

Supporting Information for  
Polyoxometalate-Enhanced Oxidation of Organic Compounds  
by Nanoparticulate Zero-Valent Iron and Ferrous Ion  
in the Presence of Oxygen

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Prepared April 4, 2008

The supporting information consists of 6 pages, including 5 figures.

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## Supporting Information S1

Estimation of  $K$  from the redox potentials of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{POM}/\text{POM}^-$



$$E_H^0(\text{POM}/\text{POM}^-) - E_H^0(\text{Fe}^{3+}/\text{Fe}^{2+}) = -\Delta G^0/nF = (RT/nF) \ln K$$

Where,  $F = 9.65 \times 10^4 \text{ C/mol}$ ,  $R = 8.314 \text{ J/mol/K}$ ,  $E_H^0(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.771$ ,  $E_H^0(\text{POM}/\text{POM}^-) = +0.218 \text{ V}$

Therefore,  $K = \text{Exp}[(0.218-0.771) \times (9.65 \times 10^4) / (8.314 \times 293)] = \underline{\underline{\mathbf{3.06 \times 10^{-10}}}}$

S1-2. Estimation of the redox potential of  $\text{Fe}^{\text{(III)}}\text{-POM}/\text{Fe}^{\text{(II)}}\text{-POM}$  from the  $K$  value determined in this study ( $2.26 \times 10^{-2}$ )

$$\begin{aligned} E_H^0(\text{Fe}^{\text{(III)}}\text{-POM}/\text{Fe}^{\text{(II)}}\text{-POM}) &= (RT/nF) \ln K + E_H^0(\text{POM}/\text{POM}^-) \\ &= 0.218 - [(8.314 \times 293) / (9.65 \times 10^4) \times \ln(2.26 \times 10^{-2})] \\ &= \underline{\underline{\mathbf{0.314 \text{ V}}}} \end{aligned}$$

## Supporting Information S2

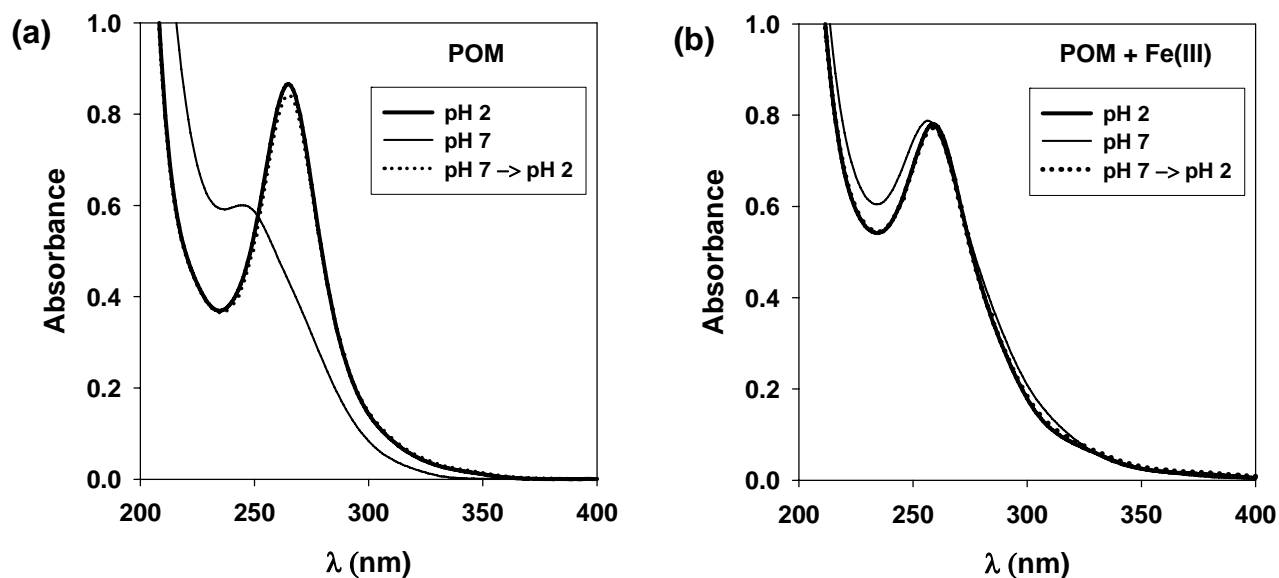


Figure S1. Reversible UV-vis absorption spectra of (a) POM and (b) Fe(III)-POM complexes:  $[\text{Fe(III)}]_0 = [\text{POM}]_0 = 20 \mu\text{M}$ ; Deaerated conditions (argon saturation).

