

Interaction between Reductive Transformation of 2-Nitrophenol and Adsorbed Fe(II) Species

Liang Tao^A and Fang-Bai Li^A

^AGuangdong Key Laboratory of Agricultural Environment Pollution Integrated Control, Guangdong Institute of Eco-environmental and Soil Sciences, Guangzhou, China, Email tlpippen@yahoo.com.cn, cefbli@soil.gd.cn

Abstract

The aim of this study was to elucidate the role of Fe(II)-complexes in heterogeneous SiO₂ suspension and homogeneous Fe(II) solution for the reductive transformation of 2-nitrophenol (2-NP) by using electrochemical method. Fe(II) adsorption onto SiO₂ surfaces was studied in view of its high reactivity towards the aqueous reductive transformation of 2-NP. Kinetic measurements demonstrated that rates of 2-NP reduction were highly sensitive to pH and Fe(II) concentration. An increase in pH or Fe(II) concentration gave rise to an elevated density of Fe(II) adsorbed to mineral surfaces, which further resulted in an enhanced reaction rate of 2-NP reduction. Furthermore, the electrochemical method of cyclic voltammetry (CV) was applied to characterize the Fe(III)-to-Fe(II) electron transfer processes in the interfacial phase. The electrochemical evidences confirmed that the oxidation potential (E_p) of Fe(II)-complexes can be significantly affected by the adsorbed Fe(II) species; and the enhanced reductive transformation of 2-NP can be related to the negative shift of the redox potential of the Fe(III)/Fe(II) couple. The linear relationships between $\ln k$ and pH values, adsorbed Fe(II) density, or E_p were all quantified.

Key Words

Interaction; surface, Fe(II) species, reductive transformation, cyclic voltammetry

Introduction

The contamination of soil by nitroaromatic compounds (NACs), one of the ubiquitous pollutants in subsurface environments, is a significant environmental concern (Colon *et al.* 2006). Recently, an increasing number of laboratory and field studies have reported that mineral-bound Fe(II) species can substantially promote the reduction transformation of nitro groups to the corresponding anilines under abiotic conditions, and this heterogeneous reaction has demonstrated that the formation of surface complexes is responsible for the enhanced reaction rate (Hofstetter *et al.* 1999; Li *et al.* 2008; Strathmann and Stone 2003). Depending on environmental factors such as pH, the concentration of Fe(II) and the type of minerals, different Fe(II) surface-complex species could exist, varying in their content (Hiemstra and Riemsdijk 2007; Nano and Strathmann 2006; Strathmann and Stone 2003). Moreover, the contribution of each individual species to the total reaction rate is different. The interpretation of remarkably enhanced reduction of organic pollutants in a heterogeneous reaction has normally been based on the change of Fe(III)/Fe(II) redox potential in the literature (Klausen *et al.* 1995). However, to our knowledge, in spite of theoretical calculations, no experimental evidence of the difference in redox potential has been available in previous reports. In fact, the electrochemical method (i.e., cyclic voltammetry (CV)) is a useful tool that enables a direct observation of the redox behavior of the investigated couple, provided that a modified electrode can be successfully produced with minerals.

In this paper, we selected 2-nitrophenol as the target organic contaminant. Experiments were carried out in sterile batch suspensions containing 2-nitrophenol and SiO₂ powders under various experimental conditions. The aim of this study was to elucidate the role of Fe(II)-complexes in heterogeneous SiO₂ suspension and homogeneous Fe(II) solution for the reductive transformation of 2-nitrophenol by using electrochemical method. The CV measurements were performed to identify the redox behavior of the adsorbed Fe(II) surface complex.

Methods

Reagents

The SiO₂ powders were ground and sifted through 200-mesh before being used. Other chemicals used see our previous reports (Tao *et al.* 2009).

Kinetic studies and adsorption studies

To study the reductive transformation of 2-NP in the presence of SiO₂, borosilicate glass serum bottles (20 mL) with aluminum crimps and Teflon-lined butyl rubber septa were employed as reactors. Due to the high

possibility of Fe(II) being oxidized at circumneutral pH, the kinetic experiments at $\text{pH} \geq 6.5$ were conducted with continuously bubbled nitrogen rather than on a rotator. The flow rate of nitrogen was 90 mL/min which allows for the sufficient stirring of the suspension. The detailed experimental stage and analytical methods were reported in the former reports (Li *et al.* 2009). The adsorption of Fe(II) onto SiO_2 was conducted under the conditions identical to kinetic experiments, except that 0.022 mM 2-NP was not added to the reactor. After equilibrium, the final pH of each suspension was recorded before filtering (0.2 μm membrane filter). The acidified filtrate was then collected for the analysis of Fe(II) content.

