

Oxidation of Organic Contaminants on Nanoparticulate Zero-Valent Iron



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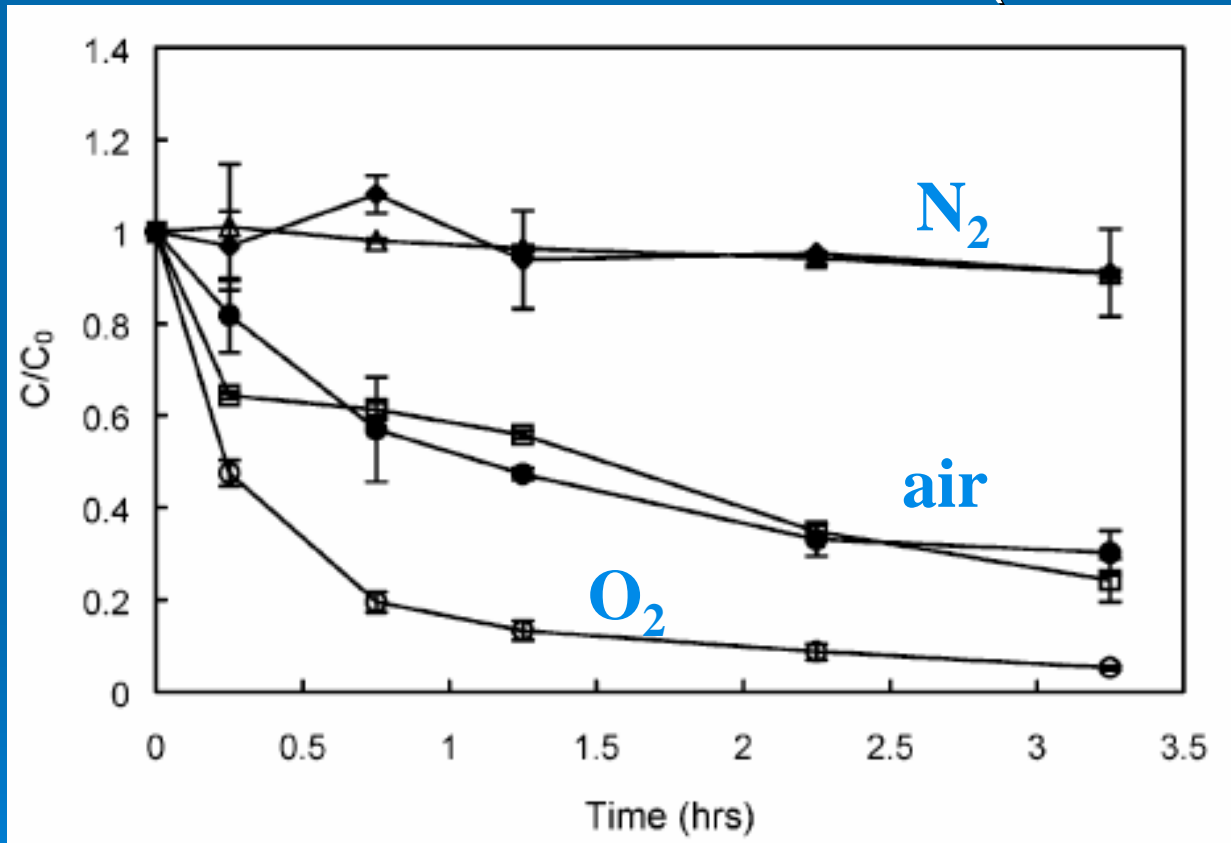
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Zero-Valent Iron (ZVI) Applications

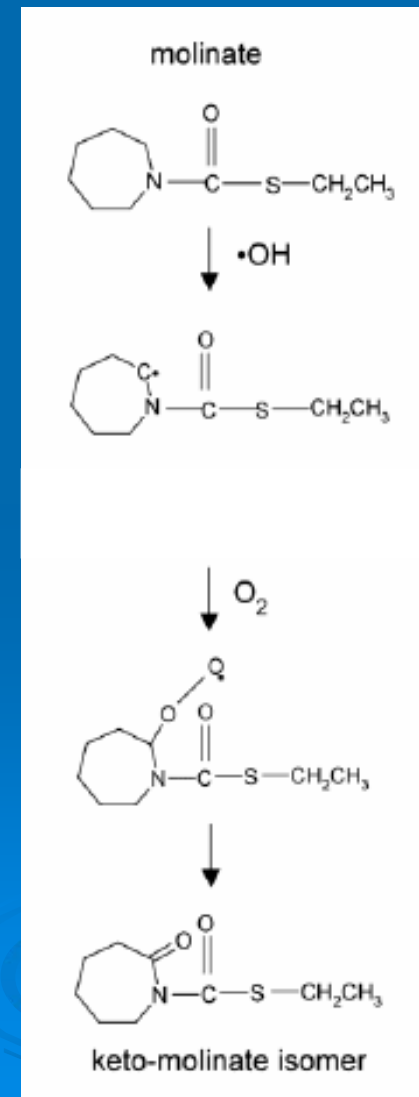
- Permeable reactive barriers
 - Reduction of halogenated organics
 - Sequestration of metals
- Iron nanoparticles
 - In situ remediation (Zhang, Tratnyek et al.)
 - Oxygen is undesirable

