# Oxidation of Organic Contaminants on Nanoparticulate Zero-Valent Iron

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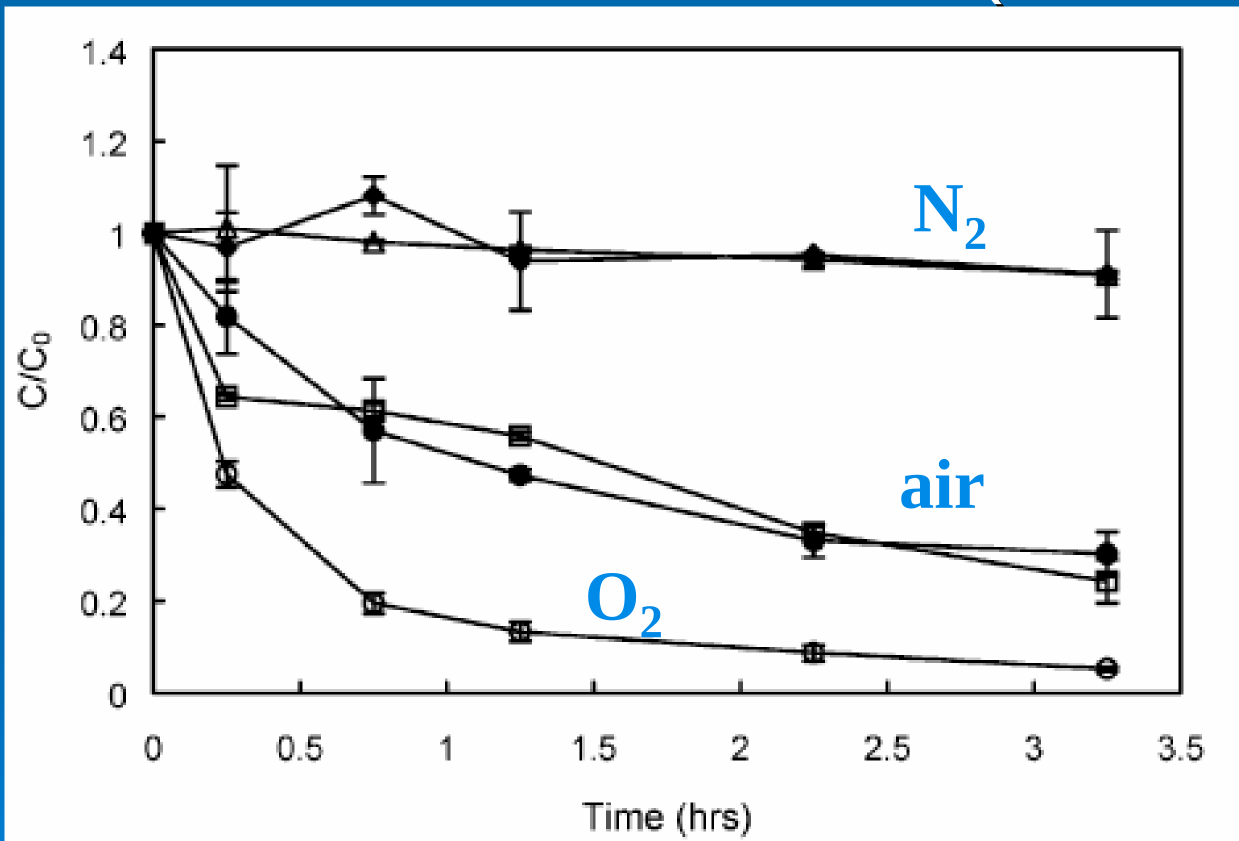
# Zero-Valent Iron (ZVI) Applications