Electrochemical tests: Reductive transformation of 2-NP by Fe(II) in SiO_2 suspension

The preparation of a SiO_2 -modified glassy carbon (GC) electrode were described in our earlier work (Tao *et al.* 2009), electrochemical measurements were carried out in a conventional three-electrode cell, equipped with a SiO_2 modified glassy carbon (GC) electrode as the working electrode, a saturated calomel electrode (SCE, +0.24 V versus standard hydrogen electrode (SHE) at 25 °C) as the reference electrode, and a platinum spiral wire as the counter electrode. Cyclic voltammograms (CV) were recorded with an Autolab potentiostat (PGSTAT 30, Eco Chemie, The Netherlands) at the scan rate of 50 mV/s. CV tests were performed under pure nitrogen atmosphere at 25 °C.

Results

Effects of pH on 2-NP transformation

The reduction of 2-NP in reaction media consisting of Fe(II) were studied at various pH conditions and a temperature of 298 K. Figure 1A, 1B show the comparisons of reaction kinetics obtained under different pH conditions in SiO_2 suspensions or in homogeneous suspensions, respectively. Notably, the rates of 2-NP reduction by Fe(II) were significantly enhanced with an increase in pH in both cases. The kinetics of 2-NP reduction in both systems (heterogeneous and homogeneous) was found to follow the pseudo-first-order kinetic model under all experimental conditions. In addition, the homogeneous reaction of Fe(II) with 2-NP gave a much lower rate than that resulting from the heterogeneous reaction in which the adsorbed Fe(II) species were involved. These observations demonstrated that Fe(II) adsorbed to SiO_2 was a reactive electron acceptor to promote the reductive transformation of 2-NP. It is interesting to note that the k values increase exponentially with pH in all cases as indicated by two straight lines shown in Figure 1C. By comparison, it was found that the addition of minerals could greatly facilitate the 2-NP reduction. Figure 1C shows that the resultant k values of 2-NP reduction at the fixed pH in the presence/absence of minerals can be ranked from low to high as non-mineral < SiO_2 . This distinctly pH-dependent k value was in good accordance with those observed for the reduction of nitroaromatic compounds (NACs) in the appearance of Fe(II) and other mineral suspensions (Colon *et al.* 2006; Klausen *et al.* 1995).

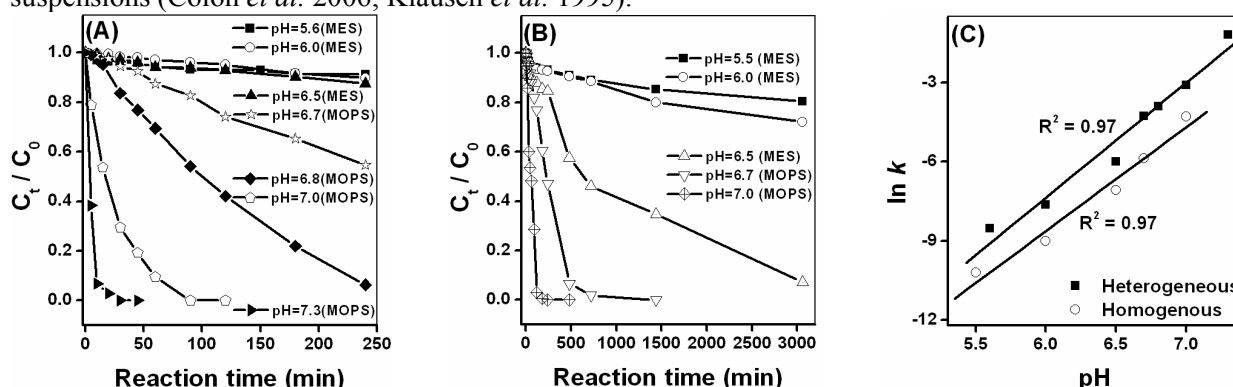


Figure 1. Effects of pH on the reductive transformation of 2-NP in the presence of SiO_2 (A), and homogeneous system (B) respectively. Effects of pH on $\ln k$ (the first-order rate constant of 2-NP transformation (C)). Reaction conditions: 3 $\text{mmol}\cdot\text{L}^{-1}$ Fe^{2+} , 0.022 $\text{mmol}\cdot\text{L}^{-1}$ 2-NP, 4.0 g/L SiO_2 , pH 5.5-7.4, and 298 K.