Oxidative ZVI Reactions

➤ Molinate transformation (Joo et al. 2004)

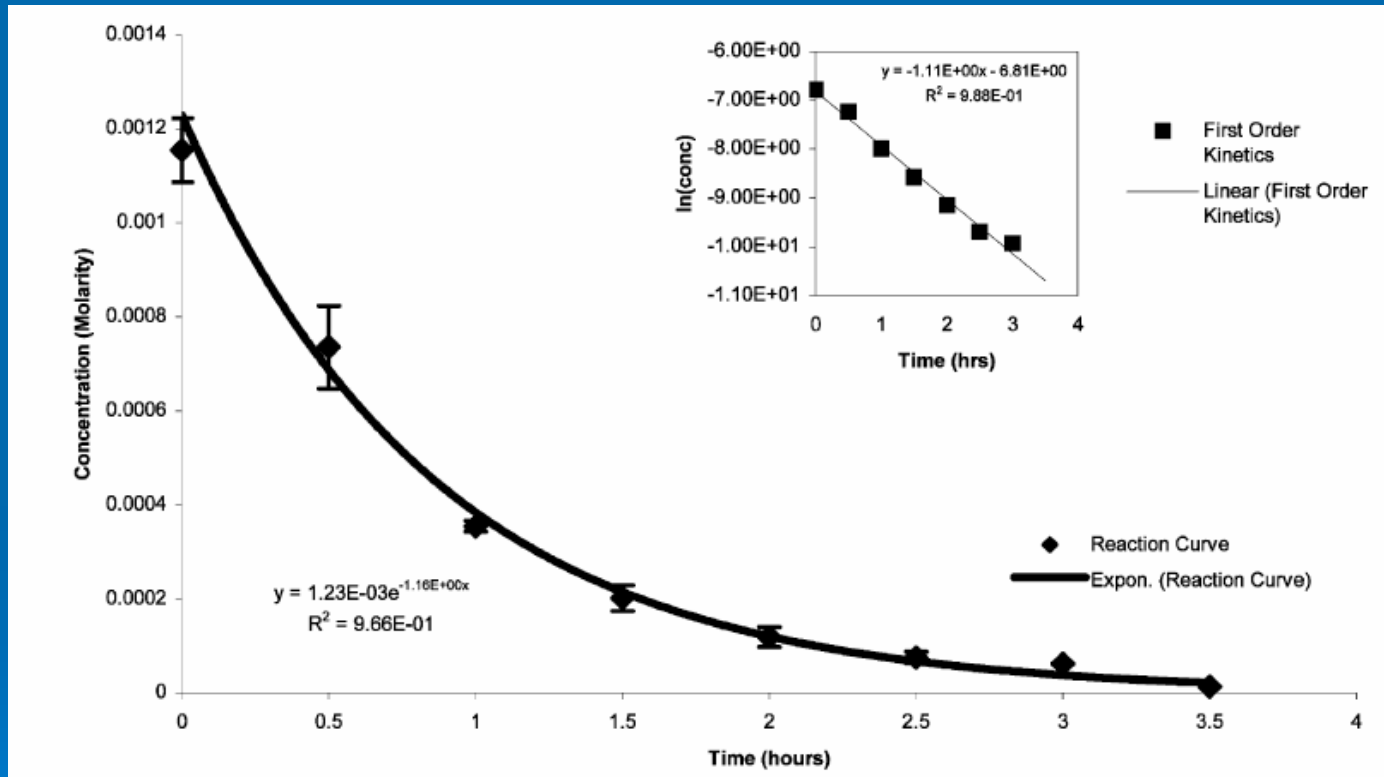


[molinate]=0.2 mg/L
[nZVI] = 560 mg/L; pH 4



Oxidative ZVI: Granular Fe

➤ Chlorophenol transformation (Noradoun et al. 2003)