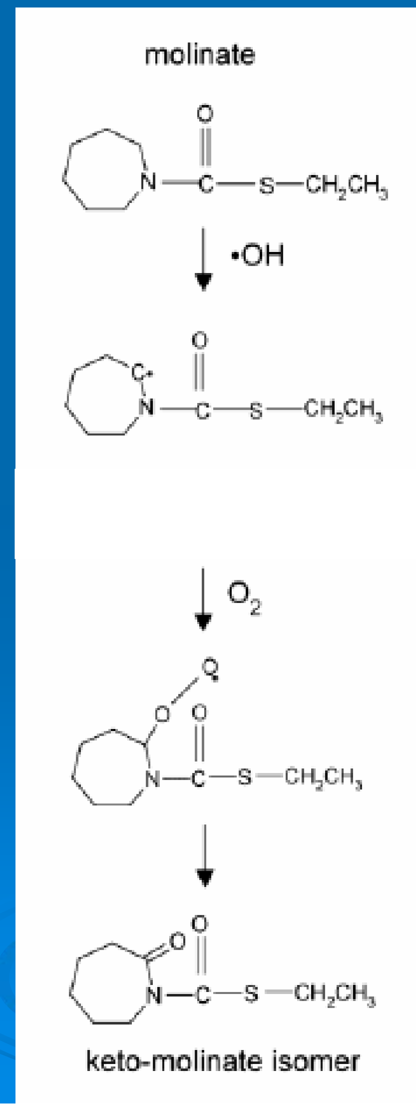
- Permeable reactive barriers
  - Reduction of halogenated organics
  - Sequestration of metals

- Iron nanoparticles
  - In situ remediation (Zhang, Tratnyek et al.)
  - Oxygen is undesireable

# Oxidative ZVI Reactions

- Molinate transformation (Joo et al. 2004)

