

# The influence of Si(IV) on the reactivity of $[\equiv\text{Fe(III)}]/[\equiv\text{Fe(II)}]$ couples for 2-nitrophenol reduction in $\gamma\text{-Al}_2\text{O}_3$ suspensions

Liang Tao <sup>a</sup>, Shan-Li Wang <sup>b</sup>, Fang-Bai Li <sup>a\*</sup>, Nin-Ya Yu <sup>c</sup>, Ke Wu <sup>a, c</sup>

<sup>a</sup> Guangdong Key Laboratory of Integrated Agro-environmental Pollution Control and Management,  
Guangdong Institute of Eco-environmental Science & Technology, Guangzhou 510650, P. R. China

<sup>b</sup> Department of Agricultural Chemistry, National Taiwan University, Taipei 10617, Taiwan, Republic of  
China

<sup>c</sup> College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, P. R.  
China

**11 Pages**

**8 Sections**

**5 Figures**

**1 Table**

Submitted to RSC Advances

---

\*Corresponding author. Tel: 86-20-37021396; Fax: 86-20-87024123. E-mail: [cefbli@soil.gd.cn](mailto:cefbli@soil.gd.cn) (Fangbai Li)

## Section S1 Adsorption Study

Batch studies were conducted to assess the influence of pH (from 4.0 to 8.0) on the extent of Fe(II) adsorption using the similar method with modification (Li et al., 2009). In detail, to prevent any Fe(II) oxidation, all experiments were conducted inside an oxygen-free glovebox (Model Bactron II, Anaerobic Chamber, 200 plate capacity, USA) at 298 K. Stock solutions of 0.5 M FeCl<sub>2</sub> (> 99.0%, Acors), 0.06 M MES (2-[N-morpholino] ethanesulfonic acid monohydrate, > 99.5%, Sigma-Aldrich), 0.06 M MOPS (3-[N-morpholino] propanesulfonic acid, > 99.5%, Sigma-Aldrich), and 0.44 M NaCl were prepared with reagent-grade water (18 MΩ cm resistivity, Milli-Q water). Equal volume of buffer (MES or MOPS) and NaCl were mixed together and the solution pH (4.0 to 8.0) was then adjusted by adding diluted HCl or NaOH solution. After that, different amount of Si(IV) was dissolved into the above solution and solutions were filtered through 0.2 μm filter prior to use. Suspensions prepared for the reactor contained 0.5 mM Fe(II), 0~0.75 mM Si(IV) (Na<sub>2</sub>SiO<sub>3</sub>·5H<sub>2</sub>O, > 99.0%, Acors), 28 mM buffer, 200 mM NaCl and 68.0 mg of γ-Al<sub>2</sub>O<sub>3</sub> mineral powder (Alu-C, 13 nm, Degussa) were then placed on a rotator at 200 rpm and 298 K. After equilibrium, the final pH of each suspension was recorded before filtering (0.2-μm membrane filter). The acidified filtrate was then collected for analysis of the Fe(II) content.

## Section S2 Analyses.

The concentration of 2-NP as a function of reaction time was monitored by HPLC 2487 (5 μm 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 λ Absorbance UV/Vis detector as described elsewhere (Li et al., 2009; Tao et al., 2010). The isocratic mobile phase contained 80/20 (v/v) methanol/water and 3 mM HCl at a flow rate of 1.0 ml min<sup>-1</sup> under isocratic conditions at 30 ± 1 °C and the wavelength was set at 213 nm. Concentrations of 2-NP were calculated by comparison with standard solutions [1]. For 2-NP 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 ( $< 60 \mu\text{L}$ ) to adjust pH to below 3 for preventing further degradation of 2-NP. The suspension was immediately centrifuged at 10000 rpm for 10 min (Sigma-3K 15) to remove the particles and the supernates were remained for further analysis.