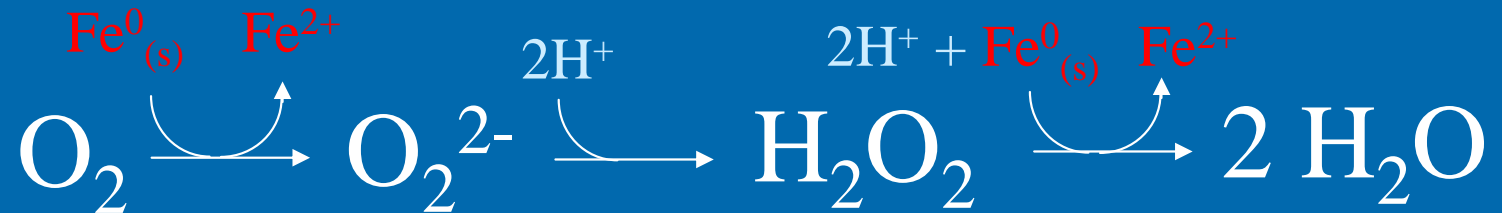
[Chlorophenol]=0.14 g/L
[ZVI] = 50 g/L; 0.32 mM EDTA

Questions

- How does oxidative ZVI work?
- How efficient is it?
- What are the potential applications?

Oxygen Activation by ZVI

➤ 4 e⁻ pathway

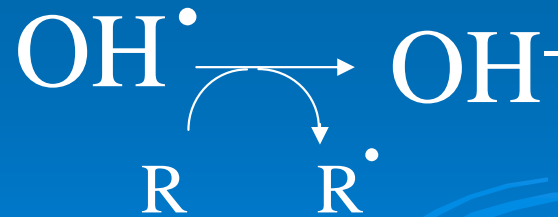
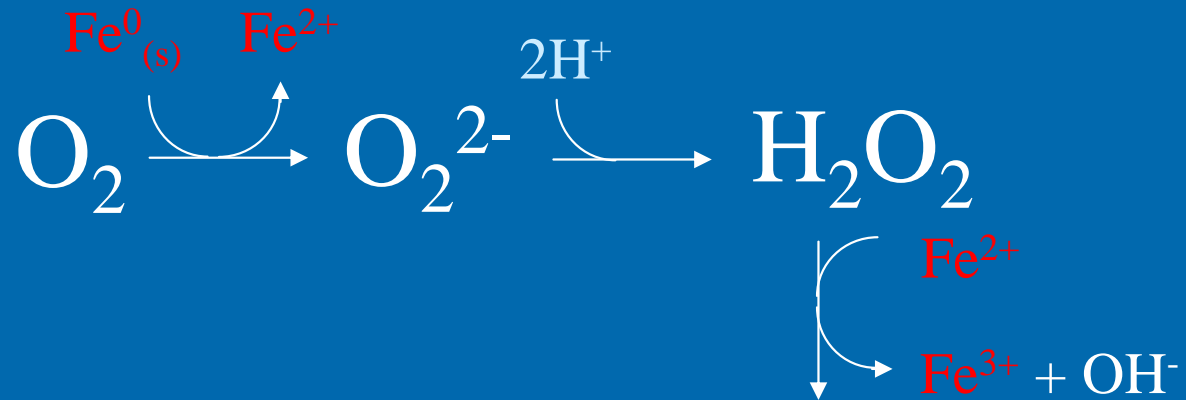


Overall:



Oxygen Activation by ZVI

➤ 2 e⁻ pathway

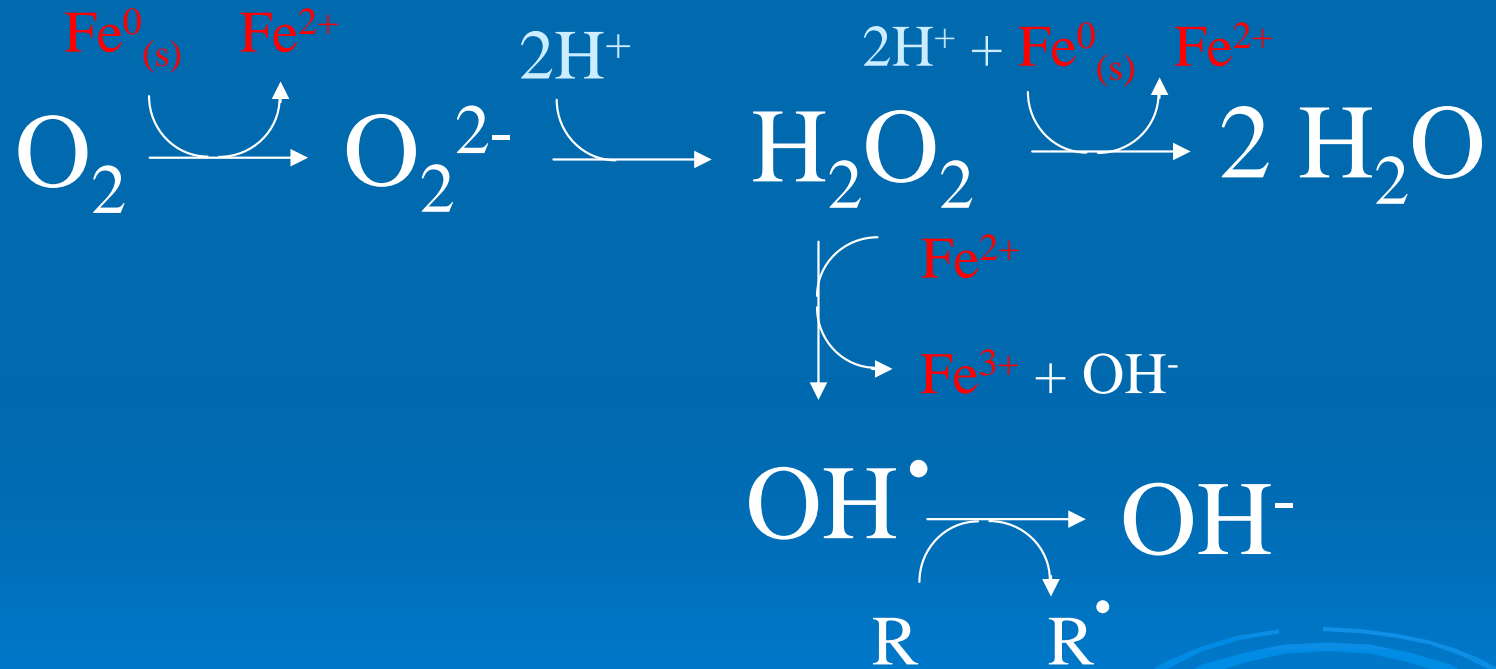


Overall:



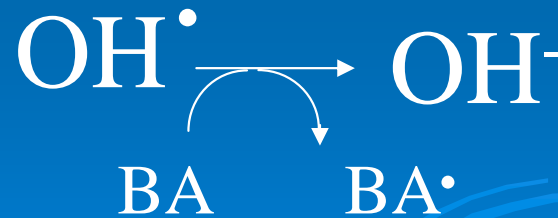
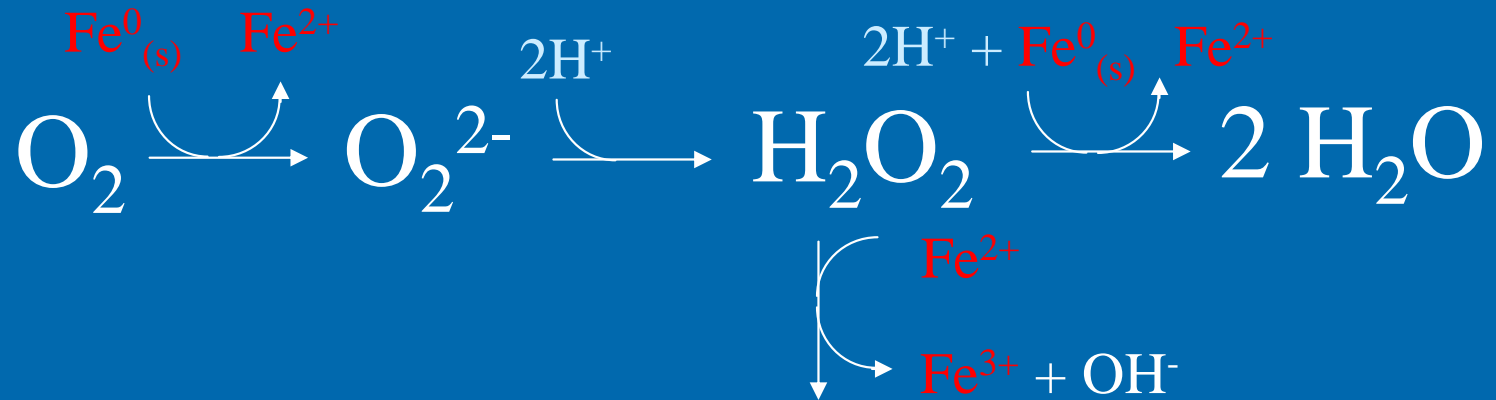
Oxygen Activation by ZVI