Fe(II) adsorption and effects of Fe(II) concentration

Figure 2A shows effects of pH and the initial Fe(II) concentration on the Fe(II) adsorption in SiO_2 suspensions. It should be noted that Fe(II) adsorption onto SiO_2 mineral exhibited the pH-dependent patterns that stronger Fe(II) adsorption occurred at higher pH values. For a constant initial Fe(II) concentration (e.g., 0.1 mM), an increase in pH resulted in enhanced rates of adsorption. The pH values less than 5.5 corresponded to a negligible Fe(II) adsorption; whereas, the extent of the maximum Fe(II) adsorption only nearly 20 % even at pH 8.0. Additionally, the increase of the initial Fe(II) concentration slightly decreased the percentage of Fe(II) adsorption, but largely increased the amounts of adsorbed Fe(II) onto the

minerals. This trend has commonly been observed for the cation sorption onto hydrous metal oxides (Benjamin and Leckie 1981; Nano and Strathmann 2006). The adsorption density (adsorption concentration divided by solid surface area), however, largely increased with the increase of the aqueous Fe(II) concentration.

Another set of experiments were performed with various Fe(II) concentrations in the range from 1 mM to 10 mM to evaluate its influence on the reduction kinetics of 2-NP transformation at a fixed pH value of 6.7. The change of k value was plotted against the density of adsorbed Fe(II) instead of the initial Fe(II) concentration as previous reports have demonstrated that the concentration of adsorbed Fe(II) plays a tremendous role in NACs reductive transformation (Hofstetter *et al.* 1999; Li *et al.* 2008; Pecher *et al.* 2002; Strathmann and Stone 2003). The concentration of aqueous Fe(II) indeed had an insignificant effect on 2-NP transformation as shown in the former section. Figure 2B reveals the pronounced linear relationship between $\ln k$ and the density of adsorbed Fe(II), indicating that 2-NP transformation was highly dependent on this parameter. For example, the concentration of the adsorbed Fe(II) equalling to $0.4 \mu\text{mol m}^{-2}$ corresponded to a k value of $5\text{E-}4 \text{ min}^{-1}$, which was much lower than a k value of $3\text{E-}3 \text{ min}^{-1}$ in the presence of $3 \mu\text{mol m}^{-2}$ adsorbed Fe(II). Figure 2C reveals the pronounced linear relationship between $\ln k$ and the Fe(II) concentration in homogeneous, the k value of 2-NP reductive transformation was increase with the increase of Fe(II) concentration.