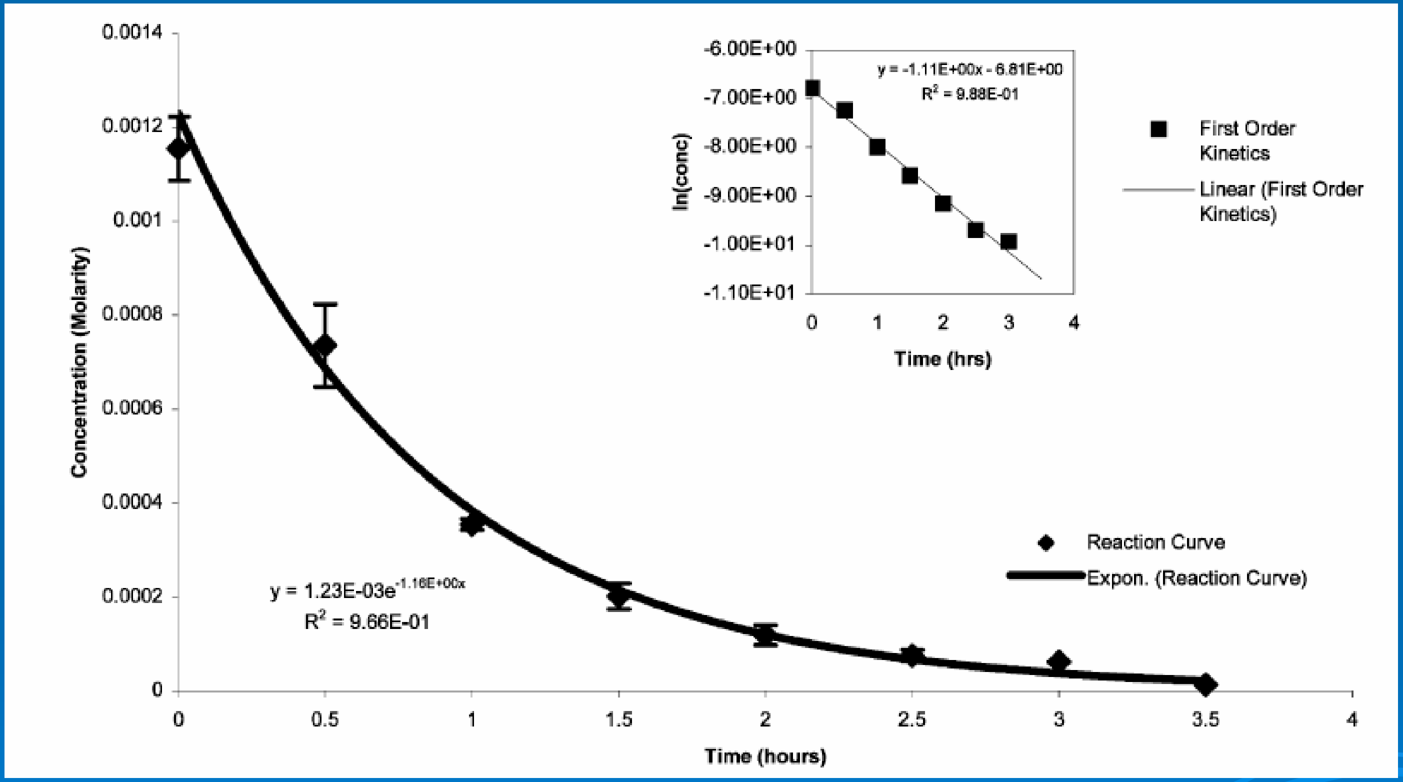



[molinate]=0.2 mg/L
[nZVI] = 560 mg/L; pH 4

# 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

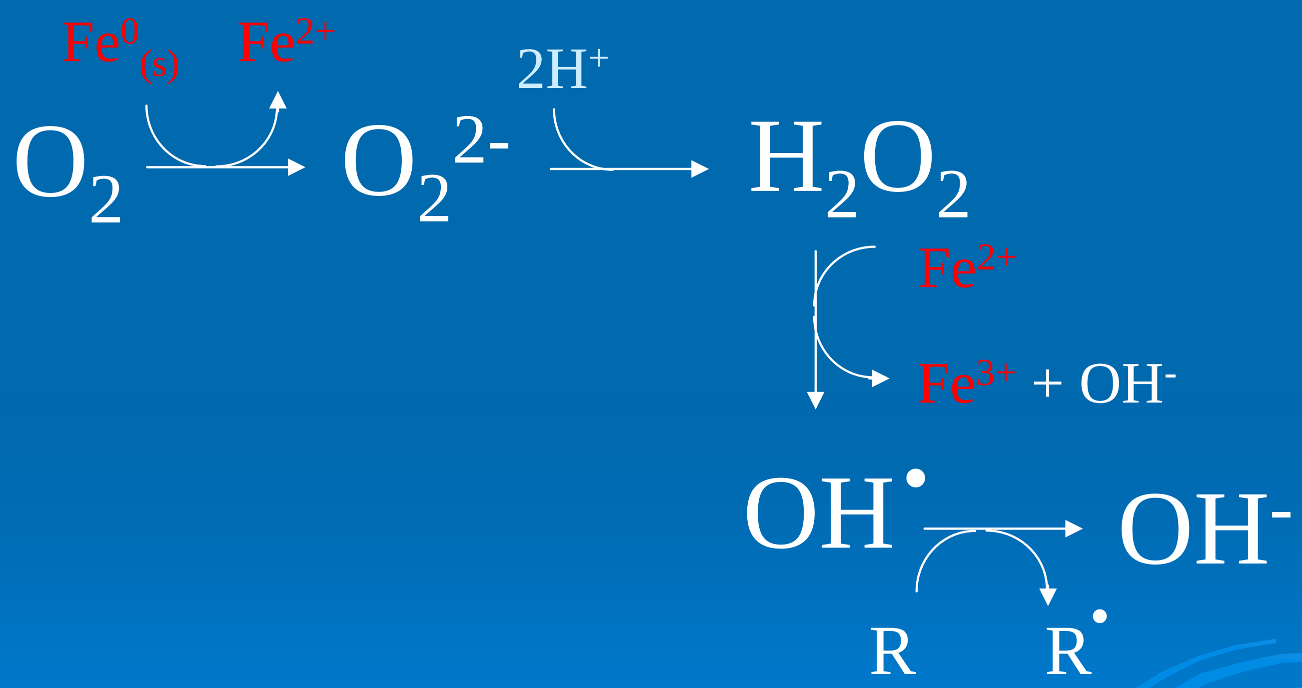
$$O_2 \xrightarrow{Fe^0_{(s)} \;\rightarrow\; Fe^{2+}} O_2^{2-} \xrightarrow{2H^+} H_2O_2 \xrightarrow{2H^+ + Fe^0_{(s)} \;\rightarrow\; Fe^{2+}} 2\ H_2O$$

