Electronic Supplementary Information

The double influence mechanism of pH to the arsenic removal by nano zero valent iron: electrostatic interactions and the corrosion of Fe⁰

Can Wu,①a Jingwei Tu,①a Weizhen Liu,①a Jing Zhang,①b Shengqi Chu,①b Guining Lu,①a Zhang Lin*①a and Zhi Dang①a

① School of Environment and Energy, South China University of Technology, The Key Laboratory of Pollution Control and Ecosystem Restoration in Industry Clusters (Ministry of Education), Guangdong Engineering and Technology Research Center for Environmental Nanomaterials, Guangzhou Higher Education Mega Center, Guangzhou, Guangdong 510006, China. E-mail: zlin@scut.edu.cn; Tel: 86-20-39380503; Fax: 86-20-39380508

①Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

Postal Address: School of Environment and Energy, South China University of Technology, Guangzhou Higher Education Mega Center, Guangzhou, Guangdong 510006, China
**Fig. S1** SEM image of nZVI after corrosion at pH 4 (a), 7 (b), and 10 (c).

**Fig. S2** Evolution of solution pH during As(V) removal by nZVI with initial solution pH of 4, 7 and 10.
The corrosion mechanism of nZVI at vary pH.

The increasing pH value condition would decreases the lepidocrocite content but increases the magnetite/maghemite content in the corrosion products of nZVI. Which has been reported in the previous study. The study by Dong\textsuperscript{1} shows that, at pH 5, the corrosion products of nZVI main is lepidocrocite, and at pH 10, the main corrosion products of nZVI is magnetite/maghemite.

The corrosion mechanism of nZVI is a complex scientific issue. How pH affects the formation of the oxide layer at the nZVI surface is not fully understood, thus more research is needed to study the effect of pH on metal removal by nZVI to determine the specific impact on each removal mechanism. Therefore, the corrosion mechanism of nZVI has been speculated.

Under basic condition, the formation mechanism of magnetite/maghemite could be shown as follows\textsuperscript{2,3}: 

Fig.S3 Fe k-edge XANES spectra and linear combination fits (LCF) of As(V)-treated nZVI at initial pH 4.0 (a) and 10.0 (b).
2 Fe⁰ + O₂ + 2 H₂O → 2 Fe²⁺ + 4 OH⁻ \quad (1)

Fe²⁺ + 2 H₂O → Fe(OH)₂ + H⁺ \quad (2)

3 Fe(OH)₂ → Fe₃O₄ + 2 H⁺ + 2 H₂O \quad (3)

4 Fe₃O₄ + O₂ → 6 Fe₂O₃ \quad (4)

Obviously, the basic condition accelerates the consumption of H⁺ in equal (3), which is in favor of the formation of Fe₃O₄ and Fe₂O₃.

Under acidity condition, the formation mechanism of lepidocrocite could be shown as follows⁴:

2 Fe⁰ + O₂ + 2 H₂O → 2 Fe²⁺ + 4 OH⁻ \quad (5)

4 Fe²⁺ + O₂ + 2 H₂O → 4 Fe³⁺ + 4 OH⁻ \quad (6)

Fe³⁺ + 3 H₂O → Fe(OH)₃ + 3 H⁺ \quad (7)

Fe(OH)₃ → FeOOH + H₂O \quad (8)

The acidity condition accelerates the consumption of OH⁻ in equal (6), which is in favor of the formation of FeOOH.