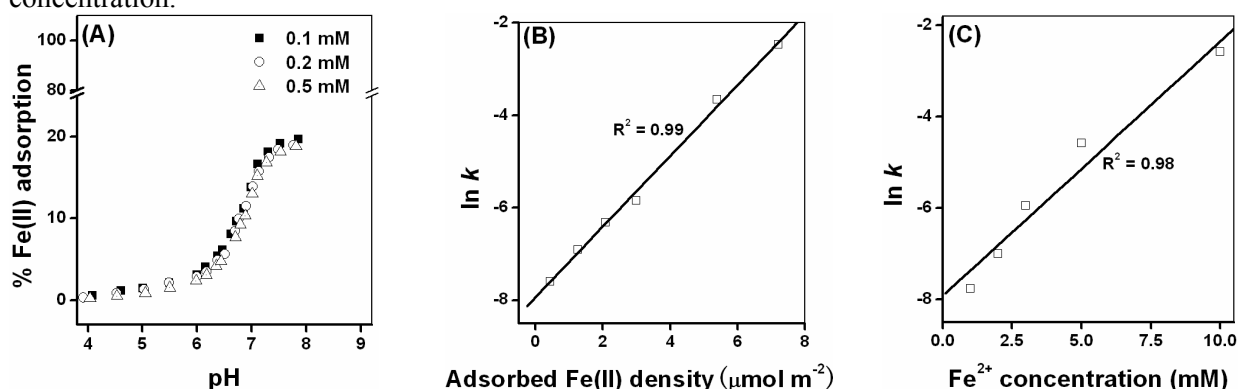


Figure 2. (A) Effects of pH and Fe(II) concentration on the adsorption of Fe(II) onto SiO₂; effects of adsorbed Fe(II) density on $\ln k$ (B) and effects of Fe(II) concentration on $\ln k$ in homogeneous system (C), respectively. Reaction conditions: 0.1-0.5 mmol/L of Fe(II), 4.0 g/L SiO₂ surfaces, pH 5-8, and 298 K for (A); 1-10 mmol/L of Fe(II), pH 6.7 and 298 K for (B) and (C).

Electrochemical evidence of the change in Fe^{III}/Fe^{II} redox potential

Voltammograms of adsorbed Fe(II) species on the SiO₂-modified GC electrode at various pH values provide a direct evidence of the change in its redox behaviour. It should be noted that repeatable scans of CV were performed, and that there was insignificant difference in the peak position with respect to the first three cycles, demonstrating the stability of the coated electrode (data not shown). Figure 3A, 3B illustrates the pH effect on the redox behaviour of the surface-complex Fe(II) and aqueous Fe(II) species onto SiO₂, and non-mineral, respectively. Clearly, all the voltammograms exhibited a pair of peaks: an anodic oxidation peak for Fe(II) at potentials ranging from -0.1 to 0.6 V (versus SCE), and a cathodic reduction peak for Fe(III) at potentials ranging from -0.6 to -0.1 V (versus SCE). Consistent with the theoretical results, both peaks shift toward more negative direction with the increase of pH. For instance, when pH was modulated from 5.5 to 6.7, the peak oxidation potential (denoted as E_p) of Fe(II) adsorbed onto SiO₂ significantly decreased from 0.230 to 0.024 V (versus SCE), and the E_p value of Fe(II) species in homogeneous system decreased from 0.443 to 0.243 V (versus SCE). The linear E_p reduction against pH was found in two sets of reactions on the SiO₂/GC, and GC electrodes. In the meantime, it can be seen that at any fixed pH, E_p values of SiO₂/GC was significant lower than that of GC electrode due to the Fe(II) adsorption onto the mineral (data not shown). In general, the negative shift of the Fe(II) oxidation potential thermodynamically reflects the movement of Gibbs free energy to a negative value. According to the linear free-energy relationship (LFER), Figure 3C presents the relationship between $\ln k$ of 2-NP transformation and E_p (versus SHE), and a good linear correlation was found. At the fixed E_p , the SiO₂ surface demonstrated the highest value of $\ln k$, while the homogeneous system had the lowest value. It thus can be concluded that an increase in the concentration of the adsorbed Fe(II) species might result in a negative shift of Fe(II) oxidation potential, which accounts for the enhanced transformation rates of 2-NP.

