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REDUCTIVE ACTIVITY OF ADSORBED Fe(II) ON IRON (OXYHYDR)OXIDES FOR 2-NITROPHENOL TRANSFORMATION

LIANG TAO[1,2], FANGBAI LI[1,*], YONGKUI WANG[1,2], AND KEWEN SUN[3]

[1] Guangdong Key Laboratory of Agricultural Environment Pollution Integrated Control, Guangdong Institute of Eco-Environmental and Soil Sciences, Guangzhou 510650, PR China
[2] Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China
[3] Institute of Health and Environmental Ecology, Wenzhou Medical College, Wenzhou, Zhejiang 325035, PR China

Abstract—Much attention has been paid to the adsorption of Fe(II) onto mineral surfaces as it is a crucial step in enhancing the reductive activity of Fe(II) species. The present study elucidates the role of Fe(II) adsorbed on Fe (oxyhydr)oxides (γ-FeOOH, α-FeOOH, and α-Fe_2O_3) for the reductive transformation of 2-nitrophenol (2-NP), using cyclic voltammetry (CV). Studies of Fe(II) adsorption and 2-NP reduction kinetics showed that an increase in pH gave rise to an elevated density of adsorbed Fe(II) on mineral surfaces, which further resulted in an enhanced reaction rate of 2-NP reduction. In addition, CV tests showed that the enhanced activity of Fe(II) species is attributed to the negative shift of peak oxidation potential (E_P) of the Fe(III)/Fe(II) couple. The dependence of adsorbed Fe(II) reactivity on pH values was proven by the three linear correlations obtained (ln *k vs.* pH, E_P *vs.* pH, and ln *k vs.* E_P). The present study demonstrated that the reductive activity of adsorbed Fe(II) species can be indicated by the E_P value of active Fe(II) species. Moreover, the electrochemical approach can be used as an effective tool to study the reductive activity of adsorbed Fe(II) species in subsurface environments.

Key Words—2-nitrophenol, Adsorbed Fe(II), Cyclic Voltammetry, Fe Oxides, Redox potential, Reductive Activity.

INTRODUCTION

The adsorption of ferrous iron [Fe(II)] onto mineral surfaces is an important environmental process that has been gaining increased attention (Hatter, 1985; Klausen *et al.*, 1995; Klupinski *et al.*, 2004; Li *et al.*, 2008; Stumm and Sulzberger, 1992). Recently, several reports have stated that, under abiotic conditions, the mineral-bound Fe(II) species can substantially promote the reductive transformation of nitroaromatic compounds (NACs, a series of widespread organic compounds mainly applied in medicine, dyes, and other industrial organic synthetic materials, such as pesticides, herbicides, pharmaceuticals, and chemical intermediates, *etc.*) to the corresponding nitroso compounds (Frank *et al.*, 1992; Hatter, 1985; Klausen *et al.*, 1995; Naka *et al.*, 2006; Rügge *et al.*, 1998; Yan and Bailey, 2001). Studies of the mechanism of heterogeneous reduction have demonstrated that the formation of surface complexes is responsible for the enhanced reaction rate (Hofstetter *et al.*, 1999; Klausen *et al.*, 1995; Li *et al.*, 2008; Pecher *et al.*, 2002; Schwarzenbach and Stone, 2003). Previous studies of Fe-free minerals (γ-Al_2O_3 and TiO_2) have shown that the greater reaction rate of reductive transformation of 2-nitrophenol (2-NP) is attributed to the enhanced concentration of the $\equiv Al_{st}OFe^+$ or $\equiv TiOFe^+$ complex in γ-Al_2O_3 or TiO_2 suspensions, respectively (Li *et al.*, 2009; Tao *et al.*, 2009). Fe-containing minerals (*e.g.* ferrihydrite, goethite, hematite, *etc*.) which are found in in lakes, rivers, and soils, *etc.* (Chen *et al.*, 2006; Schwertmann and Cornell, 1991) have also been considered.

Compared with studies using Fe-free minerals, predicting the reductive behavior of 2-NP on Fe-containing minerals is more complicated. In addition, the reductive activity of Fe(II) is very variable on Fe-containing minerals because Fe(II) can be adsorbed to form the active adsorbed Fe(II) species and react with the Fe(III) oxides to generate new surface-bound Fe(II) species (Maithreepala and Doong, 2004). Further analysis of the existing forms of adsorbed Fe(II) species and their concentrations on Fe-containing mineral surfaces is difficult (Jeon *et al.*, 2003; Liger *et al.*, 1999; Maithreepala and Doong, 2004; Schwarzenbach and Stone, 2003; Vikesland and Valentine, 2002) thus hindering their prediction. Moreover, understanding of the relationship between adsorbed Fe(II) reactivity on Fe-containing minerals and reductive kinetics of the contaminants is insufficient.

