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# An overview of the role of goethite surfaces in the environment

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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.

**Keywords:** goethite, adsorption, catalysis, environmental remediation

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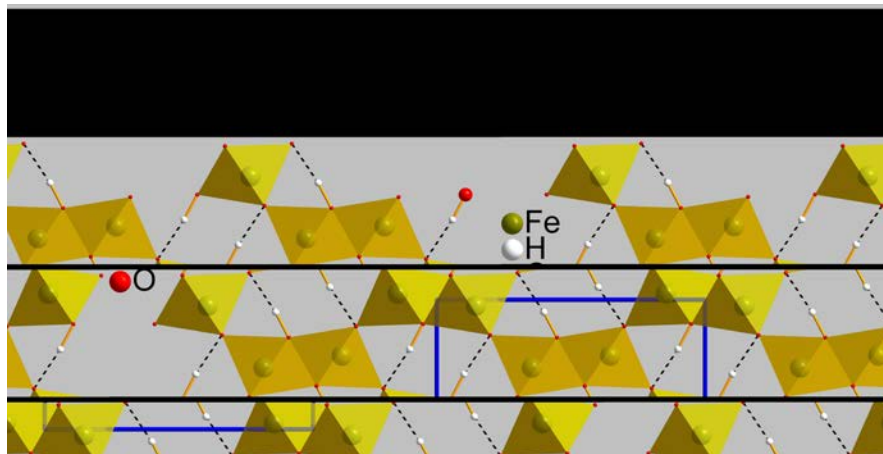
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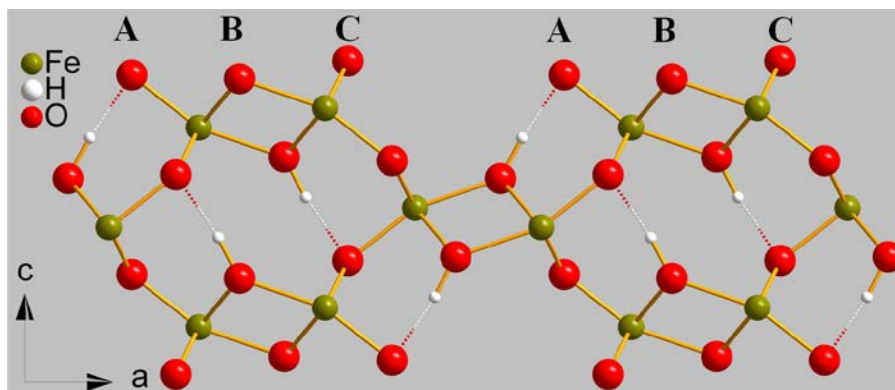
28 **1. Introduction**

29 Goethite ( $\alpha$ -FeOOH) is a widespread soil mineral and a major component of many ores,  
30 sediments and soils and it is one of the most thermodynamically stable iron oxide (Cornell  
31 and Schwertmann, 2003). Goethite can be found in both humid and semiarid regions and also  
32 appears as the weathering product of various iron-containing rocks (Kemp, 1985). The  
33 orthorhombic structure of goethite has been confirmed as hexagonally close-packed array of  
34  $O^{2-}$  and  $OH^-$  anions with  $Fe^{3+}$  in the center of the octahedral (Cornell and Schwertmann,  
35 2003). The two octahedrons compose double chains of octahedra formed by edge sharing,  
36 running parallel to the [001] direction. Fig. 1 shows these chains are linked to adjacent double  
37 chains by corner-sharing with one chain and the OH groups are linked to another O atom in a  
38 chain diagonally opposite.

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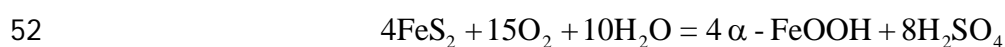
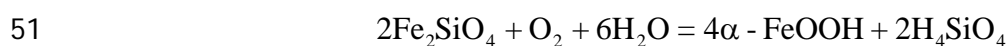


41  
42



44 Fig. 1. (010) plane of goethite (top) polyhedral framework and (bottom) ball and stick model  
45 (Blue line represents unit cell and the dash line denotes the hydrogen bonding).

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



53 The newly formed goethite has a low solubility and it is the most stable iron oxyhydroxide in  
54 nature. Generally, goethite formed from weathering is often poorly crystalline and rich in  
55 defects and impurities, which makes goethite has much good surface activity. Moreover,  
56 goethite displays nanometer sized particles in width and several microns in length for both  
57 naturally formed and the laboratory synthesized analog. Such sizes make goethite with a high  
58 specific surface area, varying from 10-132  $\text{m}^2\cdot\text{g}^{-1}$  (Atkinson et al., 1967; Strauss et al., 1997)  
59 depending on the transforming environment and the synthetic conditions. Therefore, the wide  
60 spread in nature and special physicochemical properties attracted many attentions on the  
61 study of the structure, surface physiochemical properties and adsorption capacity of goethite.  
62 As for the structure of goethite, the existence of bulk groups have been investigated widely  
63 using various techniques such as IR and TG/DTG (Russell et al., 1974; Schwertmann, 1984).  
64 In addition to this bulk groups, goethite still has a complicated surface structure especially the  
65 distribution of adsorbed water/hydroxyl group. In recent years, several reports about the fine  
66 surface structure can be found using crystal truncation rod (CTR) or model means. Ghose et  
67 al. reported that the proposed interface stoichiometry is  $(\text{H}_2\text{O})\text{-}(\text{H}_2\text{O})\text{-OH}_2\text{-OH-Fe-O-O-Fe-R}$ ,  
68 which indicates the existence of two layers of absorbed water and two types of terminal  
69 hydroxyls, a hydroxo group and a aquo group (Ghose et al., 2010). The report of Boily (Boily,  
70 2012) confirmed that interfacial water molecules adopted highly surface-specific  
71 configurations on (010), (100), (110), and (021) planes of goethite. Besides, water molecules  
72 generally had weaker hydrogen bonding strengths, as well as smaller self-diffusion  
73 coefficients, than their bulk liquid counterparts. Relevant reports on the surface functional  
74 groups (Fe-O, Fe-OH, Fe-O-Fe) calculated using density functional theory (DFT) or other

75 models can be found in the literature (Boily et al., 2001; Villalobos et al., 2003; Rustad and  
76 Boily, 2010). All these physicochemical properties imply goethite has a great potential as an  
77 adsorbent or catalyst due to its large surface area and special surface active sites.