Overall:

$$O_2 + 2\ Fe^0_{(s)} + 4\ H^+ \longrightarrow 2\ H_2O + 2\ Fe^{2+}$$

# Oxygen Activation by ZVI

- 2 e⁻ pathway

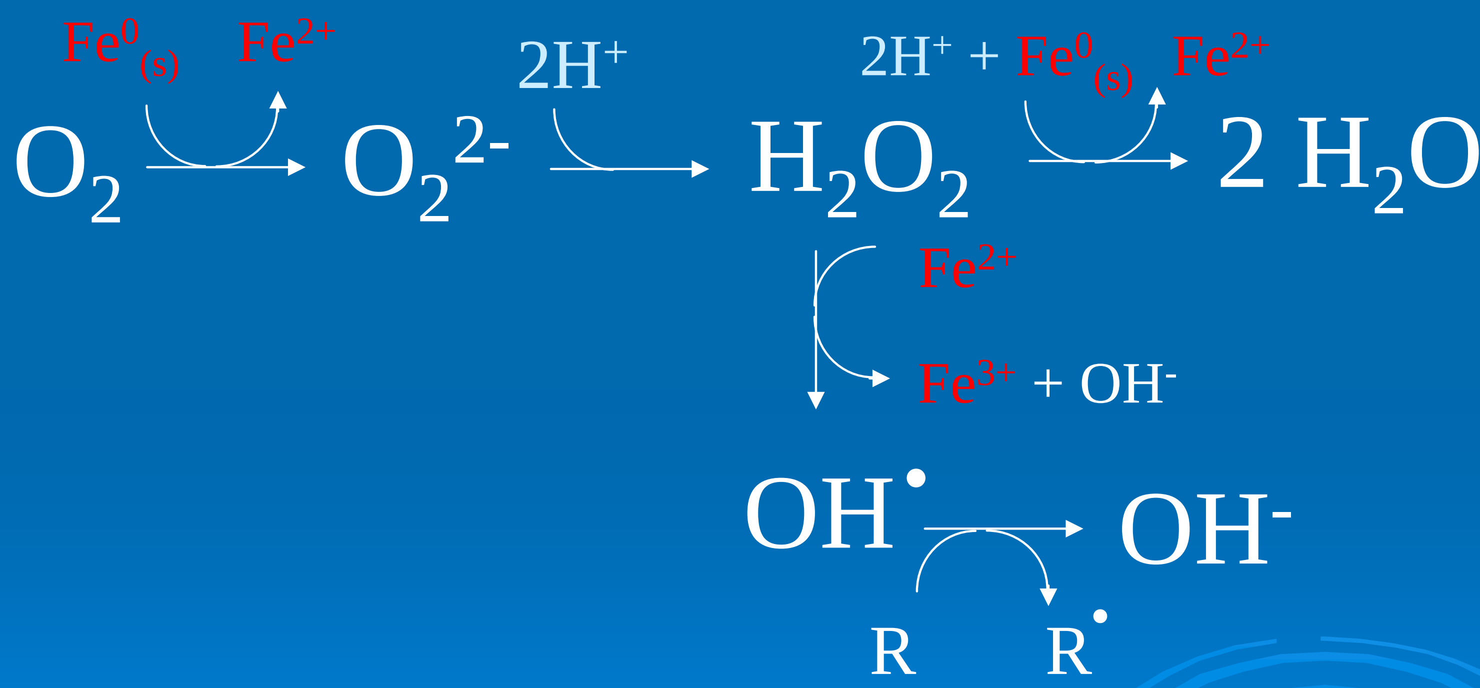



Overall:

$$O_2 + Fe^0_{(s)} + 2\,H^+ + R \longrightarrow 2\,OH^- + Fe^{3+} + R^\bullet$$

# Oxygen Activation by ZVI

- Efficiency determined by branching ratio



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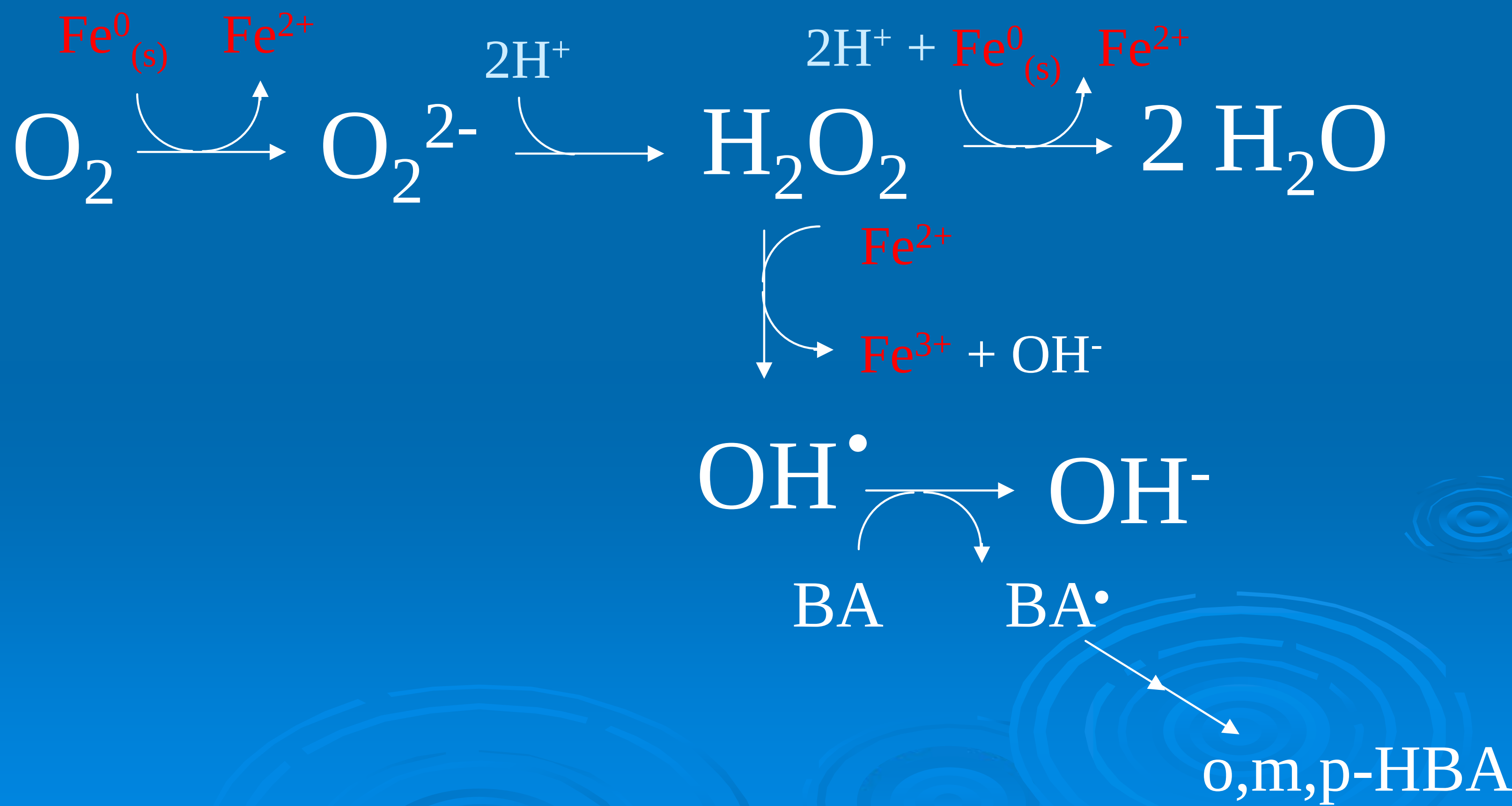
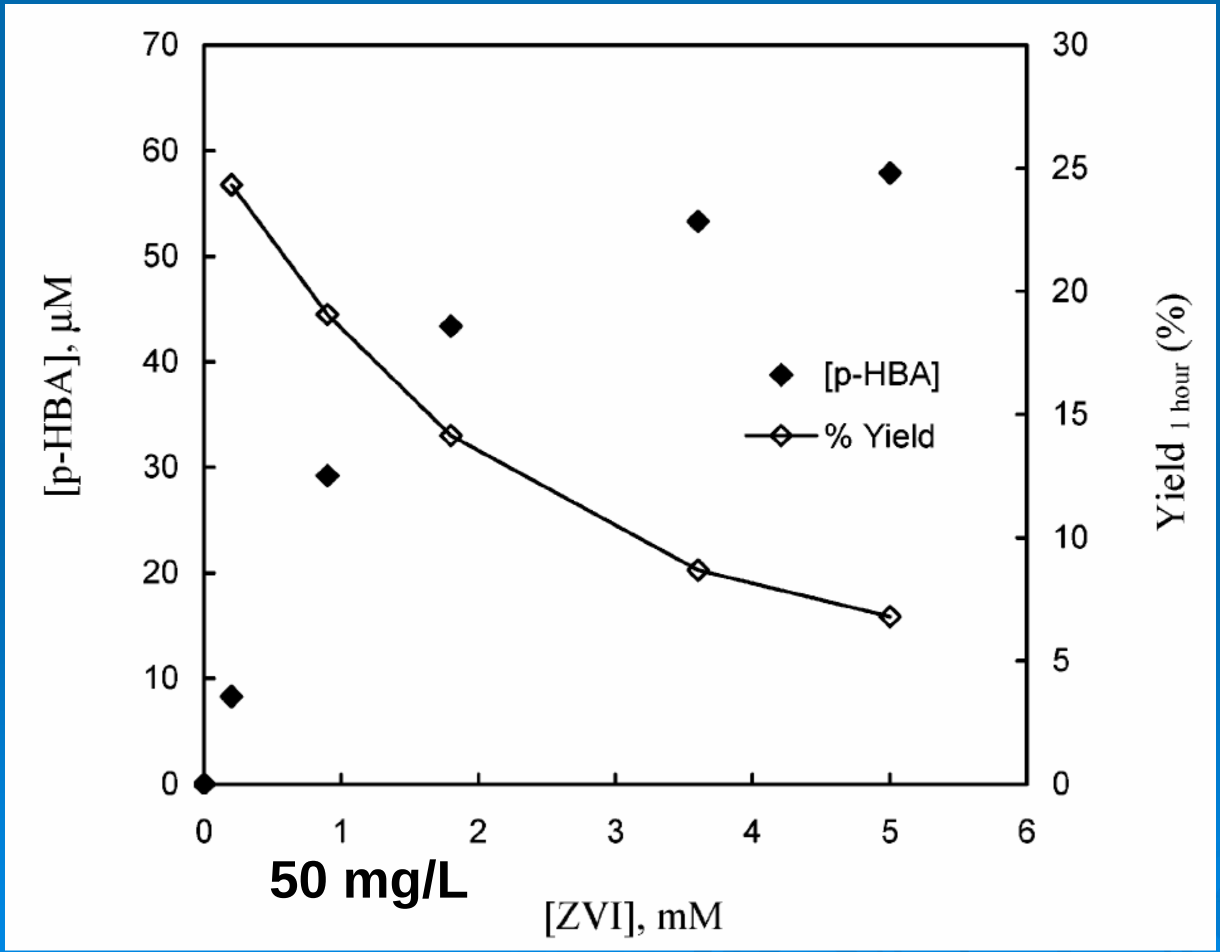