- Efficiency determined by branching ratio



Oxygen Activation by ZVI

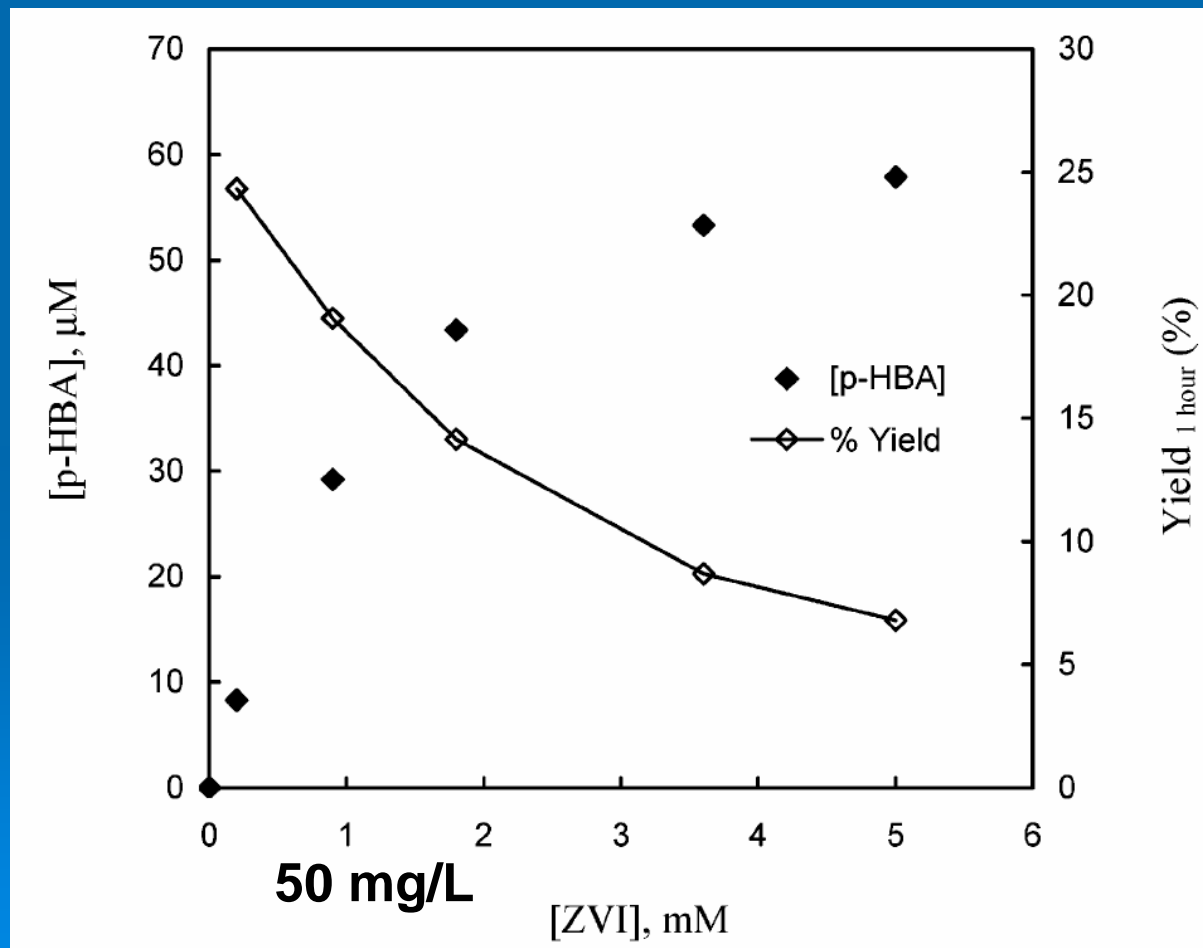
- Efficiency determined by branching ratio