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

88

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

102

## 103 **2. Surface properties of goethite**

104 As is well known, goethite is isostructural with diaspore ( $\alpha$ -AlOOH). However, it is the  
105 surface structure not the bulk structure that makes this kind of iron oxyhydroxide sensitive to  
106 the environment. From 1930s to now, several significant reports on the study of the structure

107 of goethite can be found using a range of different methods (Goldsztaub, 1932; Sampson,  
108 1969; Gast et al., 1974; Busca et al., 1978; Rochester and Topham, 1979b; Schwertmann,  
109 1984; Boily et al., 2001; Villalobos et al., 2003; Ghose et al., 2010; Rustad and Boily, 2010;  
110 Han et al., 2011; Boily, 2012) . Goldsztaub solved the crystal structure of goethite in 1932  
111 and then Sampson reported the lattice parameters of a natural single crystal and synthetic  
112 goethite in 1969 (Goldsztaub, 1932; Sampson, 1969). Russell et al. investigated the types of  
113 goethite surface hydroxyl groups by characterizing goethite and phosphated goethite (Russell  
114 et al., 1974), which proves goethite has three types of surface hydroxyl groups as is shown in  
115 Fig. 1. More details about the surface hydroxyl groups were presented in the literature  
116 (Rochester and Topham, 1979b). DFT has been used for calculations of the vibrational  
117 frequencies of OH groups of an idealized goethite (110) surface (Rustad and Boily, 2010).  
118 Later, surface adsorbed water even the number of its layers was investigated. Robert et al.  
119 studied the interaction of water with goethite compared with other amorphous ferric oxides  
120 (Gast et al., 1974) . The results indicated that the last traces of physically adsorbed water  
121 were removed from the amorphous ferric oxides by outgassing at 25 °C, however, still  
122 retained approximately a monolayer of physically adsorbed water on goethite under the same  
123 conditions. This monolayer of water on goethite was proposed presumably hydrogen-bonded  
124 at least in part with the structural hydroxyls. Ghose et al. reported that the proposed interface  
125 stoichiometry is (H<sub>2</sub>O)-(H<sub>2</sub>O)-OH<sub>2</sub>-OH-Fe-O-O-Fe-R, which indicated the existence of two  
126 layers of absorbed water and two types of terminal hydroxyls, a hydroxy group and an aquo  
127 group (Ghose et al., 2010). The bulk groups and the complicated surface functional groups  
128 results in the potential of strong affinity and high reactivity. The surface hydroxyl groups of  
129 goethite can promote more ·OH generation in the presence of ozone than that of β-FeOOH, γ-  
130 FeOOH and γ-*AlOOH* (Zhang et al., 2008). Furthermore, Liu et al. (Liu et al., 2013)  
131 postulated that not only the specific surface areas, but also the numbers of hydroxyl groups  
132 (namely effective adsorption sites) on goethite influences the adsorption capacity of goethite  
133 to phosphate.

134

### 135 **3. Adsorbent**

136 As an adsorbent, surface site density is an important factor determining the adsorption  
137 capacity of material. Villalobos et al. (Villalobos et al., 2003) investigated the surface site  
138 density of goethite by adsorption of proton and carbonate, indicating an inverse relationship  
139 between sorption capacity for protons and carbonate ions and specific surface area of goethite

140 for three synthetic goethite preparations. An explanation for this is the variability of the  
141 surface site density. Extra speculation was presumed depending on the different preparation  
142 methods which lead to different predominant faces for goethite. In addition, goethite usually  
143 presents large specific surface area as is mentioned above. All the confirmed information on  
144 the properties of goethite displays it possesses underlying predomination on physical,  
145 chemical and even biological reaction.

### 146 **3.1 For anions**

147 Table 1 lists the researched anions and relevant references in part, although it is  
148 confirmed there are more than 100 papers can be found on the research of inorganic anion  
149 adsorption on goethite. It mainly involves the effect of goethite on their transport,  
150 transformation and bioavailability. Furthermore, the effect of pH, ionic strength, exotic ions  
151 and temperature were also investigated. In these researches, some of the reported research  
152 mentioned the application of goethite for the treatment of environmental pollutants. The  
153 extent of goethite adsorption and the in-depth study of adsorption mechanisms substantially  
154 improved the understanding of the role of goethite in the environment.

155

156 According to the reported results and adsorption theory, the main adsorption  
157 mechanisms contain both non-specific adsorption and specific adsorption (ligand exchange).  
158 Hingston et al. illuminated both adsorption mechanisms in detail (Hingston et al., 1972). In  
159 aqueous suspension, the terminal iron atoms on the surface will complete their coordination  
160 shells with OH<sup>-</sup> and water molecular. When the ions in solution do not have specific affinity  
161 for the iron atoms of the surface, the surface will adsorb H<sup>+</sup> and OH<sup>-</sup>. In contrast, specific  
162 adsorption means replacement of hydroxyl groups by the adsorbing ligand. Specific  
163 adsorption frequently occurs for anions, in which phosphate and arsenate were most widely  
164 researched. At the earliest, Atkinson et al. proposed that phosphate replaces type A hydroxyl  
165 group and forms bridges between adjacent Fe<sup>3+</sup> (Atkinson et al., 1972). Afterward, many  
166 reports can be found on the adsorption model of phosphate on the surface of goethite using  
167 various methods (Tejedor-Tejedor and Anderson, 1990; Torrent et al., 1990; Torrent et al.,  
168 1992; Geelhoed et al., 1997b; Strauss et al., 1997; Nowack and Stone, 1999a; Li and  
169 Stanforth, 2000; Ler and Stanforth, 2003; Lin et al., 2004; Chitrakar et al., 2006). Adsorption  
170 of phosphate on goethite mainly involves a ligand exchange mechanism which is similar to  
171 the adsorption of arsenate. Tejedor-Tejedor et al. studied the mechanism of phosphate  
172 adsorption on goethite using in-situ CIR-FTIR, which provided evidence for the formation of

