



## Reductive transformation of 2-nitrophenol by Fe(II) species in $\gamma$ -aluminum oxide suspension

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### ABSTRACT

Fe(II) adsorption onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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, Fe(II) concentration and reaction temperature. An increase in pH, Fe(II) concentration or reaction temperature 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. By using the diffuse double layer (DDL) surface complexation model, the dominant Fe(II) surface complex that was responsible for the high reactivity was predicted to be the strongly bound  $\equiv\text{SOFe}^+$  functional group (represented by  $\equiv\text{Al}_s\text{OFe}^+$ ) onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surfaces. In addition, cyclic voltammetry tests showed that the enhanced activity of Fe(II) species was attributed to the negative shift of the redox potential of Fe(III)/Fe(II) couple, resulted from the enhanced concentration of  $\equiv\text{Al}_s\text{OFe}^+$  complex.

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### 1. 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 (Rene et al., 1990; Frank et al., 1992; Rügge et al., 1998; Yan and Bailey, 2001; Naka et al., 2006) have reported that mineral-bound Fe(II) species can substantially promote the reduction transformation of nitro groups to the corresponding anilines under abiotic conditions (Stumm and Sulzberger, 1992; Klausen et al., 1995; Klupinski et al., 2004). Mechanistic studies with this heterogeneous reaction have demonstrated that the formation of surface complexes is responsible for the enhanced reaction rate (Hofstetter et al., 1999; Pecher et al., 2002; Strathmann and Stone, 2003; Li et al., 2008). 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 (Strathmann and Stone, 2003; Hiemstra and Riemsdijk, 2007). Moreover, the contribution of each individual species to the total reaction rate is different. For example, Nano and Strathmann (2008) reported that the concentration of a hydrolyzed surface complex (e.g.,  $\equiv\text{TiOFe(II)OH}$ ), other than the concentration of aqueous species or the concentration of unhydrolyzed surface complex, was

believed to be the key parameter to influence the reactivity of Fe(II) with NACs.

In nature, various minerals included in iron-contained soils (e.g., ferrihydrite, goethite, hematite, etc.) and iron-free soils (e.g., titania, silica and  $\gamma$ -aluminum oxide) are capable of providing functional sites to stabilize Fe(II) ions (Strathmann and Stone, 2003). Of our great interest is the investigation of alumina (Al<sub>2</sub>O<sub>3</sub>) used as the sole mineral surface for the adsorption of Fe(II) ions, due to the relatively high fraction of alumina in clays, varying from very low to 75% (Schoonen et al., 1998). According to a generalized surface complex model proposed by Strathmann's group, there are two primary surface complexes (weak and strong-binding of  $\equiv\text{SOFe}^+$  functional groups) resulted from the Fe(II) adsorption to  $\gamma$ -AlOOH or  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mineral surfaces (Nano and Strathmann, 2006). The identification of one kind of surface complexes that could play a dominant role in determining the overall reaction activity of NAC transformation is environmentally important, as the concentration of each surface complex is closely correlative with a number of environmental variables. Accordingly, the establishment of such relationships between the reaction rate and the density of dominant surface complex could help to understand the influence of environmental conditions on the reduction transformation of organic pollutants in the presence of Fe(II) and Al<sub>2</sub>O<sub>3</sub> minerals.

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). As an example, the Fe oxide mineral surface-bound Fe(III)/Fe(II) couple possesses a more negative redox potential compared

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with the aqueous Fe(III)/Fe(II) couple, thus leading to a higher reaction rate (Rush and Koppenol, 1987; Klausen et al., 1995; Buerge and Hug, 1998; Strathmann and Stone, 2002a,b). However, to our knowledge, in spite of the theoretical calculations, no experimental evidence of the difference in redox potential has been available in the 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powders under various experimental conditions. The major goal of this study was to explore the interfacial reactions between Fe(II) adsorption and the reductive transformation of 2-nitrophenol. The MINEQL+ (Environmental Research Software) program was applied to calculate the individual equilibrium Fe(II) species in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> suspensions and CV measurements were performed to identify the redox behavior of the adsorbed Fe(II) surface complex.

## 2. Materials and methods

### 2.1. Reagents

The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powders (Shanghai Chemical Reagent Factory (China)) were ground and sifted through 200-mesh before being used. Chemicals including 3-[N-morpholino]propanesulfonic acid (MOPS, >99.5%) and 2-[N-morpholino]ethanesulfonic acid monohydrate (MES, >99.5%) were purchased from Sigma-Aldrich (Germany). Chemicals including 2-nitrophenol (2-NP, 99.5%), 2-aminophenol (2-AB, 99.5%), FeSO<sub>4</sub>·7H<sub>2</sub>O (>99.5%) and methanol (HPLC) were purchased from Acros (Belgium). All chemicals were of analytical or higher grade and were used without further purification.