# Benzoic Acid Experiments

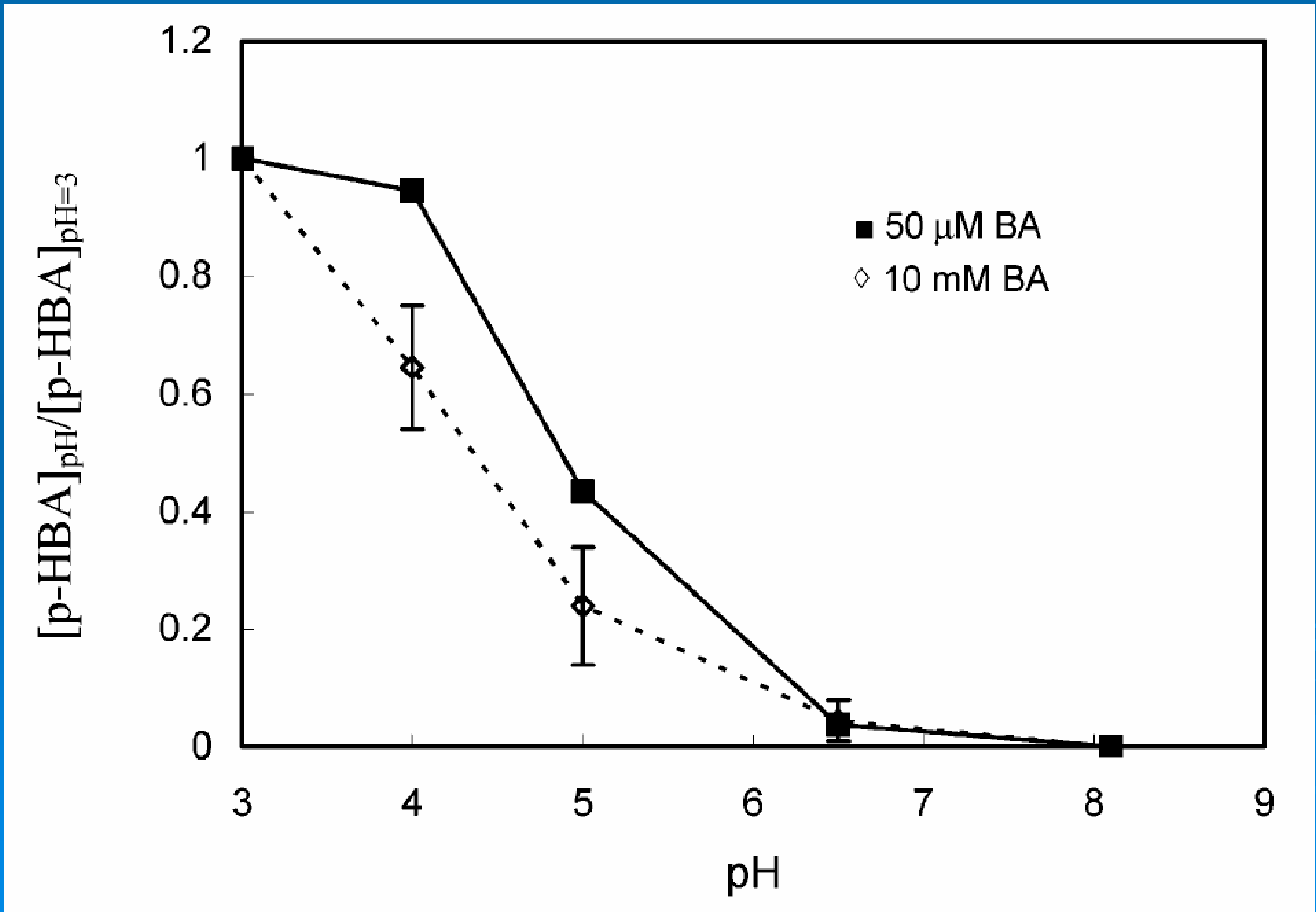
- Yields 5-25% (Joo et al. 2005)




