 \text{ m}^2 \text{ g}^{-1}$ (Atkinson et al., 1967; Strauss et al., 1997) depending on the transforming environment and the synthetic conditions. Therefore, the wide spread in nature and special physicochemical properties attracted many attentions on the study of the structure, surface physicochemical properties and adsorption capacity of goethite. As for the structure of goethite, the existence of bulk groups have been investigated widely using various techniques such as IR and TG/DTG (Russell et al., 1974; Schwertmann, 1984). In addition to this bulk groups, goethite still has a complicated surface structure especially the distribution of adsorbed water/hydroxyl group. In

recent years, several reports about the fine surface structure can be found using crystal truncation rod (CTR) or model means. Ghose et al. reported that the proposed interface stoichiometry is $(H_2O)-(H_2O)-OH_2-OH-Fe-O-O-Fe-R$, which indicates the existence of two layers of adsorbed water and two types of terminal hydroxyls, a hydroxo group and a aquo group (Ghose et al., 2010). The report of Boily (Boily, 2012) confirmed that interfacial water molecules adopted highly surface-specific configurations on (010), (100), (110), and (021) planes of goethite. Besides, water molecules generally had weaker hydrogen bonding strengths, as well as smaller self-diffusion coefficients, than their bulk liquid counterparts. Relevant reports on the surface functional groups ($Fe-O$, $Fe-OH$, $Fe-O-Fe$) calculated using density functional theory (DFT) or other models can be found in the literature (Boily et al., 2001; Villalobos et al., 2003; Rustad and Boily, 2010). All these physicochemical properties imply goethite has a great potential as an adsorbent or catalyst due to its large surface area and special surface active sites.

The widespread occurrence and special physicochemical properties determine the significant role of goethite in nature and in the man-made environment. In the past several decades, goethite has been documented playing a crucial role in regulating the mobility and transformation of species in various parts of the ecosystem and their transport between these parts. It involves the uptake of plant nutrients from soil, the transportation of pesticides and other contaminants from soil to the aquatic system, and the purification of carbon-, sulfur- and nitrogen-containing gases (Russell et al., 1975; Kaneko and Inouye, 1981; Ishiwaka and Inouye, 1983; Baltrusaitis et al., 2007; Simonetti et al., 2007). In addition, goethite has been demonstrated to be a natural catalyst for catalytic oxidation of organic compounds in soil or wastewater (Lin and Gurol, 1996; Lu, 2000).

Under this research background, we have summarized the structure and promising values of goethite in the environment, as adsorbent for nutrients and as an adsorbent or/and catalyst for contaminants especially for organic substances and cations. As an important constituent of soil and sediments, it is essential to have a comprehensive understanding for its structure, especially for the surface functional groups, the physicochemical properties and its potential applications. As an abundant and cheap natural material with a large specific surface area and high surface reactivity, it is important and worthwhile to understand its potential applications in environmental protection. Nowadays, environmental pollutions are displaying a development of multi-dimension namely from ground surface to subsurface and air with the rapid economic development. Therefore, this present work reviews the research of goethite as an adsorbent or/and catalyst and reveals the implied significance to the environment. Meanwhile, the further possible applications as a precursor of multi-porous iron oxides or nZVI, which can be used in environment protection, are also suggested.

2. Surface properties of goethite

As is well known, goethite is isostructural with diaspore ($\alpha\text{-AlOOH}$). However, it is the surface structure not the bulk structure that makes this kind of iron oxyhydroxide sensitive to the environment. From 1930s to now, several significant reports on the study of the structure of goethite can be found using a range of different methods (Goldsztaub, 1932; Sampson, 1969; Gast et al., 1974; Busca et al., 1978; Rochester and Topham, 1979b; Schwertmann, 1984; Boily et al., 2001; Villalobos et al., 2003; Ghose et al., 2010; Rustad and Boily, 2010; Han et al., 2011; Boily, 2012). Goldsztaub solved the crystal structure of goethite in 1932 and then Sampson reported the lattice parameters of a natural single crystal and synthetic goethite in 1969 (Goldsztaub, 1932;

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