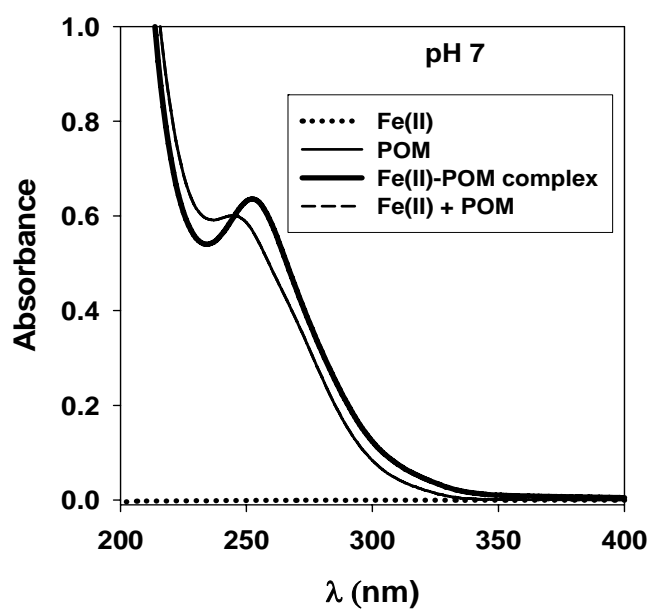


Figure S2. UV-vis absorption spectra of the solutions of POM and Fe(II) at pH 7:  $[\text{Fe(II)}]_0 = [\text{POM}]_0 = 20 \mu\text{M}$ ; Deaerated conditions (argon saturation).

## Supporting Information S3

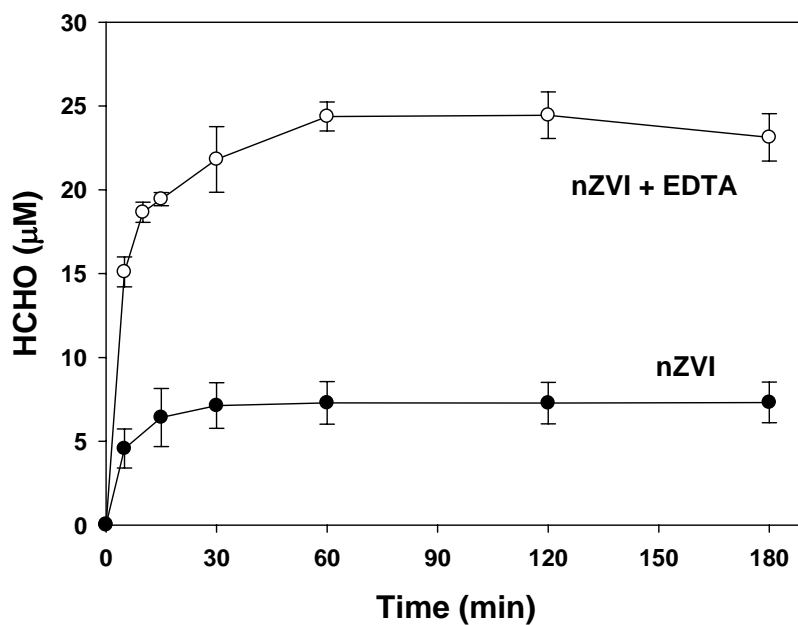


Figure S3. Effect of EDTA on HCHO production from nZVI:  $[\text{Fe}^0]_0 = [\text{Fe(II)}]_0 = 0.15 \text{ mM}$ ,  $[\text{EDTA}]_0 = 0.25 \text{ mM}$ ;  $[\text{methanol}]_0 = 100 \text{ mM}$ ;  $\text{pH} = 7$ .