173 three different type of complexes, protonated and nonprotonated bridging bidentate as well as  
174 a nonprotonated monodentate, between orthophosphate ions and surface  $\text{Fe}^{3+}$  of  $\alpha\text{-FeOOH}$   
175 particles in aqueous suspensions (Tejedor-Tejedor and Anderson, 1990). Hiemstra et al  
176 modeled phosphate adsorption on goethite with the CD-MUSIC using comparable  
177 experimental data, concluding the existence of monodentate species at very low surface  
178 loading. In fact, many researchers presented different ligand models considerably dependent  
179 on the surface coverage and solution pH. Generally, the bidentate surface complex is the most  
180 abundant for the adsorption of phosphate on goethite. Recently, the other mechanism of  
181 surface precipitation was reported by Josasson et al. (Jonasson et al., 1988), Li et al. (Li and  
182 Stanforth, 2000), and Ler et al. (Ler and Stanforth, 2003). Li et al. (Li and Stanforth, 2000)  
183 also investigated the distinction between the adsorption and surface precipitation of  
184 phosphate on goethite, which supposing the onset of surface precipitation occurs well before  
185 monolayer coverage, particularly at high pH values. Later, Ler et al. (Ler and Stanforth, 2003)  
186 confirmed the existence of surface precipitation of phosphate on goethite by monitoring the  
187 variation of  $\zeta$ -potential of the phosphated goethite. The adsorption capacity of goethite to  
188 phosphate reached 10 mg-P/g-goethite (Chitrakar et al., 2006). In general, it is slow for the  
189 diffusion of phosphate adsorption between domains and for desorption of phosphate from  
190 goethite (Torrent et al., 1990; Strauss et al., 1997). The slow and even irreversible desorption  
191 for phosphate are attributed to slow rediffusion out of micropores, to the formation of inert,  
192 binuclear surface complexes, and to the affinity making goethite crystals into aggregates  
193 (Atkinson et al., 1972; Anderson et al., 1985).

194

195 The adsorption of chromate and arsenate/arsenite is also widely investigated due to their  
196 toxicity to humans (Abdel-Samad and Watson, 1997; Fendorf et al., 1997; Manning et al.,  
197 1998; Gao and Mucci, 2001; Rietra et al., 2001a; Gräfe et al., 2004; Lakshmipathiraj et al.,  
198 2006; Luengo et al., 2007; Zhang et al., 2007; Grafe et al., 2008; Amstaetter et al., 2009;  
199 Dimirkou et al., 2009; Catalano et al., 2011; Das et al., 2011; Guo et al., 2013a; Wang et al.,  
200 2013). The chromium XPS signal indicated that initially a small amount of chromium adsorbs  
201 in the  $\text{Cr}^{3+}$  oxidation state via a redox reaction, but that the large majority of chromium  
202 remains in the  $\text{Cr}^{6+}$  oxidation state (Abdel-Samad and Watson, 1997). As for the adsorption  
203 model, Fendorf et al. (Fendorf et al., 1997) gave a detailed account that chromate or arsenate  
204 retention on goethite is due to a monodentate complex at very low coverage, both the  
205 monodentate and bidentate complexes at intermediate coverage, and predominantly the



206 bidentate complexes at very high coverage. It indicates that the adsorption model for both  
 207 chromate and arsenate is strongly dependent on the surface coverage. In case of the effect of  
 208 pH, it is different for arsenate and arsenite. Arsenite adsorption increases with increasing pH,  
 209 as compared to low pH which improves the adsorption of arsenate. Lakshmipathiraj et al.  
 210 (Lakshmipathiraj et al., 2006) reported the adsorption amount of goethite to arsenate  
 211 decreased from 4.7 to 1.1 mg·g<sup>-1</sup> as the pH increased from 5 to 8. Additionally, competitive  
 212 adsorption on goethite also has been the subject of much research because the competitive  
 213 adsorption results at least to some extent, affects the bioavailability of nutrients and  
 214 immobilization of toxic chemicals, such as the competitive adsorption between phosphate and  
 215 sulfate/arsenate (Geelhoed et al., 1997b; Gao and Mucci, 2003).

216

217 The adsorption of goethite for other anions was also studied including silicate, chloride,  
 218 fluoride and sulphate, and others, which reveals the universality of goethite adsorption. The  
 219 adsorption capacity and strong affinity of goethite to these adsorbates confirmed the  
 220 significance of goethite at least on their transport in environments.

221

222

223

**Table 1. List for inorganic anion adsorption on goethite**

Inorganic anions	References
Silicate	(Hingston et al., 1967)
Selenite /Selenate	(Hingston et al., 1968; Manceau and Charlet, 1994; Saeki and Matsumoto, 1998; Rietra et al., 2001a; Das et al., 2013)
Phosphate	(Atkinson et al., 1972; Parfitt et al., 1975; Sigg and Stumm, 1981; Geelhoed et al., 1997a; Geelhoed et al., 1997b; Strauss et al., 1997; Venema et al., 1997; Geelhoed et al., 1998; Barrow, 1999; Nowack and Stone, 1999b; Li and Stanforth, 2000; Gao and Mucci, 2001; Dideriksen and Stipp, 2003; Gao and Mucci, 2003; Ler and Stanforth, 2003; Gimsing et al., 2004; Lin et al., 2004; Wang and Xing, 2004; Antelo et al., 2005; Chitrakar et al.,