### **Section S3 Electrochemical tests.**

Electrochemical tests were applied using the same methods as previous studies (Li et al., 2009; Tao et al., 2009; 2010). In detail, mineral-modified glassy carbon (GC) electrodes were prepared using bare GC electrodes with a diameter of 3 mm, in which a GC electrode was initially polished with emery paper, followed by  $\text{Al}_2\text{O}_3$  powders (particle sizes of 0.06 and 1  $\mu\text{m}$ ). Between the two polishing steps, the electrode was thoroughly rinsed with deionized water. The polished electrode was sequentially cleaned with acetone and water in an ultrasonic bath for 10 min. Then, the mineral slurry containing 5 mg of  $\gamma\text{-Al}_2\text{O}_3$  was prepared in a dilute Nafion solution (0.5 wt%, 250  $\mu\text{L}$ ) and placed in an ultrasonic bath for 15 min. By using a micro-syringe, aliquots (2  $\mu\text{L}$ ) of the above slurry were coated on the clean GC electrode, and the electrode with the coating was air dried for 30 min prior to use. The mineral-modified glassy carbon electrode is named " $\gamma\text{-Al}_2\text{O}_3/\text{GC}$ ".

Electrochemical measurements were carried out in a standard three-electrode cell, consisting of a working electrode ( $\gamma\text{-Al}_2\text{O}_3/\text{GC}$ ), a counter electrode (platinum spiral) and a saturated calomel electrode (SCE) as the reference electrode (Li et al., 2009; Tao et al., 2009; 2010). Cyclic voltammograms were recorded with an Autolab potentiostat (PGSTAT 30, Eco Chemie, The Netherlands) at a scan rate of 50  $\text{mV s}^{-1}$ . The electrochemical cell was filled with a solution containing 3.0 mM  $\text{FeCl}_2$  and 0.20 M NaCl buffered with 28 mM MES (2-Morpholin-4-yl-ethanesulfonic acid, hydrate) or MOPS (3-N-morpholino propanesulfonic

acid) and the solution pH was adjusted by adding diluted HCl or NaOH solution. High purity nitrogen gas was bubbled through the above electrolyte to remove dissolved oxygen. CV tests were performed under nitrogen atmosphere at 25 °C.

**Table S1** The kinetic fitting results of Fe(II) and Si(IV) adsorbed onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at pH 6.9.

$Q_{e, \text{exp}}$ (mmol·g <sup>-1</sup> )			Pseudo-first-order			Pseudo-second-order		
			$K_1$ (min <sup>-1</sup> )	$Q_{e, \text{cal}}$ (mmol·g <sup>-1</sup> )	$R^2$	$K_2$ (g·mmol <sup>-1</sup> ·min <sup>-1</sup> )	$Q_{e, \text{cal}}$ (mmol·g <sup>-1</sup> )	$R^2$
Fe(II) adsorption	Only Fe(II)	0.049	0.274	0.038	0.992	14.085	0.053	0.999
	Fe(II)+ Si(IV)	0.043	0.245	0.025	0.949	18.603	0.046	0.998
Si(IV) adsorption	Only Fe(II)	0.099	0.176	0.033	0.848	10.478	0.101	0.988
	Fe(II)+ Si(IV)	0.090	0.207	0.022	0.730	13.923	0.092	0.988

**Section S4** The quantity of adsorption ( $Q_t$ ) data for Fe(II) and Si(IV) under different conditions were fit with pseudo first-order (formula 1) and pseudo second-order methods (formula 2), and the results are shown in Table S1 and Figure S2.