Using theoretical calculations, the Fe(III)/Fe(II) couple of surface-bound Fe(II) on Fe-containing minerals generally possesses a more negative redox potential compared with the aqueous Fe(III)/Fe(II) couple, thereby leading to a greater reaction rate (Buerge and Hug, 1998; Klausen *et al.*, 1995; Rush and Koppenol, 1987; Strathmann and Stone, 2002a, 2002b). For

* E-mail address of corresponding author:
cefbli@soil.gd.cn
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example, Li *et al*. (2008) found that the strong nucleophilic ability and small reductive potential of the ≡Fe(II)-polycarboxylate complexes can significantly enhance transformation of pentachlorophenol. Buerge and Hug (1998) demonstrated that the rate coefficients of Cr(VI) reductive transformation through Fe(II) increased along with decreasing electron reduction potential of the Fe(III)L/Fe(II)L redox couples. However, to the authors' knowledge, no experimental evidence of the difference in redox potential is available for Fe-containing minerals. The use of cyclic voltammetry (CV), a powerful tool in electrochemistry (Bard and Faulkner, 1980), has the potential to make such measurements of the redox potential on the solid surface (Li *et al.*, 2009; Tao *et al.*, 2009).

In the present study, 2-NP was selected as the target organic contaminant. Experiments were carried out in sterile batch suspensions containing 2-NP and Fe (oxyhydr)oxides including γ-FeOOH, α-FeOOH, and α-Fe_2O_3, under various experimental conditions. The objective of this research was to elucidate the relationship among Fe(II) adsorption, kinetics of 2-NP transformation, and electrochemical behavior of the adsorbed Fe(II) species on Fe-containing minerals. The results are expected to describe the correlations among the reductive activity of adsorbed Fe(II), the kinetics of 2-NP reductive transformation, and the peak oxidation potential of the Fe(III)/Fe(II) couple.

MATERIALS AND METHODS

Chemicals

3-[N-morpholino] propanesulfonic acid (MOPS, >99.5%) and 2-[N-morpholino] ethanesulfonic acid monohydrate (MES, >99.5%) were purchased from Sigma-Aldrich (St Louis, Missouri, USA). 2-nitrophenol (2-NP, 99.5%), 2-aminophenol (2-AP, 99.5%), $FeSO_4·7H_2O$ (>99.5%), and methanol (HPLC) were purchased from Acros (Geel, Belgium). All were of analytical or higher grade and were used without further purification.

Fe (oxyhydr)oxide synthesis and characterization

α-FeOOH was prepared as reported by Schwertmamm and Cornell (1991), γ-FeOOH was prepared by a hydrothermal method (Yen *et al.*, 2002), and α-Fe_2O_3 was formed by sintering γ-FeOOH powder at 420ºC for 2 h at a programmed heating rate of 2ºC/min (Liu *et al.*, 2006). The synthetic Fe (oxyhydr)oxides (α-FeOOH, γ-FeOOH, and α-Fe_2O_3) were ground and sieved through a 200 mesh sieve (Shangyu Shenke Test Equipment Factory, Shaoxing, Zhejiang, China) before use. The crystal structure of the samples was determined by powder X-ray diffraction (XRD) using a Rigaku D/Max-III A diffractometer at room temperature, operated at 30 kV and 30 mA with CuKα radiation (λ = 0.15418 nm). The BET surface area (Table 1) was determined using N_2 adsorption at 77 K was applied using a Carlo Erba Sorptometer.

Experimental procedures

Abiotic reduction experiments were conducted in aqueous suspensions in 20 mL borosilicate glass serum bottles with aluminum crimps and Teflon-lined butyl rubber septa using the same methods described in previous studies (Li *et al.*, 2009; Tao *et al.*, 2009). Suspensions prepared for the redox reactor contained 0.5 mM $FeSO_4$, 11.0 μM 2-NP, 28 mM buffer (MES or MOPS), 200 mM NaCl, and 68.0 mg of one of the Fe (oxyhydr)oxides (γ-FeOOH, α-FeOOH, or α-Fe_2O_3). Batch studies were conducted to assess the influence of pH (from 5.5 to 7.8) on the kinetics of 2-NP reductive transformation. A constant suspension temperature of 25ºC was achieved using a constant thermostatic shaker system. For 2-NP kinetic studies, one of the 20 mL serum bottles was taken from the shaker and transferred to the oxygen-free glove box prior to routine analysis. After vigorous mixing, the serum bottle was opened and spiked with 2 M HCl (<60 μL) to adjust the pH to <3 and to prevent further 2-NP degradation. The suspension was immediately centrifuged at 10,000 rpm for 10 min (Sigma-3K 15) to remove the particles. The supernatants were saved for further analysis.

Experiments of Fe(II) adsorption onto Fe (oxyhydr)-oxides were conducted under conditions identical to those in the kinetic experiments, except that 11.0 μM 2-NP was not added to the reactor and the pH was kept within a narrow range (from 4.5 to 7.8). Because of the possibility of Fe(II) being oxidized at circumneutral pH, the adsorption experiments at pH ⩾ 6.5 were carried out under continuous bubbling of nitrogen rather than on a rotator (Li *et al.*, 2009). The nitrogen flow rate was 90 mL min^{-1}, which allowed for sufficient stirring of the suspension. After achieving equilibrium, the final pH of each suspension was recorded before filtering (0.2 μm membrane filter); the acidified filtrate was then collected for Fe(II) concentration analysis.