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	2006; Nowack and Stone, 2006; Cheng et al., 2007; Luengo et al., 2007; Rahnemaie et al., 2007; Kim et al., 2011)
Fluoride	(Hingston et al., 1972; Sigg and Stumm, 1981; Hiemstra and Van Riemsdijk, 2000)
Chloride	(Hingston et al., 1972)
Sulphate	(Hingston et al., 1972; Sigg and Stumm, 1981; Geelhoed et al., 1997a; Geelhoed et al., 1997b; Peak et al., 1999; Rietra et al., 1999; Rietra et al., 2001a; Juang and Wu, 2002; Beattie et al., 2008)
Silicate	(Sigg and Stumm, 1981; Kersten and Vlasova, 2009)
Arsenate/Arsenite/Arsenic	(Grossl and Sparks, 1995; Fendorf et al., 1997; Matis et al., 1997; Manning et al., 1998; Gao and Mucci, 2001; Liu et al., 2001; Waltham and Eick, 2002; Gao and Mucci, 2003; Gräfe et al., 2004; Antelo et al., 2005; Gräfe and Sparks, 2005; Dixit and Hering, 2006; Lakshmipathiraj et al., 2006; Giménez et al., 2007; Luengo et al., 2007; Sahai et al., 2007; Stachowicz et al., 2007; Grafe et al., 2008; Luxton et al., 2008; Stachowicz et al., 2008; Asta et al., 2009; Dimirkou et al., 2009; Hartzog et al., 2009; Catalano et al., 2011; Mamindy-Pajany et al., 2011; Wang et al., 2013)
Chromate	(Abdel-Samad and Watson, 1997; Fendorf et al., 1997)
Carbonate	(Hiemstra et al., 2004; Rahnemaie et al., 2007)

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224

### 225 **3.2 For organic compounds and organic acids**

226

227 Table 2 displays the list of goethite adsorption of organic compound and organic acid.

228 The adsorption/desorption behavior of water-soluble organics on goethite has been

229 researched for several decades due to its significance on the transport and transformation of

230 organic compounds in soil and groundwater as well as the use of surfactants in the flotation  
231 of minerals (Tejedor-Tejedor et al., 1992). Therefore, this overview summarizes the  
232 adsorption behavior of fulvic acid, humic acid and glycophosphate, etc. on goethite.  
233 Generally, adsorption of organic on goethite is usually dominated by electrostatic effects,  
234 although ligand exchange and hydrogen bonding may also be involved (Cornell and  
235 Schwertmann, 2003).

236

237       Totally, organic compound adsorption on goethite usually depends on the solution pH,  
238 chemical composition of organic matter, ionic strength, composition of cation in solution. As  
239 for pH, solution  $\text{pH} < \text{PZC}$  will benefit the increase of adsorption capacity, and vice versa.  
240 Example is the decrease of the adsorption of lactate, tartrate and citrate with increasing pH  
241 (Cornell and Schindler, 1980). Moreover, low pH favors the inner-sphere surface complex at  
242 least for oxalate and malonate (Persson and Axe, 2005). Fu et al. (Fu and Quan, 2006) found  
243 the inner-sphere surface complex of fulvic on goethite which is consistent with the previously  
244 reported (Filius et al., 2000) which revealed a inner-sphere in low pH in contrast a out-sphere  
245 in high pH. In contrast, acetate, benzoate, and cyclohexanecarboxylate got a out-sphere  
246 surface complex as can be seen in the report (Norén and Persson, 2007). To the best of our  
247 knowledge, the adsorption model for organic also has a little difference, which has been  
248 widely researched using diffuse reflectance infrared Fourier transform, attenuated total  
249 reflectance Fourier transform infrared, X-ray photoelectron spectroscopy, atomic force  
250 microscopy, Extended X-Ray Adsorption Fine Structure, etc. Barja et al. (Barja and dos  
251 Santos Afonso, 2004) reported two predominating complexes where the phosphonate group  
252 in glyphosate or aminomethylphosphonic acid (a product of biodegradation of glyphosate )  
253 bonds monodentately or bridges bidentately to the surface of iron oxide in an inner sphere  
254 mode, while the carboxylate and amino group are noncoordinated to the surface. As for the  
255 adsorption model, different authors had different results for the same organic. Using citrate as  
256 an example, Cornell et al. (Cornell and Schindler, 1980) supported a tridentate complex  
257 according to the results of IR; however, Filius et al. (Filius et al., 1997) supported a bidentate  
258 complex based on their modeling work. Besides, organic acids, such as humic acid, still can  
259 improve the adsorption capacity of goethite for other organic compounds. Iglesias and  
260 coauthors (Iglesias et al., 2010) found the adsorption amount of paraquat dramatically  
261 increased from 0.03 to 0.24  $\mu\text{mol}\cdot(\text{m}^2)^{-1}$  as goethite was replaced by humic-coated goethite  
262 which was confirmed by Brigante et al. (Brigante et al., 2010) and later proposed the

263 adsorption mechanism. The same authors made another similar conclusion that humic-coated  
264 goethite favored the adsorption of MCPA ((4-chloro-2-methylphenoxy)-acetic acid, a kind of  
265 acid pesticide) at all concentrations of this pesticide. In addition, fulvic acid increased the  
266 adsorption of cadmium on goethite at low pH(<7) and decreased that at high pH(>7), and  
267 improved the adsorption of mercury within the whole pH interval (Bäckström et al., 2003).  
268 This adsorption, especially for natural organic matter (NOM), has another important  
269 significance in affecting the global carbon balance by protecting NOM from enzymatic  
270 oxidation to CO<sub>2</sub> in soil and sediments. Goethite not only influences the transport of these  
271 organic/organic acid listed in the table below, but also passively affects their transformation  
272 by surface complexation.