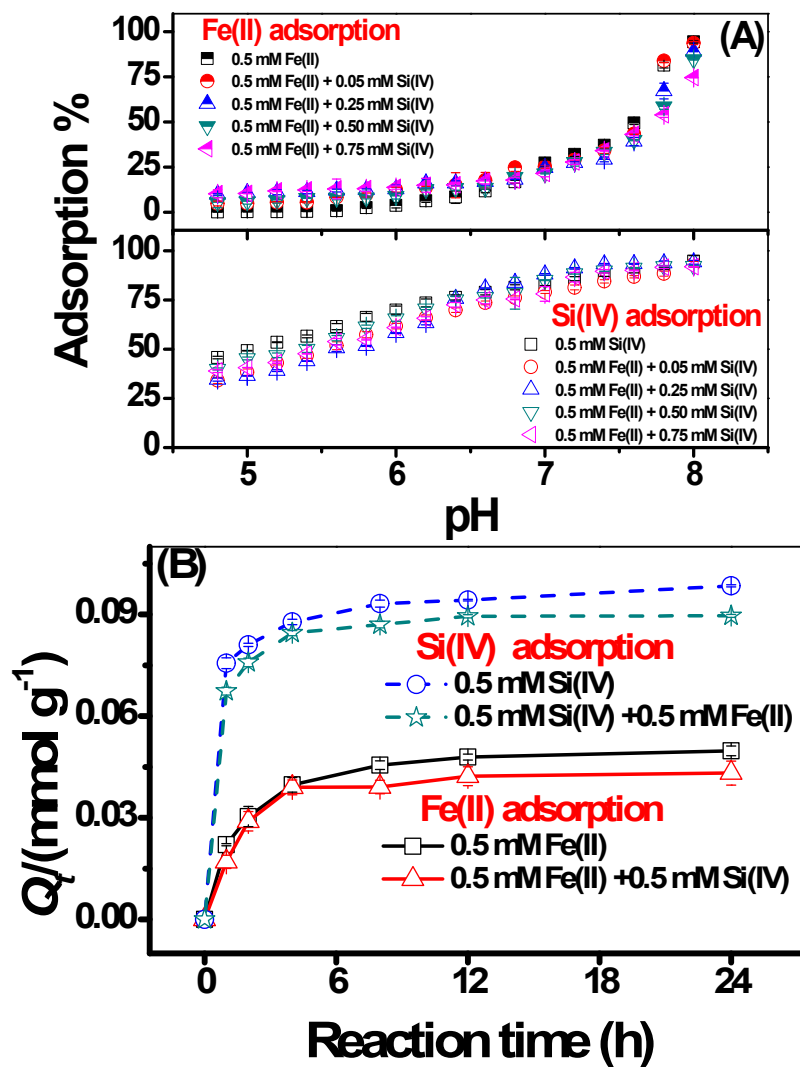
$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (\text{formula 1})$$

$$t/Q_t = 1/k_2 Q_e^2 + t/Q_e \quad (\text{formula 2})$$

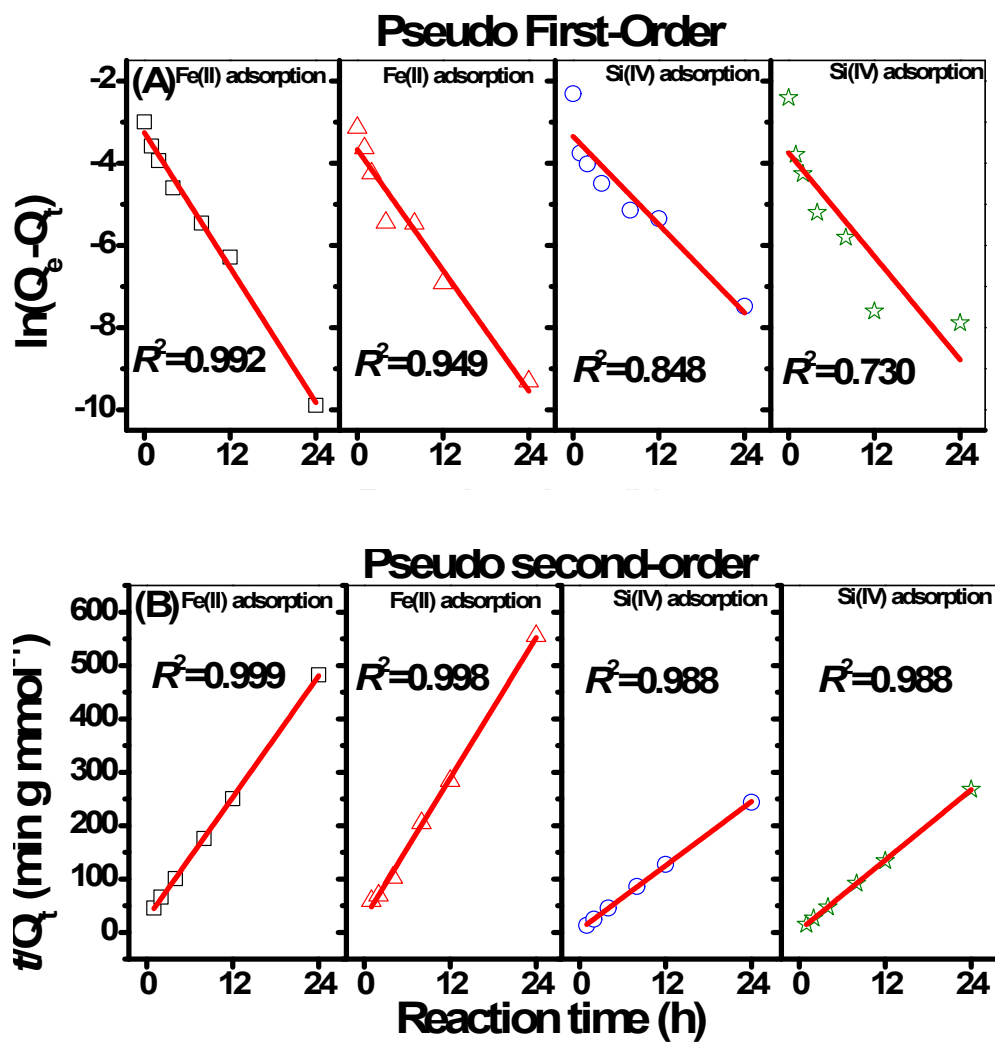
where  $t$  is the adsorption time,  $Q_e$  is the equilibrium adsorption quantity,  $Q_t$  is the adsorption quantity at adsorption time  $t$ , and  $k_1$  and  $k_2$  are the pseudo first-order kinetic adsorption constant and the pseudo second-order kinetic adsorption constant, respectively.