Electrochemical tests

Cyclic voltammograms were obtained using the methods described by Li *et al*. (2009). The preparation of a mineral-modified glassy carbon (GC) electrode started from a bare GC electrode (3 mm in diameter). Prior to use, the GC electrode was polished with emery paper, followed with γ-Al_2O_3 powders of 1 and 0.06 μm particle sizes, and was thoroughly rinsed with double-distilled water between the two polishing steps. Then, the GC electrode was cleaned successively with acetone and double-distilled water in an ultrasonic bath for 10 min. To obtain the mineral slurry, 0.5 mg of mineral (α-FeOOH, γ-FeOOH, or α-Fe_2O_3) was dispersed in a dilute Nafion solution (0.5 wt.%, 250 μL) in an ultrasonic bath for 15 min. Using a micro-syringe, an aliquot (2 μL) of the above suspension was allowed to

coat the clean GC electrode and air-dry for 30 min prior to measurements. Three mineral-modified glassy carbon electrodes were prepared and labeled 'γ-FeOOH/GC,' 'α-FeOOH/GC,' and 'α-Fe_2O_3/GC.'

Electrochemical measurements were carried out in a conventional three-electrode cell, equipped with the mineral-modified glassy carbon (GC) electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum spiral wire as the counter electrode. Cyclic voltammograms were recorded with an Autolab potentiostat (PGSTAT 30, Eco Chemie, The Netherlands) at a scan rate of 50 mV s^{-1}. The electrochemical cell was filled with a solution containing 0.5 mM $FeSO_4$ and 0.20 M NaCl buffered with 28 mM MES or MOPS; in addition, the pH of the solution was adjusted by adding dilute HCl or NaOH solution. High-purity N_2 gas was bubbled through the above electrolyte to remove dissolved oxygen.

Analytical methods

The 2-NP concentration as a function of reaction time was monitored by High Performance Liquid Chromatography (HPLC) using a Waters model 2487 (5 mm Symmetry-C18, 4.6 mm, 250 mm) system, which consists of a Waters 1525 binary pump, an analytical reversed-phase column, and a dual-wavelength UV-visible Absorbance detector. The isocratic mobile phase contained 80/20 (v/v) methanol/water and 3 mM HCl at a flow rate of 1.0 mL min^{-1} under isocratic conditions at 30 ± 1ºC, and the wavelength was set at 213 nm. The concentrations of 2-NP were calculated through a comparison with standard solutions (Klupinski *et al.*, 2004).

The Fe(II) concentration was determined colorimetrically by the 1,10-phenanthroline method at 510 nm using a UV-visible spectrophotometer (TU-1800PC) (Fadrus and Malý, 1975; Jeon *et al.*, 2005; Maithreepala and Doong, 2004). Solutions containing dissolved Fe(II) were filtered through 0.22 μm filters to remove particles in the samples prior to analysis. The total Fe(II) in the samples was extracted using 0.5 mM HCl for 1.5 h (Fadrus and Malý, 1975; Jeon *et al.*, 2005; Maithreepala and Doong, 2004) and then analyzed using the same procedures as for dissolved Fe(II). Adsorbed Fe(II) was calculated as the difference between total Fe(II) and dissolved Fe(II).

RESULTS AND DISCUSSION

Reductive transformation of 2-NP by Fe(II) in Fe (oxyhydr)oxide suspension

The reaction kinetics obtained under various conditions were compared (Figure 1). No significant 2-NP transformation was observed in the absence of Fe(II). 2-NP adsorption studies on Fe (oxyhydr)oxides (Figure 1) showed that the level of adsorption under all conditions was small; in addition, the adsorption behavior, with respect to γ-FeOOH, α-FeOOH, and α-Fe_2O_3, showed negligible difference. Compared with the homogeneous reaction of aqueous Fe(II) with 2-NP, the heterogeneous reactions in Fe (oxyhydr)oxide suspensions proceeded at a much faster rate because of the existence of active adsorbed Fe(II) species (Li *et al.*, 2009). From the kinetics of 2-NP reductive transformation, the rate of 2-NP reduction decreased in the order: γ-FeOOH < α-FeOOH < α-Fe_2O_3.

Effects of pH on 2-NP transformation

The effects of pH on the kinetics of 2-NP reductive transformation in Fe(II)/γ-FeOOH (Figure 2a), Fe(II)/α-FeOOH (Figure 2b), and Fe(II)/α-Fe_2O_3 (Figure 2c) suspensions revealed that the rate of 2-NP reductive transformation significantly increased with increase in pH. The results also revealed that the transformation of 2-NP generally follows the pseudo-first-order kinetics rate law, from which the rate constants (k) were calculated. In the Fe(II)/γ-FeOOH suspension (Figure 2a), the k value of 2-NP transformation was 1.1×10^{-3} min^{-1} at pH 5.5, ~25 times smaller than that obtained at pH 7.7. In all cases, the k values increased exponentially with pH, as illustrated by the straight lines (with high coefficients of determination) in the ln k *vs.* t plots (Figure 2d). At a fixed pH of 6.5, the rate constant increased in the order: γ-FeOOH < α-FeOOH < α-Fe_2O_3. The value of k was slightly more sensitive to changes in pH in the Fe(II)/α-Fe_2O_3 suspension than in the case of the two oxyhydroxides (Table 1).