273

274

**Table 2. List for organic compound and organic acid adsorption on goethite**

Organic/organic acid	References
Acetate	(Sigg and Stumm, 1981; Norén and Persson, 2007)
Benzoic/benzoate	(Tejedor-Tejedor et al., 1992; Norén and Persson, 2007)
Phenolic	(Tejedor-Tejedor et al., 1992)
Citrate	(Geelhoed et al., 1998; Barrow, 1999; Lindegren et al., 2009)
Methylphosphonic Acid	(Barja et al., 1999)
Malonate	(Filius et al., 1999; Persson and Axe, 2005; Axe et al., 2006)
Phosphonate	(Nowack and Stone, 1999a; Mustafa et al., 2006)
Benzenecarboxylate/benzencarboxylic	(Boily et al., 2000; Lindegren and Persson, 2010)
Fulvic acid	(Filius et al., 2000; Weng et al., 2005; Fu and Quan, 2006; Weng et al., 2006b)
Humic acid	(Saito et al., 2003; Weng et al., 2006a; Kang and Xing, 2008)
Anthracene	(Angove et al., 2002)
Glyphosate	(Dideriksen and Stipp, 2003; Sheals et al., 2003; Barja and dos Santos Afonso, 2004; Gimsing et al., 2004; Jonsson et al., 2008)
Aminomethylphosphonic Acid	(Barja and dos Santos Afonso, 2004)
Oxalate	(Persson and Axe, 2005; Axe et al., 2006)
Mellitic acid	(Angove et al., 2006)
Bisphenol A (BPA)	(Shareef et al., 2006)
17 $\alpha$ -ethynylestradiol (EE2)	(Shareef et al., 2006)
Estrone (E1)	(Shareef et al., 2006)
Molybdate	(Xu et al., 2006a, b)
Tetrathiomolybdate	(Xu et al., 2006a)

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1-hydroxy-2-naphthoic acid	(Hanna and Carteret, 2007)
Silicic acid	(Hiemstra et al., 2007)
Fipronil	(Miranda Masutti and Mermut, 2007)
Ciprofloxacin	(Trivedi and Vasudevan, 2007; Carrasquillo et al., 2008)
p-Arsanilic Acid	(Depalma et al., 2008)
Polycyclic aromatic hydrocarbon	(Tunega et al., 2009)
Paraquat	(Brigante et al., 2010)
2-Ketogluconate	(Journey et al., 2010)
Glucose	(Olsson et al., 2011)
Methylene Blue	(Nassar and Ringsred, 2012)
Catechol	(Yang et al., 2012)
Tylosin	(Guo et al., 2013b)
Sulfamethazine	(Guo et al., 2013b)

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276

277 **3.3 For cations**

278

279 Table lists the cations adsorption on goethite. On the whole, the possibility of adsorption  
280 on goethite to these mentioned metal ions have been documented and the strength of some of  
281 them on goethite decreases in the order: Cu>Pb>Zn>Cd>Co>Ni>Mn (Grimme, 1968; Gerth  
282 and Brümmer, 1983). Cation adsorption may be suppressed as the ionic strength increases  
283 and generally this is considered as an out-sphere adsorption (R-O-M, M presents the cations,  
284 R denotes the bulk), although it may be also the result of ion pairing in solution. Moreover,  
285 the affinity of cations for goethite is strongly dependent on the temperature of the system and  
286 on the time allowed for adsorption (Bruemmer et al., 1988). It was proposed that the process  
287 involved rapid adsorption on the external surface surfaces of crystals followed by slow  
288 diffusion into the internal sites, possibly along the domain boundaries, with finally,  
289 adsorption on internal sites (Cornell and Schwertmann, 2003). Hu et al. (Hu et al., 2010)  
290 investigated the effect of adsorption temperature, pH and ionic strength on the adsorption of  
291 radionickel on goethite. The results showed that the adsorption of Ni<sup>2+</sup> was strongly  
292 dependent on the pH, ionic strength and temperature, indicating high temperature and high  
293 pH, low ionic strength favored the increase of Ni<sup>2+</sup> adsorption. Still, the adsorption of Ni<sup>2+</sup>  
294 was dominated by out-sphere surface complex at low pH in contrast to the inner-sphere at

295 high pH. Desorption is unavoidable after adsorption, which depends on the types of metal and  
 296 surface complexes formed. For example,  $Pb^{2+}$  can desorb completely from goethite whereas  
 297 Cu, Zn, Cd, Ni and Co displayed hysteresis and Al as well as Np showed a extremely slow  
 298 desorption (Padmanabham, 1983a, b; Lövgren et al., 1990; Tinnacher et al., 2011). The slow  
 299 desorption should be ascribed to the inner-sphere surface complex and high affinity between  
 300 metal and goethite. Besides, ternary adsorption, usually formed in the presence of anions and  
 301 organic acids, also devotes a lot for the slow desorption of adsorbed metal ions. Fulvic acid  
 302 can improve the adsorption of mercury and cadmium, citric acid and tartaric acid (at low  
 303 concentration < 1.0 mM) increased the adsorption of  $Cd^{2+}$  onto goethite (Huang et al., 2010).  
 304 Fulvic acid and phosphate enhanced the adsorption of  $Th^{4+}$  was also confirmed (Yan et al.,  
 305 2011). Perelomov et al. revealed the final  $Cu^{2+}$  adsorbed/ $Pb^{2+}$  adsorbed molar ratio was 1.58  
 306 in the absence of oxalic acid but greater than 2 in the presence of the organic ligand.  
 307 Furthermore, most of previous investigations have suggested that humic substance promoted  
 308 the adsorption of metal ions at low pH, such as the report of Ali et al. (Ali and Dzombak,  
 309 1996). The increase of adsorption was attributed to the adsorption of anions/organic acid on  
 310 the mineral surface followed by the interaction of heavy metal ions with modified surface and  
 311 generally formed ternary adsorption. Therefore, goethite is playing an important role in the  
 312 water/particles system on the adsorption/desorption of metal ions, which is also affected in  
 313 the presence/absence of natural organic matter, such as humic acid and fulvic acid.