## Supporting Information S4

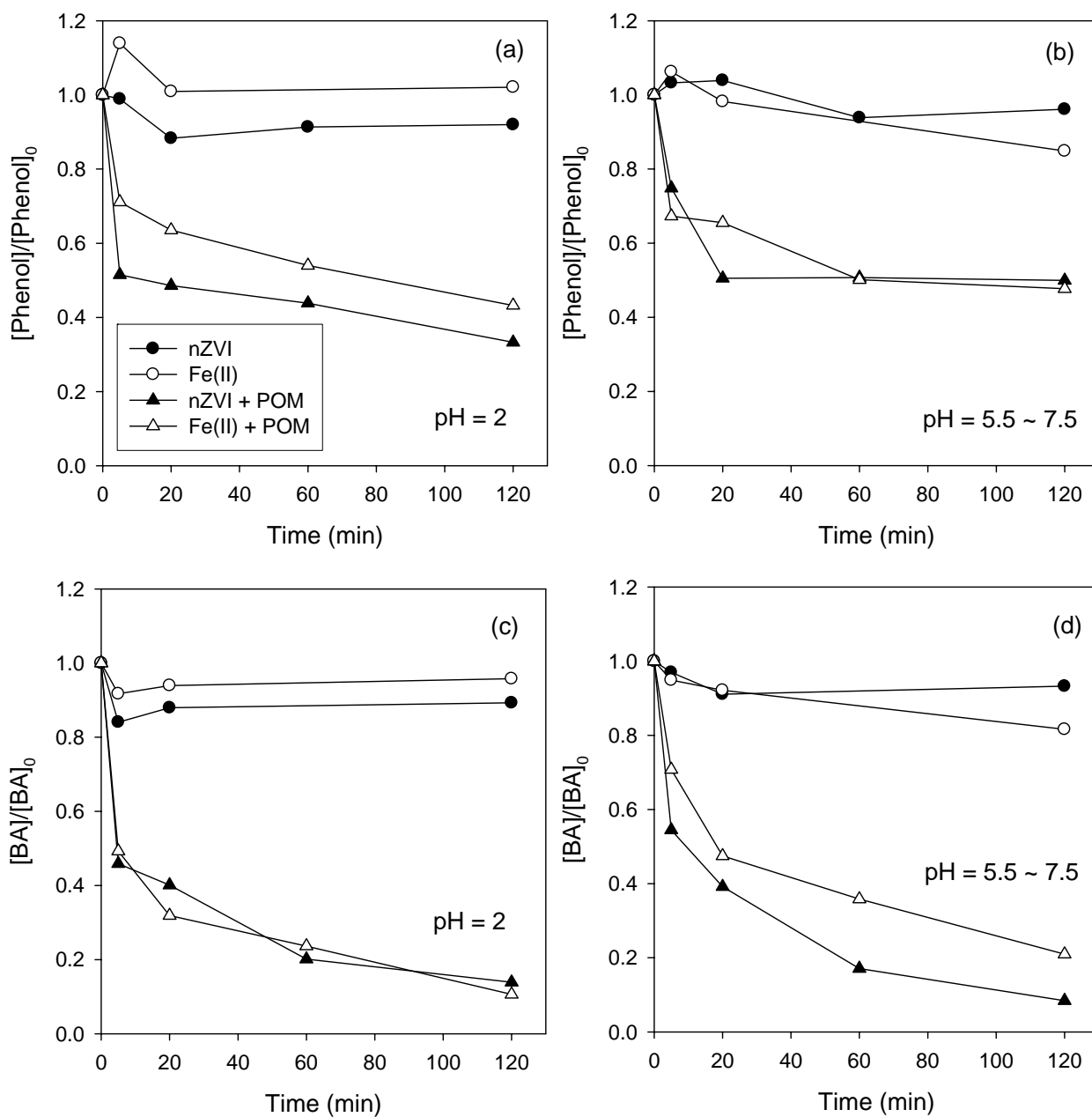


Figure S4. Degradation of organic compounds by nZVI and Fe(II) in the absence and presence of POM:  $[Fe^0]_0 = [Fe(II)]_0 = 1 \text{ mM}$ ;  $[POM]_0 = 1 \text{ mM}$ ;  $[phenol]_0 = [benzoic \text{ acid}]_0 = 10 \text{ }\mu\text{M}$

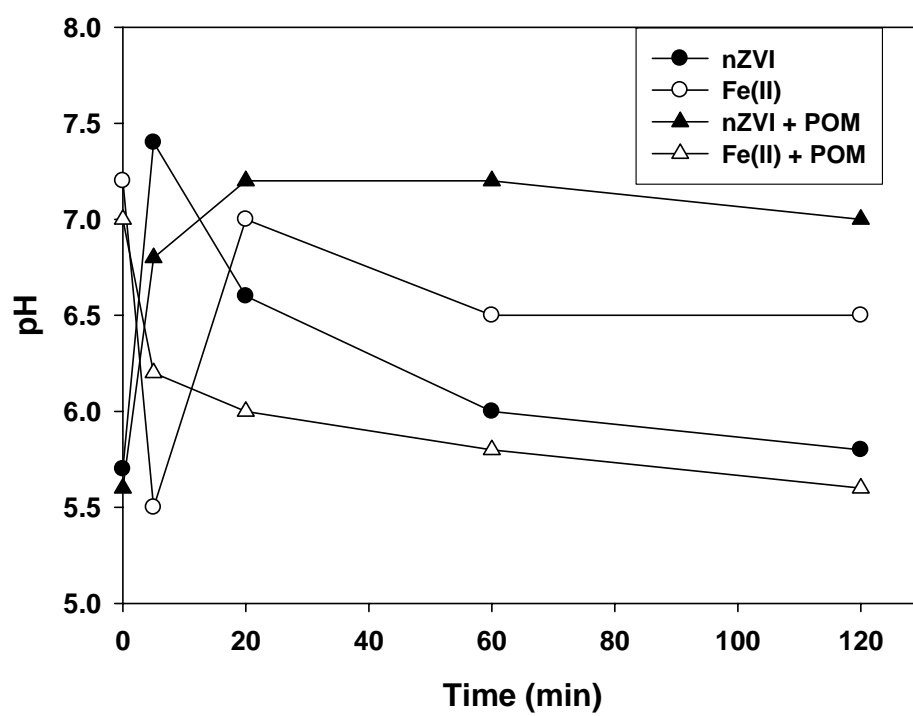


Figure S5. pH variation in the condition of Figure S4-1b