o,m,p-HBA

Benzoic Acid Experiments

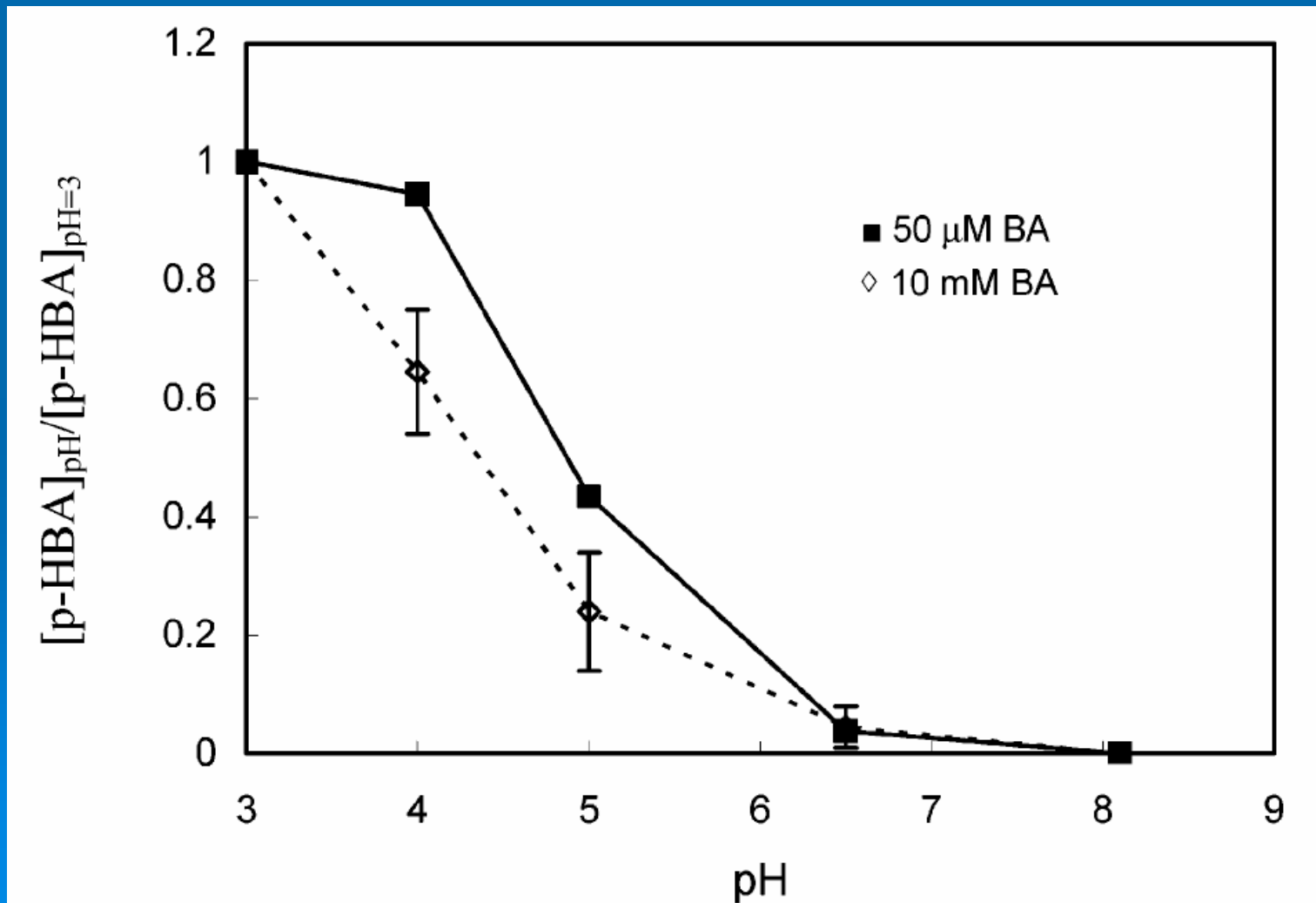
- Yields 5-25% (Joo et al. 2005)



pH = 3
[BA] = 10 mM

Effect of pH

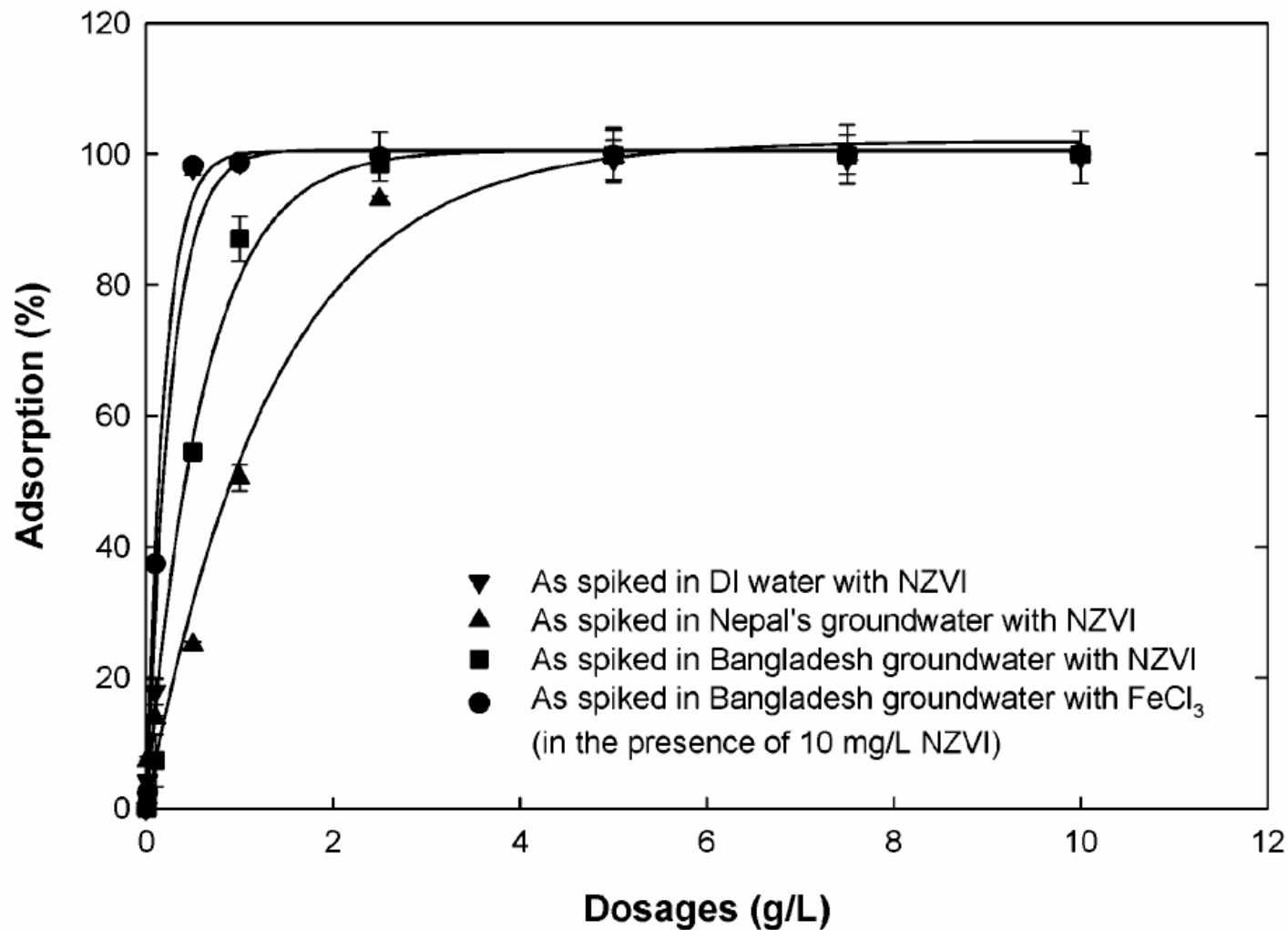
- pH slows corrosion processes
- efficiency at high pH unknown