314

315 **Table 3. List for cation adsorption on goethite**

Cation	References
$Cd^{2+}$	(Forbes et al., 1976; Angove et al., 1999; Buerge-Weirich et al., 2002; Wang and Xing, 2002; Bäckström et al., 2003; Buerge-Weirich et al., 2003; Mustafa et al., 2004; Wang and Xing, 2004; Mustafa et al., 2006; Dimirkou et al., 2009; Swedlund et al., 2009)
$Co^{2+}$	(Forbes et al., 1976; Angove et al., 1999)
$Cu^{2+}$	(Forbes et al., 1976; Grossl and Sparks, 1995; Kooner et al., 1995; Ali and Dzombak, 1996; Rodda et al., 1996; Robertson and Leckie, 1998; Buerge-Weirich et al., 2002; Juang and Wu, 2002; Buerge-Weirich et al., 2003; Sheals et al., 2003; Lin et al., 2004; Huerta-Diaz, 2006; Jonsson et al., 2006; Grafe et al.,

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	2008; Weng et al., 2008; Swedlund et al., 2009; Perelomov et al., 2011)
Pb <sup>2+</sup>	(Forbes et al., 1976; Kooner et al., 1995; Abdel-Samad and Watson, 1998; Kraemer et al., 1999; Kovačević et al., 2000; Ostergren et al., 2000a; Ostergren et al., 2000b; Villalobos et al., 2001; Glover et al., 2002; Wu et al., 2003; Orsetti et al., 2006; Garman et al., 2007; Swedlund et al., 2009; Perelomov et al., 2011)
Zn <sup>2+</sup>	(Forbes et al., 1976; Kooner et al., 1995; Kosmulski et al., 2003; Gräfe and Sparks, 2005; Xu et al., 2006c; Wang et al., 2008; Perelomov et al., 2011)
Ca <sup>2+</sup>	(Ali and Dzombak, 1996; Rietra et al., 2001b; Kosmulski et al., 2003; Weng et al., 2005; Weng et al., 2008)
Cd <sup>2+</sup>	(Davis and Upadhyaya, 1996; Venema et al., 1996; Collins et al., 1999a; Glover et al., 2002; Granados-Correa et al., 2011)
Cr <sup>6+</sup>	(Villalobos et al., 2001)
Ni <sup>2+</sup>	(Buerge-Weirich et al., 2002; Buerge-Weirich et al., 2003; Xu et al., 2006c; Marcussen et al., 2009)
Hg <sup>2+</sup>	(Collins et al., 1999b; Bäckström et al., 2003)
Sr <sup>2+</sup>	(Sahai et al., 2000)
U <sup>6+</sup>	(Giammar and Hering, 2001; Villalobos et al., 2001; Missana et al., 2003; Cheng et al., 2004; Cheng et al., 2007; Sherman et al., 2008; Guo et al., 2009; Yusan and Erenturk, 2011; Singh et al., 2012)
V <sup>5+</sup>	(Peacock and Sherman, 2004)
Sb <sup>3+</sup> /Sb <sup>5+</sup>	(Leuz et al., 2006; Watkins et al., 2006; Martínez - Lladó et al., 2008)
Ga <sup>3+</sup>	(Persson et al., 2006)
Ge <sup>4+</sup>	(Pokrovsky et al., 2006)
Se <sup>4+</sup> /Se <sup>6+</sup>	(Rovira et al., 2008)
Np <sup>5+</sup>	(Tinnacher et al., 2011)
Th <sup>4+</sup>	(Yan et al., 2011)
Nd <sup>3+</sup>	(Armstrong and Wood, 2012)

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### 317 **3.4 For gases**

318         Goethite was seldom used as a gas adsorbent. On the other hand, various gases were  
319 often utilized as probe molecules and provide information about the surface properties, such  
320 as surface acid-base nature and surface adsorption sites. Russell et al. (Russell et al., 1975)  
321 reported the CO<sub>2</sub> is strongly adsorbed as CO<sub>3</sub><sup>2-</sup> on moist goethite surface, but as both CO<sub>3</sub><sup>2-</sup>  
322 and HCO<sub>3</sub><sup>-</sup> on dry surfaces. The adsorbed carbonate played a role in redistributing surface  
323 charge and similar role was proposed to extent to other anions such as phosphate. Afterward,  
324 infrared spectra were recorded of pyridine, acetic acid, nitric acid and trimethylchlorosilane  
325 adsorbed on the surface of goethite, which confirmed the relationship between the adsorption  
326 characteristic and the surface Lewis acid sites of goethite (Rochester and Topham, 1979a).  
327 Furthermore, NO was demonstrated to be adsorbed more strongly than SO<sub>2</sub> and CO<sub>2</sub> and NO  
328 can displace previously adsorbed SO<sub>2</sub> and CO<sub>2</sub> from the surface of goethite (Ishiwaka and  
329 Inouye, 1983). The adsorption of SO<sub>2</sub> and NO on the surface of the goethite increased the  
330 electrical conductivity which accelerated atmospheric corrosion of steel (Kaneko and Inouye,  
331 1981; Kaneko and Matsumoto, 1989; Baltrusaitis et al., 2007). The bright side is the potential  
332 application as a catalyst or catalyst carrier for selective catalytic reduction (SCR) to be  
333 determined in future, which is being investigated by our research group. Recently, Simonetti  
334 et al. investigated the electronic structure of S and H<sub>2</sub>S adsorbed on the goethite (110) surface  
335 by AESD-MO cluster calculations (Simonetti et al., 2006; Simonetti et al., 2007). The results  
336 showed that S-H<sub>(goethite)</sub> is the major interaction for S and H<sub>2</sub>S, indicating hydrogen bonding  
337 contributed the interaction between S and H<sub>2</sub>S and goethite. Although goethite has not been  
338 researched as adsorbent or catalyst for sulfide at present, it is presumed this will attract much  
339 attention on desulfurization and denitrification in industries due to goethite affinity to N-  
340 containing and S-containing gases. The significance of goethite in the environment still  
341 embodies the immobilization of dissolved goethite to generated CO<sub>2</sub>. Yao et al. (Yao et al.,  
342 2013) investigated the effect of goethite on the release of methane in the anaerobic  
343 biochemical system consisted of dissimilar iron-reducing bacteria and methane-producing  
344 bacteria. The results indicated that the maximum cumulative production of methane was  
345 brought forward by 60 to 78 d in the presence of goethite and CO<sub>2</sub> was decreased by 30 to  
346 67% compared with that without goethite.