As revealed by the coefficient of determination (i.e.,  $R^2$  value), the pseudo second-order model provided fit the experimental data better than the pseudo first-order model. The calculated  $Q_e$  ( $Q_{e, \text{cal}}$ ) values from the pseudo second-order model were closer to the experimental  $Q_e$  ( $Q_{e, \text{exp}}$ ) values than their counterparts from the pseudo first-order model under all the experimental conditions. Hence, Fe(II) and Si(IV) adsorptions onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> followed the pseudo second-order model.

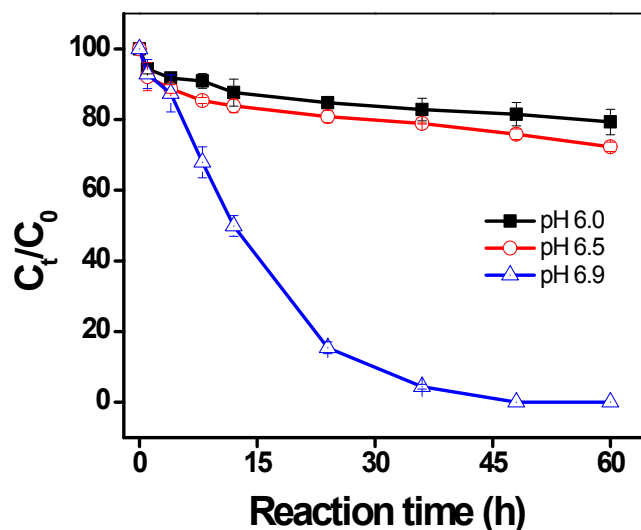
**FIGURE S1** Fractional adsorption of Fe(II) and Si(IV) on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a function of pH (A). The kinetic curves of Fe(II) and Si(IV) adsorbed onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under different conditions (B). Reaction conditions: 0.5 mM Fe(II), 0 to 0.75 mM Si(IV), pH 4-8, 4.0 g·L<sup>-1</sup> mineral, and 298 K.



**FIGURE S2** Kinetic plots fitted by pseudo first-order (A) and pseudo second-order methods (B) under different conditions. Reaction conditions: 0.5 mM Fe(II), 0.5 mM Si(IV), pH 6.9, 4.0 g·L<sup>-1</sup> mineral, and 25 °C.



**FIGURE S3.** The kinetic curves of 2-NP transformation under different pH concentrations. Reaction conditions: 0.5 mmol·L<sup>-1</sup> Fe(II), 5.5 μM 2-nitrophenol, 4.0 g L<sup>-1</sup> mineral and 25 °C.