50 mg/L nZVI
1 hr reaction

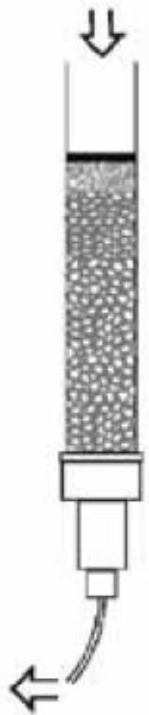
Potential nZVI Applications

➤ As(III) removal (Kanel et al. 2005)

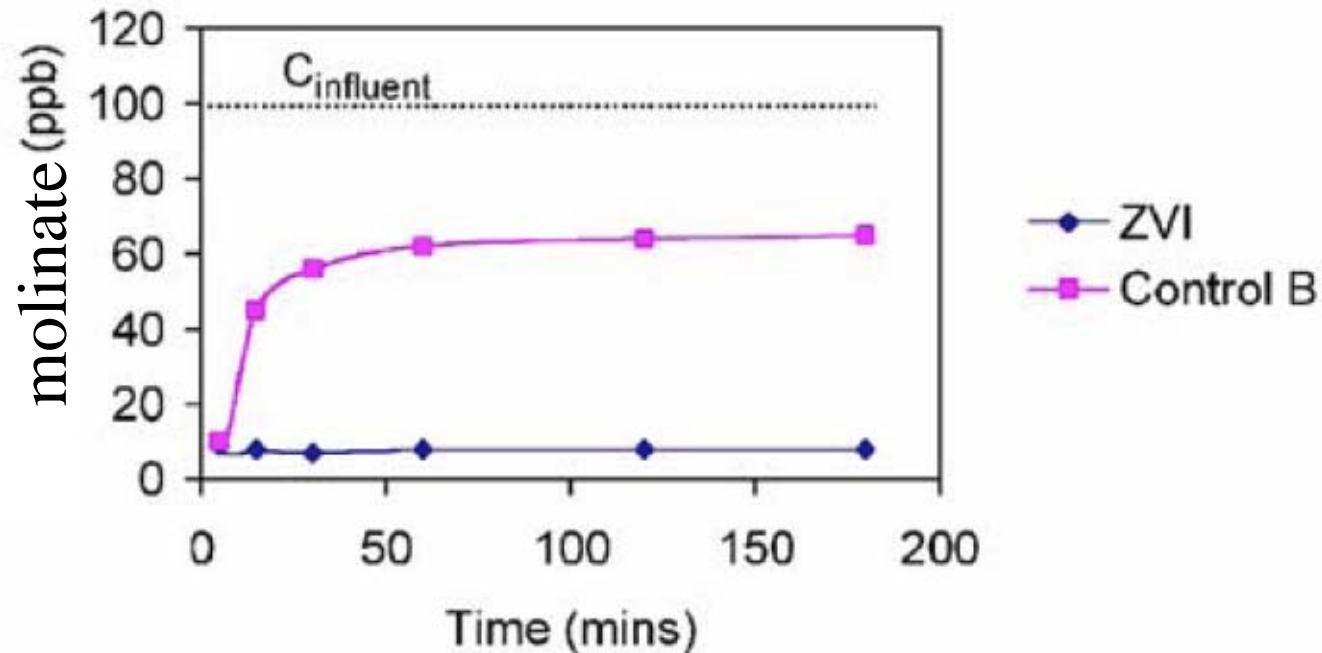


Potential nZVI Applications

- Treatment of runoff (Feitz et al. 2005)