347

### 348 **4. Catalysts**

349 Except for the adsorption of anions, organics and organic acid, cations and gases,  
350 goethite still decomposes or catalytic decomposition of some contaminants in the absence and  
351 presence of hydrogen peroxide and/or UV radiation. Recently, Han et al. first reported that  
352 aqueous goethite can generate singlet oxygen and hydroxyl radical under room light and  
353 aeration conditions investigated using spin-trapping electron paramagnetic resonance and  
354 H<sub>2</sub>O<sub>2</sub> can improve the generation of both reactive species (Han et al., 2011). Table 4 lists the  
355 references on the application of goethite as a catalyst. The main mechanism for catalytic  
356 reactions involved the generation of hydroxyl radicals both directly or indirectly. Like the  
357 adsorption of goethite to organics, the catalysis behavior is also strongly dependent on the  
358 solution pH. As a catalyst, goethite was seldom researched before the 21th century.  
359 Hydroquinone can be converted into quinone in the presence of finely divided goethite in  
360 slightly acid solutions (Shindo and Huang, 1984). Cunningham et al. (Cunningham et al.,  
361 1988) reported benzoate, oxalate, and succinate adsorbed goethite in slightly acid solution  
362 were degraded under in the presence of UV and revealed the reaction mechanism by  
363 detecting the products of Fe<sup>2+</sup> and ·OH. In the recent decade, increasing attention was paid to  
364 this kind of natural phenomenon and potential environmental application related to goethite  
365 due to its special surface properties, such as large surface area and high surface hydroxyl  
366 content. Muruganandham et al. (Muruganandham and Wu, 2007) investigated the  
367 decomposition of dissolved ozone in the presence of granular goethite to reduce the residual  
368 ozone in treated water and the decomposition of ozone increased from 53.2 to 98% as the  
369 goethite loading increased from 2 to 30 g·L<sup>-1</sup>. The results indicated granular goethite is a  
370 promising catalyst for the decomposition of ozone in aqueous medium. Oxalate and salicylate  
371 have a competitive adsorption on goethite, however, the existence of oxalate improved the  
372 photodegradation of salicylate by reacting with goethite producing OH radicals (Krýsa et al.,  
373 2011). BPA also can be degraded by goethite suspensions and acidic solutions accelerated the  
374 reaction, which implies goethite may play a crucial role in the abiotic attenuation of BPA in  
375 the natural environment (Lin et al., 2012). A direct evidence for the significance of goethite  
376 in environment is the photooxidation of arsenite to lowly toxic arsenate in the natural goethite  
377 suspension. In addition, improved oxidation will substantially occur in the presence of  
378 hydrogen peroxide and/or UV radiation in the presence of goethite. Lu et al. (Lu, 2000)  
379 reported the 2-chlorophenol can be decomposed with hydrogen peroxide catalyzed by  
380 goethite and the oxidation rate increased with the decrease of goethite particle size. He et al.  
381 (He et al., 2005) found that aromatic compounds could undergo rapid decomposition and

382 mineralization (even to 100% yield) in the presence of both  $\alpha$ -FeOOH and  $H_2O_2$  under UV  
 383 irradiation, and the degradation rates of the organics were related to their sorption ability of  
 384 the surface of  $\alpha$ -FeOOH and were in the following order: salicylic acid  $\approx$  m-hydroxybenzoic  
 385 acid > p-hydroxybenzoic acid  $\approx$  benzoic acid > p-biphthalic acid > phenol > benzenesulfonic  
 386 acid. The results imply the role of goethite in the transportation and photochemical processes  
 387 of NOM in the natural environment. Not only UV, but also ultrasonic irradiation can enhance  
 388 the catalytic activity of goethite- $H_2O_2$  system. The decoloration of dye was strongly  
 389 enhanced by ultrasonic irradiation on Fenton-like process, namely goethite- $H_2O_2$  system,  
 390 based on the research of Muruganandham et al. (Muruganandham et al., 2006). The similar  
 391 result can be found in the report (Wu et al., 2012) indicating goethite surfaces catalysed a  
 392 Fenton-like reaction responsible for the decolorizing of azo dye Orange G. Furthermore,  
 393 goethite still can catalyze ozonation. Zhang et al. (Zhang and Ma, 2008) reported that  
 394 catalytic ozonation with goethite can substantially enhance nitrobenzene decomposition  
 395 compared with ozonation alone. It is speculated this phenomenon is closely related to the  
 396 decomposition of dissolved ozone in goethite suspension as is mentioned above.

397

398

**Table 4. List for the catalytic reaction**

Reactant	References
N-butyl chloride	(Lin and Gurol, 1996)
2-chlorophenol	(Lu, 2000; Lu et al., 2002)
2,6-dimethylphenol	(Mazellier and Bolte, 2000)
3,4-dihydroxybenzoic acid	(Andreozzi et al., 2002a)
1,2-benzenediol (catechol)	(Andreozzi et al., 2002b)
2-aminophenol	(Andreozzi et al., 2002b)
2,3-dihydroxybenzoic acid	(Andreozzi et al., 2002b)
Disinfection Byproducts	(Chun et al., 2005)
Aromatic compounds	(He et al., 2005)
4-chloronitrobenzene	(Chun et al., 2006)
Trichloronitromethane	(Chun et al., 2006)
Direct Orange 39 (DO39) azo dye	(Muruganandham et al., 2006)
Polyethylene	(Liu et al., 2009)
C.I. Acid Orange 7	(Zhang et al., 2009)

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Bisphenol A	(Lin et al., 2012)
Trimethyl Phosphate	(Mäkie et al., 2012)
Triethyl Phosphate	(Mäkie et al., 2012)
Azo dye Orange G	(Wu et al., 2012)
Oxalate	(Krýsa et al., 2011)

