



## Reductive transformation of p-nitrophenol by Fe(II) species: The effect of anionic media

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### HIGHLIGHTS

- p-NP reduction is the best at pH 7.6 by Fe(II) species in chloride medium.
- Sulfate and its dosage have markedly inhibitory effect on p-NP reduction.
- Chloride and its dosage have no obvious effect on p-NP reduction.
- Sulfate has selective adsorption on Fe hydroxide.
- Sulfate can form surface complexes on Fe hydroxide.

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### ABSTRACT

Electron exchange between aqueous Fe(II) and structural Fe(III) of iron minerals has been illustrated for understanding the reduction of nitroaromatic compounds (NAC). However, factors influencing Fe(II)-induced the reduction of NAC still remain elusive. In this paper, p-nitrophenol (1.5 mM) was selected to explore the effects of pH, the stabilizing ligands ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) of ferrous ions and the extra addition of iron hydroxide on the reduction of NAC via Fe(II) species. The results indicate that the reduction degree of is much lower in  $\text{SO}_4^{2-}$  medium than that in  $\text{Cl}^-$  medium at pH 7.6. p-Nitrophenol reduction increased in  $\text{SO}_4^{2-}$  medium and slightly decreased in  $\text{Cl}^-$  medium when Fe hydroxide was extra added.  $\text{Cl}^-$  strength ( $0.01\text{--}0.1\text{ mol L}^{-1}$ ) has no obvious effect on p-NP reduction.  $\text{SO}_4^{2-}$  species and its dosage have markedly inhibitory effect on p-NP reduction due to the selective adsorption of  $\text{SO}_4^{2-}$  and the formation of sulphated surface complexes on the fresh Fe hydroxide.

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### 1. Introduction

Nitroaromatic compounds (NAC) are toxic toward humans and animals. They widely exist in industrial wastewaters derived from farm chemicals, pharmaceuticals, and synthetic dyes [1]. Conventional biological methods are found to be ineffective for their degradation. Hence, a chemical reduction (oxidation) is necessary before the resulting aniline [2–4] or hydroquinone/catechol [5,6] can be further treated by enzyme-mediated oxidative polymerization. Studies [2–4] have reported that mineral-bound Fe(II) species can substantially promote the reduction transformation of nitro group to the corresponding aniline under anaerobic conditions.

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Mechanism of this heterogeneous reaction still remains elusive. Some studies [7–10] have demonstrated that the formation of surface complexes is responsible for the enhanced reaction rate. The mineral surface-bound Fe(III)/Fe(II) couple possesses a more negative redox potential compared with the aqueous Fe(III)/Fe(II) couple. Other studies [11–13] have demonstrated that electron exchange between adsorbed Fe(II) ( $\text{Fe(II)}_{\text{ads}}$ ) and structural Fe(III) of iron (hydr)oxides ( $\text{Fe(III)}_{\text{oxide}}$ ) is important for understanding the degradation of NAC. Recent studies [14–18] have provided strong evidence for interfacial  $\text{Fe(II)}_{\text{ads}}\text{--Fe(III)}_{\text{oxide}}$  electron transfer without change in mineralogy species under circumneutral pH and low  $[\text{Fe(II)}]$ . Studies [14,17] have observed exchange of Fe atoms between  $\text{Fe(II)}_{\text{ads}}$  and  $\text{Fe(III)}_{\text{oxide}}$  by Fe isotope tracer. However, the enhanced reduction of NAC has no direct relationship with exchange of Fe atoms because NAC reduction by  $\text{Fe(II)}_{\text{ads}}\text{--Fe(III)}_{\text{oxide}}$  is noticeably more rapid than the exchange of Fe atoms.

Additionally, factors such as structure, location, or Fe oxide species are important for contaminant reduction [9]. For example,

composition of Fe bearing mineral noticeably influences the reaction rate of NAC reduction by adsorbed Fe(II) [9,19]. However, when the Fe(II) sorption density are normalized on different iron oxides, the reaction rates are all within a half order of magnitude [19,20].