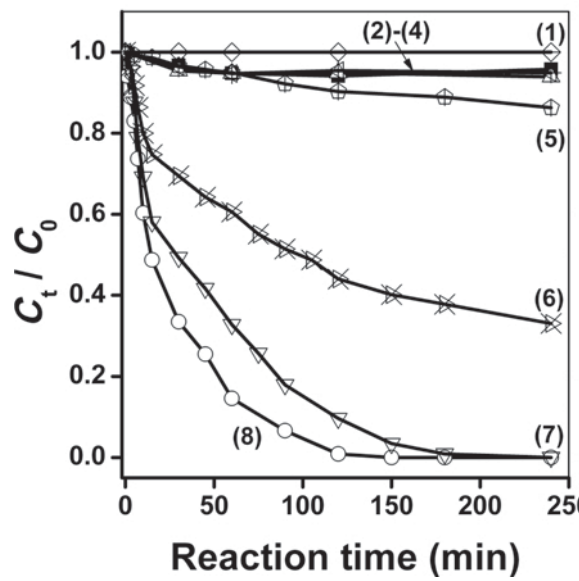

Figure 1. Reductive transformation of 2-NP at pH 6.5 (28 mM MES) and 25ºC under various conditions: blank reaction (1); 2-NP with γ-FeOOH, α-FeOOH, or α-Fe_2O_3 suspension, respectively (2–4); 2-NP with Fe(II) (5); and 2-NP with Fe(II) sorbed to γ-FeOOH, α-FeOOH, or α-Fe_2O_3, respectively (6–8). Reaction conditions: 0.5 mM $FeSO_4$, 11.0 μM 2-NP, 4.0 g L^{-1} mineral, 0.2 M NaCl.

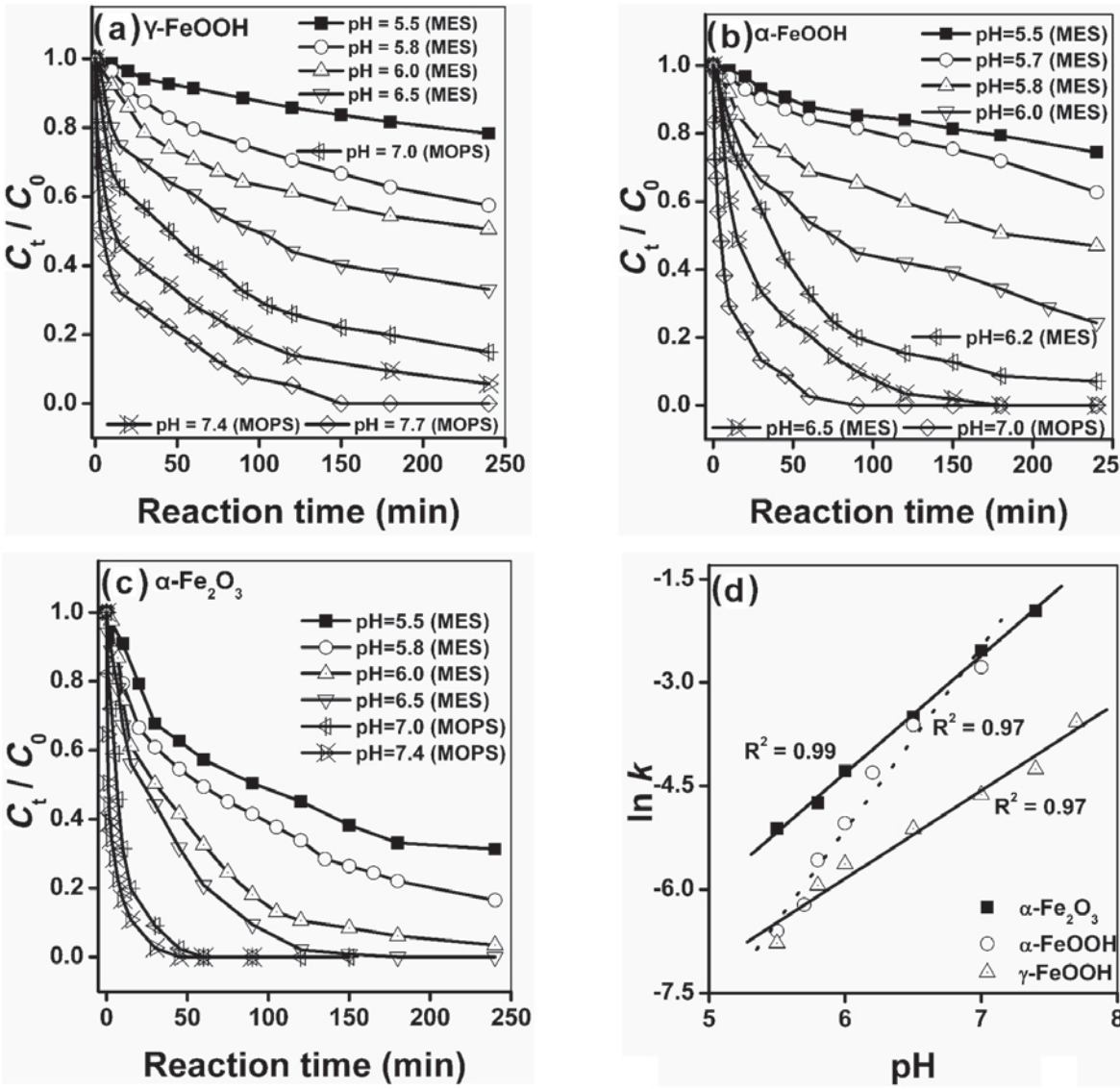

Figure 2. Effects of pH on the reductive transformation of 2-NP in γ-FeOOH (a), α-FeOOH (b), and α-Fe_2O_3 (c) suspensions, respectively. Plot of ln *k vs.* pH in γ-FeOOH, α-FeOOH, or α-Fe_2O_3 suspension (d). Reaction conditions: 0.5 mM $FeSO_4$, 11.0 μM 2-NP, 4.0 g L^{-1} mineral, pH = 5.5−7.7, 0.2 M NaCl, and 25°C.