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399

## 400 **5. Effect of Al substitution**

401       Goethite has a similar structure with diaspore and the 6-fold coordinated Fe has been  
402 demonstrated to be replaced usually by Al, Co, Mn, Cr, Ni, etc., among which the  
403 substitution of Al for Fe was well documented and was also demonstrated to occur in natural  
404 goethite (Norrish and Taylor, 1961; Mendelovici et al., 1979; Fitzpatrick and Schwertmann,  
405 1982; Cornell and Schwertmann, 2003). In addition, Al-substituted goethite can also be  
406 synthesized easily in the laboratory. The Al substitution for Fe significantly affects the  
407 physicochemical properties, which has been studied by many researchers using different  
408 modern techniques, such as XRD, TG/DTG/DTA, TEM, IR, SEM, Mössbauer spectra, etc.  
409 (Golden et al., 1979; Mendelovici et al., 1979; Fey and Dixon, 1981; Goodman and Lewis,  
410 1981; Fysh and Fredericks, 1983; Schulze, 1984; Schulze and Schwertmann, 1984; Schulze  
411 and Schwertmann, 1987; Schwertmann and Murad, 1990; Ruan and Gilkes, 1995; Scheinost  
412 et al., 1999; Ruan et al., 2002; Blanch et al., 2008; Morozov and Vasil'ev, 2010; Liu et al.,  
413 2012b; Liu et al., 2012c). Ainsworth et al. (Ainsworth and Sumner, 1985; Ainsworth et al.,  
414 1985) postulated that the occurrence of Al substitution for Fe in the structure of goethite may  
415 sterically hinder the sorption of phosphate on goethite, although the substitution increased the  
416 specific surface area and improved the isotopic exchange rates. However, in recent years, Al-  
417 substituted-goethite also exhibited higher specific surface area and higher adsorption capacity  
418 for Cu, Zn and Cd ions compared to pure goethite (Spathariotis and Kallianou, 2007). The  
419 results were similar with the current report indicating the presence of structural Al in the  
420 goethite enhanced considerably the As uptake capacity and also decreased the mobilization of  
421 Fe and As adsorbed as the substitution amount increased. However, whether the increased  
422 specific surface area or the substitution of Al for Fe improved the adsorption capacity is still  
423 not confirmed since the substitution of Al generally favors the increase of surface area.

424

## 425 **6. Conclusions and summary**

426 As is mentioned above, goethite has an isostructure with diaspore. However, it generally  
427 has a size in nanometers in width and several microns in length, which presumably results in  
428 the large specific surface area. Combining with the abundant surface hydroxyl groups,  
429 goethite is playing an important role in the transport and transformation of nutrients and  
430 contaminants containing anions, organic/organic acid (including soil organic carbon), cations  
431 and some gases. The adsorption of goethite to nutrients can decrease their loss; the adsorption  
432 to heavy metals can reduce their concentration in aqueous solution; the adsorption to soil  
433 organic carbon can reduce the release of carbon from soil, which at some degree can fix  
434 carbon. Although these gases were selected as probe molecule to characterize the surface  
435 properties of goethite, the results still displayed a selective adsorption of goethite to NO  
436 compared with SO<sub>2</sub> and CO<sub>2</sub>. As for other nutrients and contaminants, goethite showed a  
437 good affinity by non-specific adsorption, specific adsorption (ligand exchange) and ternary  
438 adsorption. Non-specific adsorption, in general, occurs for the ions which have specific  
439 affinity for the metal atoms of the surface, e.g. NaNO<sub>3</sub>, and then was absorbed by  
440 electrostatic interaction. Specific adsorption frequently happened for organic/organic acid by  
441 surface complexation (inner-sphere complexation), such as phosphate and citrate, while  
442 ternary adsorption generally takes place for the mixture of organic/organic acid and cations  
443 where cations were adsorbed by the linkage of organic/organic acid. Basically, all the  
444 adsorption is strongly dependent on the solution pH. In addition, goethite surfaces showed  
445 preferential adsorption of P-containing and high molar mass organic solutes, but not of N-  
446 containing compounds. The strength of surface affinity of goethite to metals generally  
447 decreases in the order: Cu>Pb>Zn>Cd>Co>Ni>Mn.

448

449 According to the overview, goethite has a crucial significance in the natural environment.  
450 Based on the property, recently, natural goethite and synthetic goethite were also researched  
451 as catalyst carrier and precursor of nano zero valent iron (NZVI) for treatment of aqueous  
452 contaminants in our group. Liu et al. (Liu et al., 2012a) investigated the effect of carrier  
453 (natural goethite, synthetic goethite and palygorskite) on catalytic cracking of biomass tar,  
454 which indicated that goethite as a carrier had the best catalytic reactivity. Afterward, natural  
455 goethite was selected to prepare NZVI to remove nitrite and nitrate and compared with the  
456 ordinary iron powder, which also presented the natural goethite as a precursor had a good  
457 reactivity in decomposition of nitrite and nitrate (Liu et al., 2012d). This year, NZVI prepared  
458 by reducing natural goethite in hydrogen was considered to remove phosphate and p-

459 nitrophenol (PNP). This kind of NZVI displayed good adsorption efficiency and reduction  
460 efficiency, respectively, and the former is in the process of under review and the latter is  
461 being completed. In addition, the role of goethite in accelerating the generation of methane  
462 and hindering the production of CO<sub>2</sub> in anaerobic decomposition of organics was confirmed.  
463 Therefore, goethite is really playing a crucial role in the transport and transformation of  
464 anions, organic/organic acid, cations and gases in environments. Furthermore, the  
465 significance of goethite is presumably to be expanded based on the inherent properties, such  
466 as large specific surface area and abundant hydroxyl groups in the bulk as well as on the  
467 surfaces. Goethite as the precursor of nano-hematite, nano-magnetite and NZVI is being or  
468 going to be considered in the future.

469

470

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**Table captions**

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1009 **Table 1. List for inorganic anion adsorption on goethite**

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1011 **Table 2. List for organic compound and organic acid adsorption on goethite**

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1013 **Table 3. List for cation adsorption on goethite**

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1015 **Table 4. List for the catalytic reaction**

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**Figure captions**

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1020 **Fig. 1. (010) plane of goethite (top) polyhedral framework and (bottom) ball and stick**  
1021 **model**

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