In view of the investigation above, the effect of chemical control on Fe(II)-induced NAC reduction is still complex. Herein p-nitrophenol (p-NP) was selected as the representative of NAC. Factors such as solution pH, stabilizing ligands ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) to ferrous ions, and extra addition of iron hydroxide were investigated in detail regarding their effects on Fe(II)-induced p-NP reduction. These investigations will provide important information on the reduction of NAC in the heterogeneous reaction via non-Fe or Fe mineral surface-bound Fe(II).

## 2. Experimental

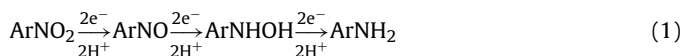
### 2.1. Materials

Ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), ferrous sulfate ( $\text{FeCl}_2 \cdot 7\text{H}_2\text{O}$ ), sodium hydroxide (NaOH), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), sodium chloride (NaCl) and p-nitrophenol were of analytical purity and were purchased from Zhiyuan Chemical Reagen Co., Ltd. (Tianjin, China). Distilled water was used. Goethite and lepidocrocite used in this paper were synthesized according to Ref. [21].

### 2.2. Reaction studies

Experiments of Fe(II)-induced p-NP reduction were performed in degassed p-NP solutions ( $1.5 \text{ mmol L}^{-1}$ , 150 mL). Reactions were conducted in a normal lab temperature (298–300 K).  $\text{Fe}^{2+}$  ions ( $0.50 \text{ mol L}^{-1}$ , 2.80 mL) and NaOH solution ( $1.5 \text{ mol L}^{-1}$ ) were dripped simultaneously into the reactor via peristaltic pump under stirring. The dripped speed of aqueous Fe(II) was  $0.45 \text{ mL min}^{-1}$ . The titration rate of NaOH solution was regulated by maintaining a desired pH. Suspension was periodically sampled and immediately centrifuged at 4000 rpm for 2 min. The supernate was collected for the measurement of p-NP concentration by HPLC. All experiments were performed in duplicate. Pure nitrogen was bubbled throughout the reaction system for the removal of dissolved oxygen as possible.

The reduction of the nitro group has been intensely studied electrochemically [22,23]. As illustrated in Eq. (1), transformation of one nitro group into corresponding aniline needs  $6e^-$ , whereas, transformation of one Fe(II) into corresponding Fe(III) lose only one  $e^-$ . So, the molar ratio of Fe(II) to p-NP in all experiments herein was designated as 6:1.



Goethite ( $\alpha\text{-FeOOH}$ ) was selected as a Fe hydroxide to study the interaction of sulfate ions ( $\text{SO}_4^{2-}$ ) with Fe hydroxide since it had no interference for the absorbency peaks at  $900\text{--}1250 \text{ cm}^{-1}$ . The experiment was performed by mixing 0.020 g of  $\alpha\text{-FeOOH}$  with 30 mL of  $\text{Na}_2\text{SO}_4$  solution ( $0.05 \text{ mol L}^{-1}$ ) in a 50 mL glass vial to reach reaction equilibrium in a constant temperature shaker (ZHWY-2102C, Shanghai, China) with rotation speed of 200 rpm at 298 K. After the interaction of  $\text{SO}_4^{2-}$  with  $\alpha\text{-FeOOH}$  for 2 h, the resulting product was immediately separated by suction filtration and rinsed with distilled water and ethanol for several times and dried at  $40^\circ\text{C}$  for 4 h in a vacuum oven.