ZVI on sand/gravel
6,000 mg/kg



Potential nZVI Applications

- Treatment of dilute plume (e.g., MTBE, 1,4-dioxane)



Potential nZVI Applications

- Treatment of dilute plume (e.g., MTBE, 1,4-dioxane)

$$\Delta[\text{O}_2] = 0.25 \text{ mM}$$

$$20\% \text{ yield (2 e}^- \text{ pathway)} = 50 \text{ }\mu\text{M OH}^\bullet$$

Potential nZVI Applications

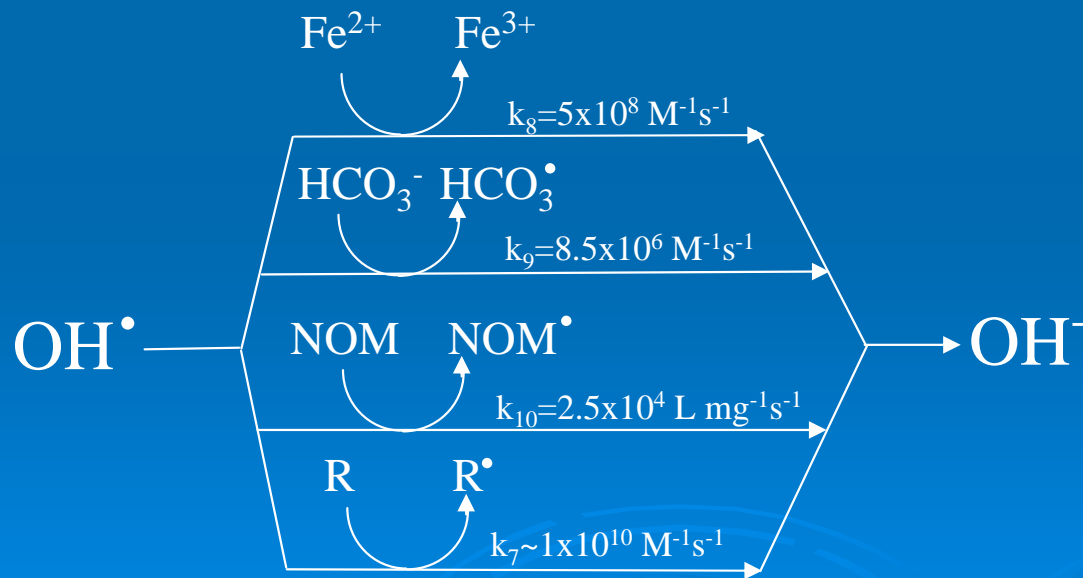
➤ Treatment of dilute plume (e.g., MTBE, 1,4-dioxane)

$\Delta[\text{O}_2] = 0.25 \text{ mM}$

20% yield (2 e⁻ pathway) = 50 μM OH^\bullet

OH^\bullet scavengers: 0.1 mM Fe(II), 1 mM HCO_3^- , 2 mg/L NOM, 1 μM R

~8% of OH^\bullet to R (4 μM)



Conclusions

- OH formed by nZVI reactions with O_2
- Efficiency depends on pathway
- Preliminary results suggest applications
 - As(III) removal
 - Runoff/soil treatment
 - Dilute groundwater plumes

References

- Joo SH, Feitz AJ, Waite TD (2004) Oxidative degradation of the carbothioate herbicide, molinate, using nanoscale zero-valent iron. *Environ. Sci. Technol.* 38: 2242-2247.
- Joo SH, Feitz AJ, Sedlak DL, Waite TD (2005) Quantification of the oxidizing capacity of nanoparticulate zero-valent iron. *Environ. Sci. Technol.*, 39, 1263-1268.
- Feitz AJ, Joo SH, Guan J, Sun Q, Sedlak DL, Waite TD (2005), *Coll. & Surfaces A*, 265, 88-94
- Kanel SR, Manning B, Charlet L, Choi H (2005) Removal of arsenic(III) from groundwater by nanoscale zero-valent iron. *Environ. Sci. Technol* 39 (5): 1291-1298.
- Noradoun C, Engelmann MD, McLaughlin M, Hutcheson R, Breen K, Paszczyński A, Cheng IF (2003) Destruction of chlorinated phenols by dioxygen activation under aqueous room temperature and pressure conditions. *Ind. Eng. Chem. Res.* 42, 5024-5030.