**Section S5** Reduction of 2-NP in reaction media consisting of Fe(II) and minerals were studied at pH 6.7 and 25 °C. Figure S2 shows the comparison of reaction kinetics obtained under different pH conditions. Apparently, the rates of 2-NP reduction by Fe(II) were significantly enhanced with an increase in pH. Further analysis of the linear relationship between  $\ln \frac{[2-NP]_t}{[2-NP]_0}$  and reaction time reveals that the transformation of 2-NP generally

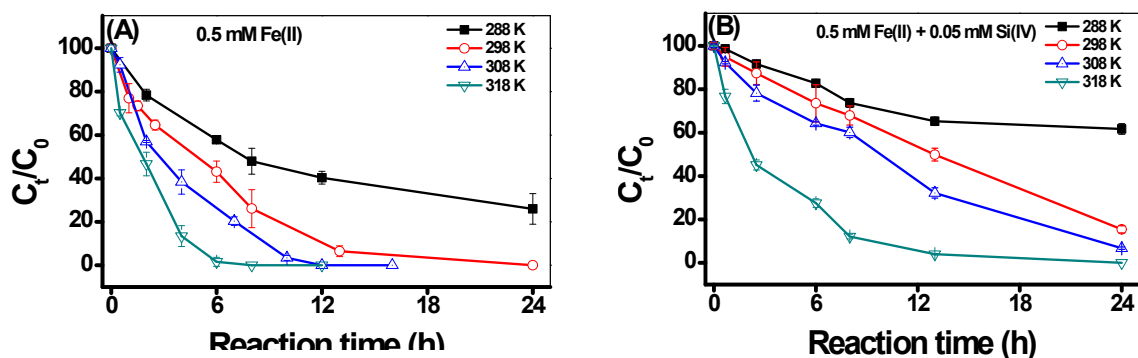
follows the pseudo-first-order kinetic rate law in the media consisting of Fe(II), 2-NP and minerals. That is,

$$\ln \frac{[2-NP]_t}{[2-NP]_0} = -kt \quad (1)$$

where  $[2-NP]_0$  and  $[2-NP]_t$  (M) are concentrations of 2-NP detected at the initial time and the reaction time, respectively;  $k$  (min<sup>-1</sup>) value is the pseudo-first-order kinetic constant for 2-NP transformation; and  $t$  (min) is the reaction time. The calculated reduction rate ( $k$ ) using pseudo -first-order rate was  $0.32 \times 10^{-2}$ ,  $0.42 \times 10^{-2}$ , and  $8.74 \times 10^{-2}/h^{-1}$ , respectively.