### 2.3. Analytical and characteristic techniques

HPLC analysis was performed with the following system: Agilent1100 Series, USA with a UV detector ( $\lambda = 316 \text{ nm}$ ) and methanol/water/acetic acids (v/v/v) at 50/49.8/0.2 mobile phase

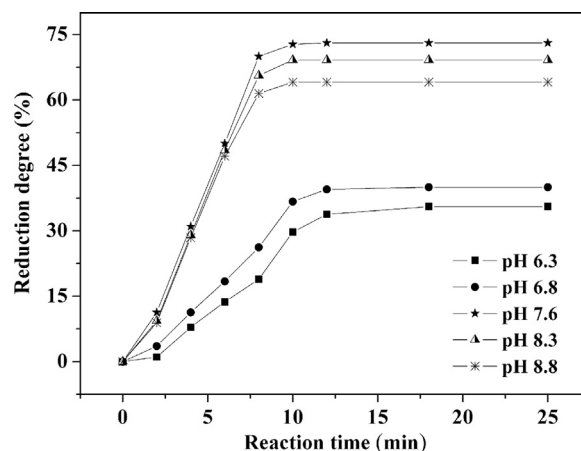


Fig. 1. Effect of pH on p-NP reduction by Fe(II) species in  $\text{Cl}^-$  medium.

at a flow rate of  $1.0 \text{ mL min}^{-1}$ . Components were separated on a reverse-phase column (ZORBAX Eclipse XDB-C18, Agilent, USA,  $5 \mu\text{m}$ ,  $4.6 \text{ mm} \times 150 \text{ mm}$ ) with column temperature at 303 K. Samples were injected in volume of  $15 \mu\text{L}$ . FTIR spectrophotometer (Japan Hitachi 8900series) was used for spectral analysis. Fe(II) concentration was determined spectrophotometrically using a modified phenanthroline method [24].

## 3. Results and discussion

### 3.1. Role of pH

Fe(II)-induced p-NP reduction varies as a function of pH (Fig. 1). The final extent of p-NP reduction at different pHs follows the precedence relationship:  $\text{pH } 6.3 < \text{pH } 6.8 < \text{pH } 8.8 < \text{pH } 8.3 < \text{pH } 7.6$ . p-NP reduction at pH 6.3–6.8 markedly lags behind that at pH 7.30–8.8. Tjisse H. et al. [10] have calculated by charge distribution model that at  $\text{pH} < 7$ , adsorbed ferrous iron is present as adsorbed  $\text{Fe}^{2+}$  while above  $\text{pH} > 7.5$ , it is adsorbed as a  $\text{Fe(III)(OH)}_2$  ion with electron transfer to the surface of iron oxides. And these results also agree with a recent mossbauer study [25]. Here the highest degree of p-NP reduction occurs at pH 7.6, consistent with the pH that favors electron transfer between Fe(II) and ferric minerals reported by studies [8,10,26].

The reduction degree of p-NP decreases at pH 8.3–8.8 compared with that at pH 7.6. This may be ascribed to the different phase transformation of Fe(II). The post-reaction sludges, obtained at different pH values, were characterized by FTIR and XRD, respectively. The assignments of the prominent absorption peaks are marked in Figs. 2 and 3, respectively. For  $\gamma\text{-FeOOH}$ , the bands appear at  $1022 \text{ cm}^{-1}$  and  $745 \text{ cm}^{-1}$  for the in-plane and out-of-plane Fe—O—H bending vibrations [27,28], whereas, the band at  $567 \text{ cm}^{-1}$  is assigned to characteristic peak of  $\text{Fe}_3\text{O}_4$ . The results show that a single phase of  $\gamma\text{-FeOOH}$  is obtained at pH 7.6 (Figs. 2a and 3a). A mixture of  $\gamma\text{-FeOOH}$  and  $\text{Fe}_3\text{O}_4$  occurs (Figs. 2b, c and 3b, c) with an increase in the pH value ( $\text{pH} > 8.3$ ), i.e., part of Fe(II) forms  $\text{Fe}_3\text{O}_4$  lattice rather than enters p-NP reduction.

### 3.2. Role of ligands

Mineral assemblage is impacted by ligand ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) type at circumneutral pH as it follows abiotic reaction of ferrous Fe with ferrihydrite [29,30]. Fe(II)-induced p-NP reduction also varies with ligand species of ferrous Fe (Fig. 4a). The degree of p-NP reduction is strikingly lower at various time points in  $\text{SO}_4^{2-}$  medium than that in  $\text{Cl}^-$  medium at pH 7.6. About 73% of p-NP was finally reduced

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