Effects of sorbed Fe(II) density on 2-NP transformation

Comparison of the adsorption behavior of Fe(II) onto γ-FeOOH (Figure 3a), α-FeOOH (Figure 3b), and α-Fe_2O_3 (Figure 3c) revealed that the percentage of Fe(II) adsorbed decreased as the initial Fe(II) concentration increased slightly, even though at the same time the amount of Fe(II) adsorbed onto the minerals increased. This trend has commonly been observed for cation sorption onto hydrous metal oxides (Benjamin and Leckie, 1981; Nano and Strathmann, 2006). In addition, Fe(II) adsorption exhibited similar pH-dependent patterns, indicating that stronger Fe(II) adsorption occurred at greater pH. At a constant initial Fe(II) concentration (*e.g.* 0.1 mM), increasing pH enhanced adsorption rates. Moreover, Fe(II) adsorption was negligible at pH < 4.0 but ~90% at pH 7.0.

As reported previously (Hiemstra and Riemsdijk, 2007; Li *et al.*, 2009; Stumm and Sulzberger, 1992; Schwarzenbach and Stone, 2003; Tao *et al.*, 2009), the amount of Fe(II) adsorbed on the mineral surface is indeed a crucial factor affecting the reduction rate of organic pollutants. The impact of adsorbed Fe(II) density on the reductive transformation of 2-NP was, therefore, investigated in γ-FeOOH, α-FeOOH, and α-Fe_2O_3 suspensions with the same initial Fe(II) concentration of 0.5 mM Fe(II) but with different pH.

Table 1. The relationship among the surface area, the sorbed Fe(II) density, the normalized k value, the kinetics of 2-NP transformation, and the electrochemical parameters. The pH was controlled at 6.5 in 0.2 M NaCl and 28 mM MES solution.

Mineral surface	Fe (oxyhydr)oxide			– Fe-free mineral[f,g] –	
	γ-FeOOH	α-FeOOH	α-Fe_2O_3	γ-Al_2O_3	TiO_2
Surface area (m^2 g^{-1}) [a]	126	36.23	43.72	127.4	50
Sorbed Fe(II) density (μmol m^{-2})	3.45[b]	6.21[b]	10.75[b]	0.38	2.09
k/sorbed Fe(II) (min^{-1} M^{-1})	13.7[c]	109.6[c]	130.4[c]	55.13	314.6
Peak oxidation potential (E_P /V)	0.255[d]	0.229[d]	0.203[d]	0.241	0.220
Rate constant of 2-NP reduction ($k \times 10^{-2}$ min^{-1})	0.598[e]	2.691[e]	3.027[e]	0.285	3.99

[a] The specific surface area (m^2 g^{-1}) was measured by the BET method
[b] Data from Figure 3
[c] Data from Figure 4
[d] Data from Figure 5
[e] Data from Figure 2
[f] Data from Li *et al.* (2009)
[g] Reaction conditions: 0.5 mM $FeSO_4$, 5.5 μM 2-NP, 4.0 g L^{-1} mineral, pH = 6.5, 0.2 M NaCl, and 25ºC.

Differences were observed (Figure 3d) in the densities of Fe(II) adsorbed (adsorption concentration divided by solid surface area) for the three Fe (oxyhydr)oxides when the pH was changed. In all cases, an increase in pH resulted in an increase in adsorbed Fe(II) density. For a constant pH (*e.g.* 6.5), the adsorbed Fe(II) densities on γ-FeOOH, α-FeOOH, and α-Fe_2O_3 suspensions were 3.45, 6.21, and 10.75 μmol m^{-2}, respectively (Table 1), and the overall trend for the adsorbed Fe(II) densities at all reaction pH values was γ-FeOOH <