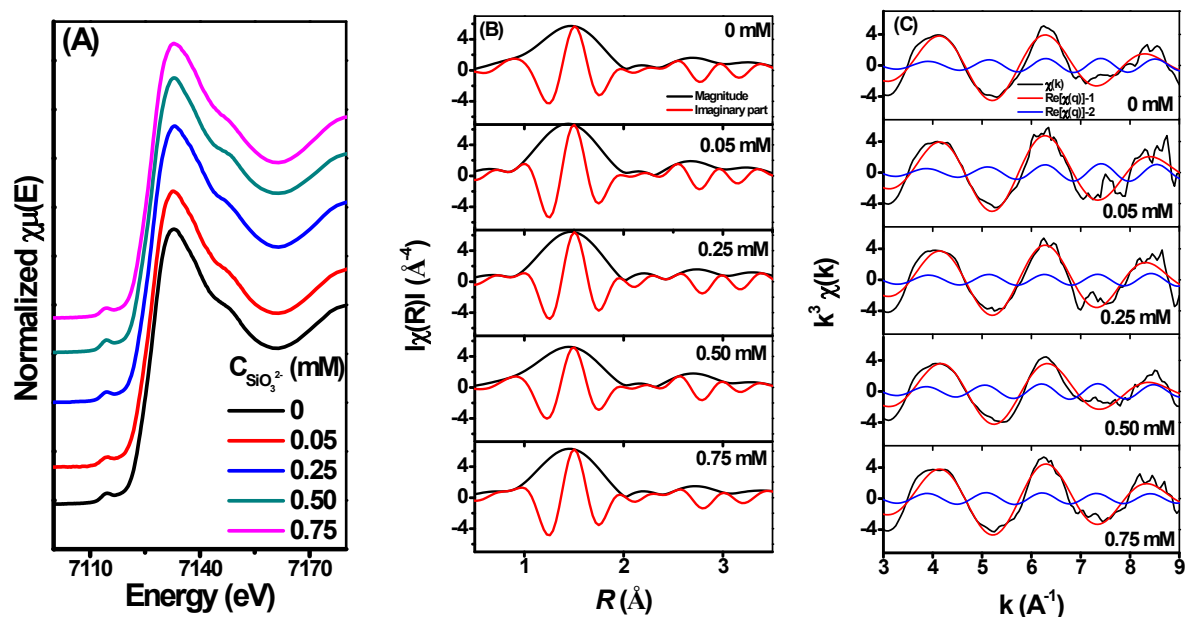


**FIGURE S4** Effects of temperature on the transformation of the 2-NP in  $\gamma\text{-Al}_2\text{O}_3$  suspension under different conditions with Fe(II) (A), and Fe(II) with Si(IV) (B). Reaction conditions:  $0.5\text{ mmol}\cdot\text{L}^{-1}\text{Fe(II)}$ ,  $0\text{ to }0.75\text{ mmol}\cdot\text{L}^{-1}\text{Si(IV)}$ ,  $5.5\text{ }\mu\text{mol}\cdot\text{L}^{-1}\text{2-NP}$ ,  $4.0\text{ g L}^{-1}\text{ mineral}$ , pH 6.9, and 288-318 K.



**Section S6** Figure S4 shows the effects of Si(IV) concentration on the reductive transformation of 2-NP under different temperatures. The calculated  $k$  values was increased from  $7.61 \times 10^{-2}$  to  $52.7 \times 10^{-2}\text{ h}^{-1}$  (with only Fe(II)) and from  $2.78 \times 10^{-2}$  to  $29.6 \times 10^{-2}\text{ h}^{-1}$  (with Fe(II) and Si(IV)) with the increase of temperature from 288 to 318K, respectively, indicating the reduction of 2-NP is a endothermic reaction. The obtained results also indicate that the addition of Si(IV) decreased the reductive transformation of 2-NP under all the reaction temperatures.

**FIGURE S5.** The Fe *K*-edge XANES spectra (A), *R* space (B), and the Fe *K*-edge  $k^3$ -weighted EXAFS spectra (C) under different Si(IV) concentrations at pH 6.9.



**Section S7** Under these different Si(IV) concentrations, all of the samples showed similar Fe *K*-edge XANES spectra (Figure S4A) characteristic features: the position and shape of the pre-edge peak, the inflection point of the absorption edge and the white line. Meanwhile, the *R* space (Figure S4B) of these samples showed no significant difference between the experimental line (black) and the calculated imaginary part line (red). Furthermore, Figure S4C shows the Fe *K*-edge  $k^3$ -weighted EXAFS spectra of these samples with the contribution of the first shell ( $R=0.8\sim 2.2$ ) presented by the red line and the contribution of the second shell ( $R=2.2\sim 3.2$ ) presented by the green line. The fits, demonstrated by the dotted line in Figure S4C, were in excellent agreement with the corresponding measured spectra (black line).

## Section S8 REFERENCES

- Li, F., Tao, L., Feng, C., Li, X., Sun, K., 2009. Electrochemical Evidences for Promoted Interfacial Reactions: The Role of Fe(II) Adsorbed onto  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> in Reductive Transformation of 2-Nitrophenol. *Environmental science & technology* 43, 3656-3661.
- Tao, L., Li, F., Feng, C., Sun, K., 2009. Reductive transformation of 2-nitrophenol by Fe(II) species in  $\gamma$ -aluminum oxide suspension. *Applied Clay Science* 46, 95-101.
- Tao, L., Li, F.B., 2010. Interaction between reductive transformation of 2-nitrophenol and adsorbed Fe(II) species. *Proceedings of the 19th World Congress of Soil Science: Soil solutions for a changing world, Brisbane, Australia, 1-6 August 2010.*, 86-89.