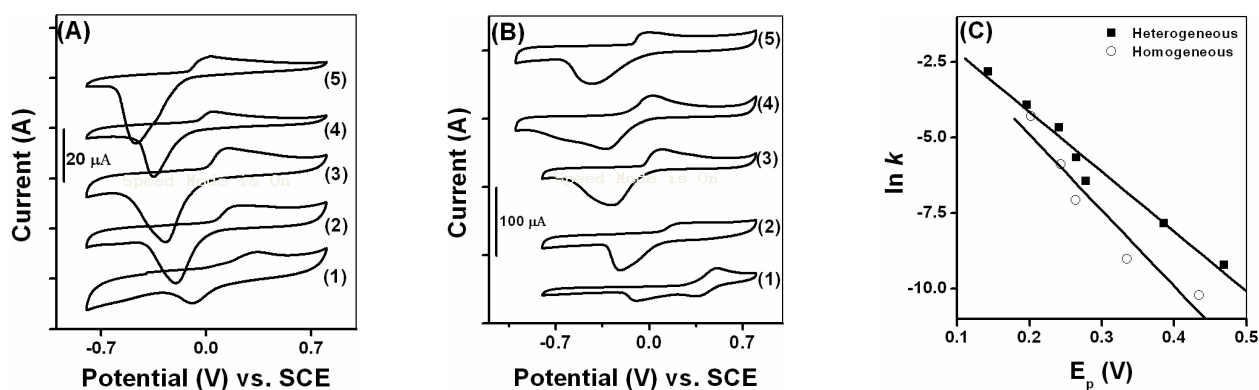


Figure 3. Cyclic voltammograms of Fe(II) adsorbed onto SiO₂-modified glassy carbon (GC) electrodes for (A) and bare glassy carbon (GC) electrodes for (B). Electrochemical measurements were conducted in 0.2 M NaCl solution at different pH values. Scan rate was 50 mV/s. (1) pH = 5.0; (2) pH = 5.5; (3) pH = 6.0; (4) pH = 6.5; and (5) pH = 6.7. Dependence of ln *k* on the *E_p* obtained from CV tests (C).

Conclusion

We have successfully demonstrated the role of Fe(II)-complexes in heterogeneous SiO₂ suspension and homogeneous Fe(II) solution for the reductive transformation of 2-NP by using electrochemical method. The first-order rate constant (*k* value) was found to be highly dependent on the experimental pH conditions. The resulting enhanced reaction rates were contributed to the increase in the adsorption concentration of surface-complexed Fe(II). An increase in pH or Fe(II) concentration gave rise to an elevated density of Fe(II) adsorbed to mineral surfaces, which further resulted in an enhanced reaction rate of 2-NP reduction. Moreover, CV tests provided direct evidence of negative shift of the peak oxidation potential of Fe(II) with the increase of pH. A good linear relationships between ln *k* and pH values, adsorbed Fe(II) density, or *E_p* were all quantified. These findings have implications for our general understanding of Fe(II) redox reactivity in more complicated heterogeneous anoxic environments.

References

- Benjamin MM, Leckie JO (1981) Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. *Journal of Colloid Interface Science* **79**(2), 209-221.
- Colon D, Weber EJ, Anderson JL, Winget P, Suarez LA (2006) Reduction of Nitrosobenzenes and *N*-Hydroxylanilines by Fe(II) Species: Elucidation of the Reaction Mechanism. *Environmental Science & Technology* **40**(14), 4449-4454.
- Hiemstra T, Riemsdijk WH (2007) Adsorption and surface oxidation of Fe(II) on metal (hydr)oxides. *Geochimica et Cosmochimica Acta* **71**(24), 5913-5933.
- Hofstetter TB, Heijman CG, Haderlein SB, Holliger C, Schwarzenbach RP (1999) Complete Reduction of TNT and Other (Poly)nitroaromatic Compounds under Iron-Reducing Subsurface Conditions. *Environmental Science & Technology* **33**(9), 1479-1487.
- Klausen J, Trober SP, Haderlein SB, Schwarzenbach RP (1995) Reduction of substituted nitrobenzenes by Fe(II) in aqueous mineral suspensions. *Environmental Science & Technology* **29**(9), 2396-2404.
- Li FB, Wang XG, Li YT, Liu CS, Zeng F, Zhang LJ, Hao MD, Ruan HD (2008) Enhancement of the reductive transformation of pentachlorophenol by polycarboxylic acids at the iron oxide-water interface. *Journal of Colloid Interface Science* **321**(2), 332-341.
- Li FB, Tao L, Feng CH, Li XZ, Sun KW (2009) Electrochemical Evidences for Promoted Interfacial Reactions: The Role of Adsorbed Fe(II) onto γ-Al₂O₃ and TiO₂ in Reductive Transformation of 2-Nitrophenol. *Environmental Science & Technology* **43** (10), 3656-3661.
- Nano GV, Strathmann TJ (2006) Ferrous iron sorption by hydrous metal oxides. *Journal of Colloid Interface Science* **297**(2), 443-454.
- Strathmann TJ, Stone AT (2003) Mineral surface catalysis of reactions between Fe^{II} and oxime carbamate pesticides. *Geochimica et Cosmochimica Acta* **67**(15), 2775-2791.
- Tao L, Li FB, Feng CH, Sun KW (2009) Reductive Transformation of 2-Nitrophenol by Fe(II) Species in γ-Aluminum Oxide Suspension. *Applied Clay Science* **46**, 95-101.