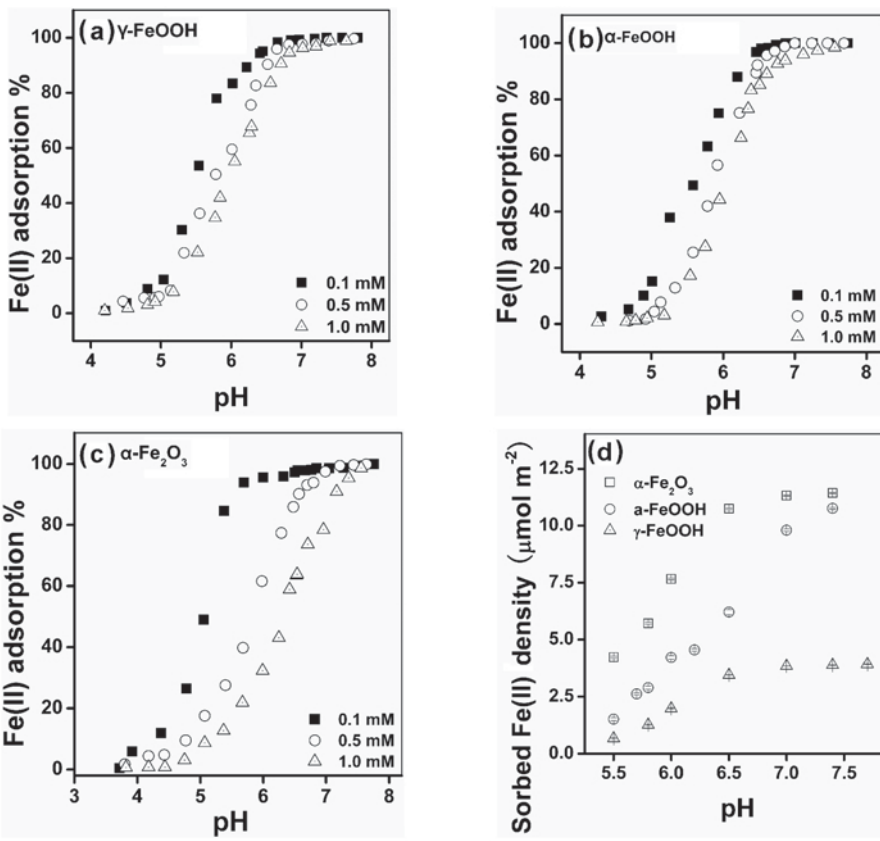

Figure 3. Fractional adsorption of Fe(II) onto γ-FeOOH (a), α-FeOOH (b), or α-Fe_2O_3 (c) as a function of pH. Plot of sorbed Fe(II) density *vs.* pH (d). Adsorption conditions: 0.1–1.0 mM $FeSO_4$, 4.0 g L^{-1} mineral, 0.2 M NaCl, pH 4.0–7.8 (28 mM buffer), and 25ºC.

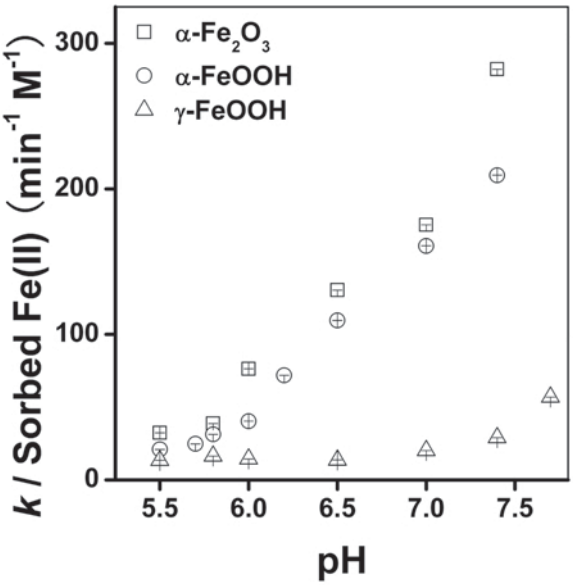

Figure 4. Comparison between k normalized to the amount of adsorbed Fe(II) for γ-FeOOH, α-FeOOH, and α-Fe_2O_3 as a function of pH. Reaction conditions: 0.5 mM $FeSO_4$, 11.0 μM 2-NP, 4.0 g L^{-1} mineral, 0.2 M NaCl, pH 5.5−7.8 (28 mM buffer), and 25ºC.

α-FeOOH < α-Fe_2O_3, which is the same as the order of k values for 2-NP reduction.

Considering the different extents of adsorption of Fe(II) under the same reaction conditions (Li *et al.*, 2009), the k values were normalized to the amount of Fe(II) adsorbed for γ-FeOOH, α-FeOOH, and α-Fe_2O_3 as a function of pH (Figure 4). The k values normalized to the moles of adsorbed Fe(II) at fixed pH (*e.g.* 6.5), values of k/sorbed Fe(II) in γ-FeOOH, α-FeOOH, and α-Fe_2O_3 suspensions, were 13.7, 109.6, and 130.4 min^{-1} M^{-1}, respectively (Table 1). The resultant k values were ranked from low to high as γ-FeOOH < α-FeOOH < α-Fe_2O_3. Fe(II) adsorbed onto α-Fe_2O_3 may also be more reactive than Fe(II) adsorbed onto α-FeOOH and γ-FeOOH for the reductive transformation of 2-NP.

Electrochemical behavior of adsorbed Fe(II) on the mineral-modified electrodes

Using home-made mineral-modified electrodes, cyclic voltammograms were performed to evaluate the Fe(II) → Fe(III) electron transfer behavior of adsorbed Fe(II) and provide direct evidence of changes in redox potential. The effects of pH on the redox behavior of the surface-complexed Fe(II) onto γ-FeOOH, α-FeOOH, and α-Fe_2O_3 are illustrated by their voltammograms (Figure 5a−c, respectively). All voltammograms clearly exhibited a pair of peaks: an anodic oxidation peak for Fe(II) at potentials ranging from −0.2 to 0.3 V (*vs*. SCE) and a cathodic reduction peak for Fe(III) at potentials ranging from −0.7 to −0.2 V (*vs*. SCE). Consistent with theoretical results (Nano and Strathmann, 2006), both peaks shifted toward a more negative value as the pH increased (Figure 5). For instance, when pH was modulated from 5.5 to 7.4, the peak oxidation potential (denoted as E_P) of Fe(II) adsorbed onto γ-FeOOH decreased significantly from 0.237 to −0.338 V (*vs.* SCE). Similar behaviors were also observed for α-FeOOH and α-Fe_2O_3 minerals.