### 2.2. Kinetic studies

To prevent Fe(II) oxidation, all experiments were conducted inside an oxygen-free glovebox (Model Bactron II, Anaerobic Chamber, 200 plate capacity, USA). The glovebox atmosphere (99.999% N<sub>2</sub>) was continuously bubbled through NaOH solution (1 M) to remove dissolved CO<sub>2</sub>. Stock solutions of NaCl (0.20 M), MES (0.05 M), and MOPS (0.05 M) were prepared with reagent-grade water (18 M $\Omega$  cm resistivity, Milli-Q water). Stock solution of 2-NP (1.1 mM) was dissolved in methanol in the oxygen-free glovebox, and preserved in a dark-brown container. All solutions were filtered through 0.2  $\mu$ m filters prior to use. To study the reductive transformation of 2-NP in the presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, borosilicate glass serum bottles (20 mL) with aluminum crimps and Teflon-lined butyl rubber septa were employed as reactors. After adding 0.022 mM 2-NP, 3.0 mM FeSO<sub>4</sub>, 28 mM buffer, and 0.20 M NaCl together with 68.0 mg of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powders to these reactors, the reduction reactions were started by transferring the serum bottles to an orbital shaker at 200 rpm and 25  $\pm$  1 °C in the dark. Furthermore, to investigate the influences of various factors on the reaction rates, kinetic measurements were carried out over a wide range of conditions (pH from 5.5 to 7.3, Fe(II) concentration in the range between 1.0 mM and 10.0 mM, temperature from 288 K to 318 K). Due to the high possibility of Fe(II) being oxidized at circumneutral pH, the kinetic experiments at pH  $\geq$  6.5 were conducted with continuously bubbled nitrogen rather than on a rotator. The flow rate of nitrogen was 90 mL min<sup>-1</sup> which allows for the sufficient stirring of the suspension.

### 2.3. Adsorption studies

The adsorption of Fe(II) onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was conducted under the conditions identical to kinetic experiments, except that 0.022 mM 2-

NP was not added to the reactor. Individual batch studies were used to evaluate the influence of pH, Fe(II) concentration and temperature on the extent of Fe(II) adsorption. In detail, pH was changed from 4 to 8; Fe(II) concentrations were varied in the range between 0.1 mM and 0.5 mM; and temperature was modulated from 288 K to 318 K for this investigation. For equilibrium adsorption experiments, Fe(II) species were mixed with solid  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powders for a desired period of time at the controlled pH and temperature. After equilibrium, the final pH of each suspension was recorded before filtering (0.2  $\mu$ m membrane filter). The acidified filtrate was then collected for the analysis of the Fe(II) content.

### 2.4. Electrochemical tests

The preparation of a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-modified glassy carbon (GC) electrode started from a bare GC electrode (diameter: 3 mm). Prior to use, the GC electrode was polished with emery paper, followed with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powders of 1 and 0.06  $\mu$ m particle size and was thoroughly rinsed with double-distilled water between two polishing steps. Then it was successively cleaned with acetone and double-distilled water in an ultrasonic bath for 10 min, respectively. To obtain a Al<sub>2</sub>O<sub>3</sub> slurry, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (0.5 mg) was dispersed in a dilute Nafion solution (0.5 wt.%, 250  $\mu$ L) in an ultrasonic bath for 15 min. By use of a micro-syringe, aliquots (2  $\mu$ L) of the above suspension was allowed to coat on the clean GC electrode and dry in the air for 30 min prior to measurements.

Electrochemical measurements were carried out in a conventional three-electrode cell, equipped with a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> modified glassy carbon (GC) electrode as the working electrode, a saturated calomel electrode (SCE, +0.24 V versus the 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<sup>-1</sup>. The electrochemical cell contained 3.0 mM FeSO<sub>4</sub> and 0.20 M NaCl solution buffered with 0.028 M MES or MOPS and the solution pH was adjusted by adding diluted HCl or NaOH solution. Pure nitrogen was bubbled through the electrolyte to remove dissolved oxygen. CV tests were performed under pure nitrogen atmosphere at 25 °C.

### 2.5. Analytical methods

The concentration of 2-NP as a function of time was monitored by HPLC 2487 (5 mm Symmetry-C18, 4.6 mm, 250 mm, Waters, USA), which consists of a Waters 1525 Binary pump, an analytical reversed-phase column and a Waters dual  $\lambda$  Absorbance UV/Vis detector. The isocratic mobile phase contained 80/20 (V/V) of methanol/water and 3 mM of HCl at a flow rate of 1.0 mL min<sup>-1</sup> under isocratic conditions at 30  $\pm$  1 °C and the wavelength was set at 213 nm. Concentrations of 2-NP were calculated by comparison with standard solutions (Klupinski et al., 2004). For kinetic studies, one of the 20-ml serum bottles was taken from the shaker and transformed to the oxygen-free glovebox prior to routine analysis. After being mixed vigorously, the serum bottle was opened and spiked with 2 M HCl (<60  $\mu$ L) to give a pH < 3, preventing further degradation of 2-NP. The suspension was immediately centrifuged at 10,000 rpm for 10 min (Sigma-3K 15) to remove the particles and the supernates were remained for further analysis.

The remaining Fe(II) concentration was determined by the 1,10-phenanthroline method at 510 nm using a UV-visible spectrophotometer (TU-1800PC, Beijing Purkinje General Instrument Co. Ltd.) (Fadrus and Malý, 1975; Maitheepala and Doong, 2004; Jeon et al., 2005). The surface complexation of Fe(II) to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surfaces was obtained according to a two-site model that considers the formation of  $\equiv$ SOFe<sup>+</sup> complexes at both weak-binding and strong-binding sites (Nano and Strathmann, 2006). The MINEQL+ (Environmental Research Software) program was applied to calculate individual

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