According to previous reports (Li *et al.*, 2009; Tao *et al.*, 2009), the correlation between E_P reduction and pH in Fe-free minerals is linear, and E_P is indeed a crucial factor affecting the rate of reduction of organic pollutants. The reduction in E_P *vs.* pH was, therefore, investigated in γ-FeOOH, α-FeOOH, and α-Fe_2O_3 suspensions. Linear E_P reduction *vs.* pH was found in all three sets of reactions on the γ-FeOOH/GC, α-FeOOH/GC, and α-Fe_2O_3/GC electrodes (Figure 5d). At any fixed pH value, the E_P values of the electrodes were ranked from low to high as α-Fe_2O_3/GC < α-FeOOH/GC < γ-FeOOH/GC. The measured E_P values for γ-FeOOH/GC, α-FeOOH/GC, and α-Fe_2O_3/GC at pH 6.5, for example, were 0.255 V, 0.229 V, and 0.203 V (*vs.* SCE), respectively (Figure 5d, Table 1). The declining trend in E_P is reasonably consistent with the order of increase of adsorbed Fe(II) density and the increase in ln k.

For each Fe (oxyhydr)oxide surface, the plot of ln k *vs.* E_P [relative to RHE, +0.24 V standard hydrogen electrode (SCE) at 25ºC] (Figure 6) revealed that the ln k values increased with decreasing E_P values in all cases, as indicated by the three linear correlations with high coefficient values. At all fixed E_P in the three Fe (oxyhydr)oxide suspensions, the ln k values of 2-NP reduction, ranked from low to high, were γ-FeOOH < α-FeOOH < α-Fe_2O_3. The α-Fe_2O_3 mineral demonstrated the greatest values of ln k, while the γ-FeOOH mineral yielded the smallest values, indicating that α-Fe_2O_3 was slightly more sensitive to the E_P change than the other two.

The k values obtained from the three Fe (oxyhydr)-oxides at pH 6.5 (Table 1) increased in the order γ-FeOOH < α-FeOOH < α-Fe_2O_3, whereas the rankings of the sorbed Fe(II) density values (Table 1) were γ-FeOOH < α-FeOOH < α-Fe_2O_3. By normalizing the k value to the amount of Fe(II) sorbed, the k value based on moles of sorbed Fe(II) was also ranked from smallest to greatest as γ-FeOOH < α-FeOOH < α-Fe_2O_3. On the other hand, the E_P value increased in the opposite order, α-Fe_2O_3 < α-FeOOH < γ-FeOOH. The trend in E_P values in the three Fe (oxyhydr)oxides was consistent with the order of variation in the sorbed Fe(II) density and the ln k increase. The corresponding results obtained from Fe-free minerals at pH 6.5 (Li *et al.*, 2009) (Table 1) also showed that: (1) the sorbed Fe(II) density on Fe-free minerals ranked from low to high as γ-Al_2O_3 < TiO_2, while the k value increased in the order γ-Al_2O_3 < TiO_2; (2) the trend of k values based on moles of Fe(II) sorbed

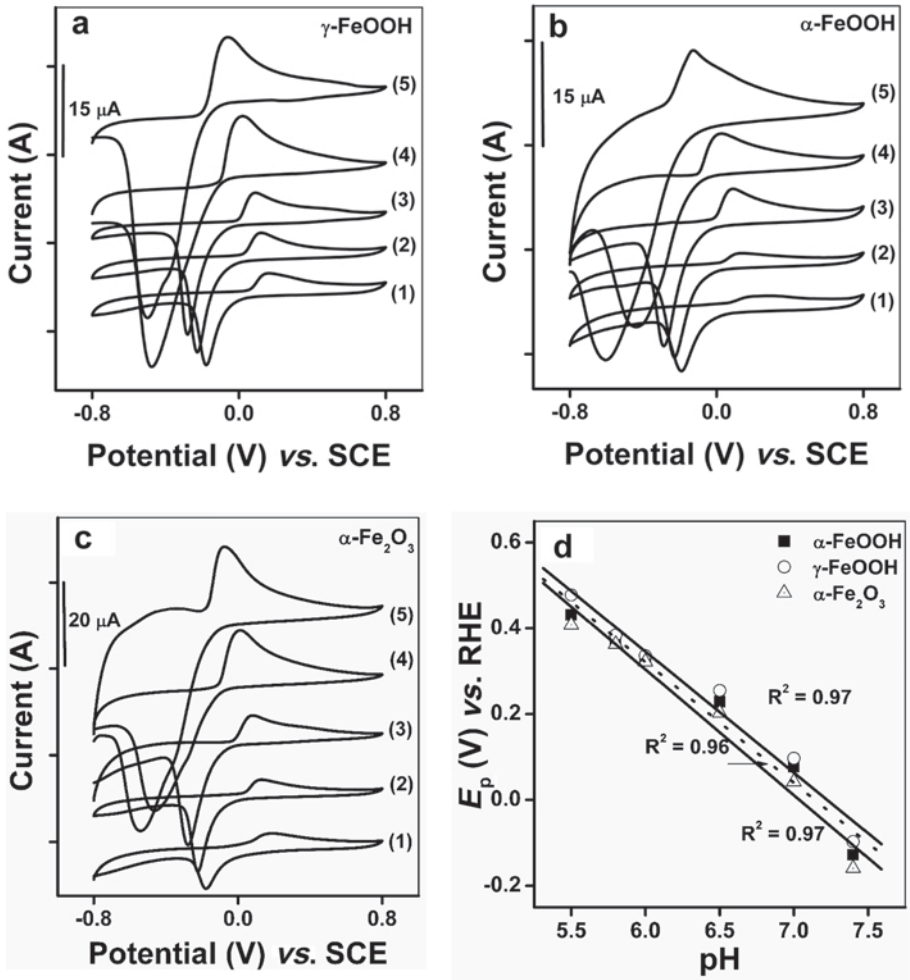

Figure 5. Cyclic voltammograms of Fe(II) species adsorbed on the γ-FeOOH/GC electrode (a), α-FeOOH/GC (b), and α-Fe_2O_3/GC (c). Plot of E_P *vs.* pH (d). Electrochemical measurements were conducted in the cell (25 mL) containing 0.5 mM $FeSO_4$, 0.2 M NaCl solution, and 28 mM buffer at 25ºC. Solution pH was varied: (1) pH = 5.5; (2) pH = 5.8; (3) pH = 6.0; (4) pH = 6.5; and (5) pH = 7.0. The scan rate was 50 mV s^{-1}.

on Fe-free minerals also ranked from low to high as γ-Al_2O_3 < TiO_2; and (3) the trend of the decline in E_P as γ-Al_2O_3 > TiO_2 was quite consistent with the order of increase in ln *k* values.

Compared with studies conducted on Fe (oxyhydr)-oxides and Fe-free minerals, the variation trends of the specific values of *k*, sorbed Fe(II) density, *k* value based on moles of sorbed Fe(II), and E_P were the same whether they were obtained from Fe (oxyhydr)oxides or from Fe-free minerals. A functional linear relationship between ln *k* and E_P was observed. The pronounced effect of E_P on ln *k* is consistent in all three Fe (oxyhydr)oxides and all Fe-free minerals (Li *et al.*, 2009), *i.e.* the negative shift of E_P due to elevated pH accounts for the enhanced rates of 2-NP reduction. At fixed pH, the E_P values for different minerals were also different, resulting in different reaction rates. Hence, E_P for the active Fe(II) species can be regarded as an important indicator of the reductive activity of adsorbed Fe(II) species; in addition, the electrochemical approach (*i.e.* CV) can be used to study the relationship between interfacial adsorption and reactivity of active species in real subsurface environments.

Attenuation of NACs in natural systems can be through biotic and abiotic processes. The biodegradation of such pollutants has been reported widely (Roldan *et al.*, 2008), while the contributions of abiotic reactions still need to be clarified and their mechanisms of reductive transformation further disclosed. In real subsurface environments, the active Fe(II) species comes mainly from dissimilatory Fe reduction (Jaisi *et al.*, 2007, 2008; Lovley *et al.*, 1996; 2004; Lee *et al.*, 2006; Seabaugh *et al.*, 2006), which would promote the reductive transformation of NACs. Nevertheless, certain aspects of their correlations, such as activity of Fe(II) species and the reduction reaction mechanism, are not well understood. Combined with former studies (Li *et al.*, 2009; Tao *et al.*,

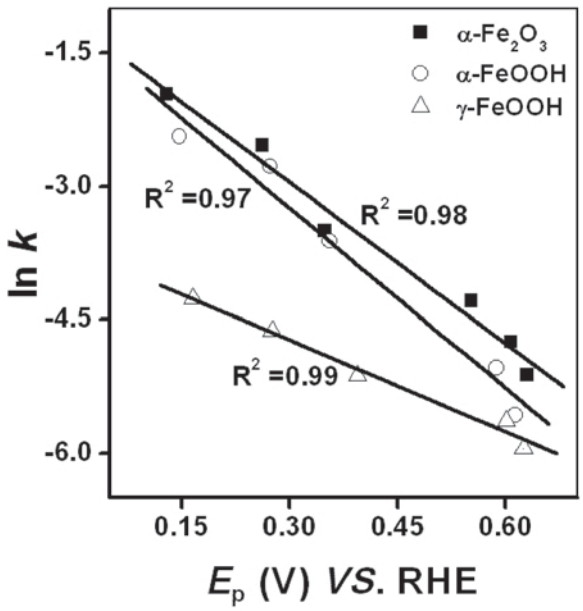

Figure 6. Dependence of ln k on E_P in γ-FeOOH, α-FeOOH, and α-Fe_2O_3 suspensions. Reaction conditions: 0.5 mM $FeSO_4$, 11.0 μM 2-nitrophenol, 4.0 g L^{-1} of mineral, 0.2 M NaCl, pH 5.5−7.8 (28 mM buffer), and 25ºC.

2009), the electrochemical approach can be a useful tool in studying these correlations. It also has application in studying the mechanism of NAC transformation in real subsurface environments.

CONCLUSIONS

The present study provides direct electrochemical evidence confirming previous understandings of interfacial reactions involving sorbed Fe(II) on Fe (oxyhydr)-oxides. 2-NP reduction by adsorbed Fe(II) depends mainly on two key factors: the sorbed Fe(II) density and the E_P value for the Fe(III)/Fe(II) redox couple. Three linear correlations (ln k *vs.* pH, E_P *vs.* pH, and ln k *vs.* E_P) were observed, which can be used to describe the pH dependence of adsorbed Fe(II) reactivity. These findings enhance understanding of Fe(II) redox reactivity in complicated heterogeneous anoxic environments. As a result, the investigation of Fe(II) adsorbed onto soil minerals and its roles in pollutant degradation are progressing.

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