pH = 3
[BA] = 10 mM

# Effect of pH

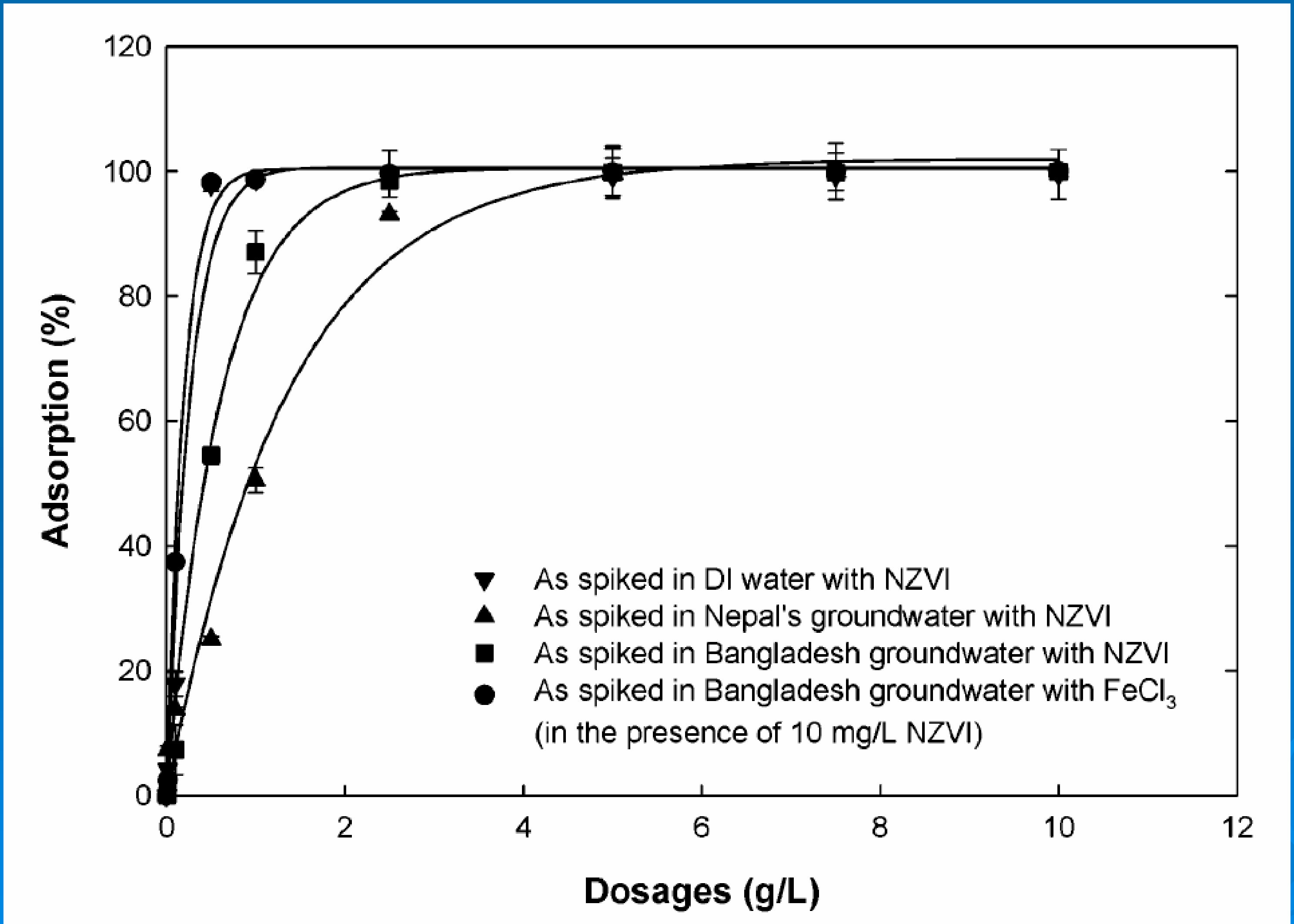
- pH slows corrosion processes
- efficiency at high pH unknown




50 mg/L nZVI
1 hr reaction

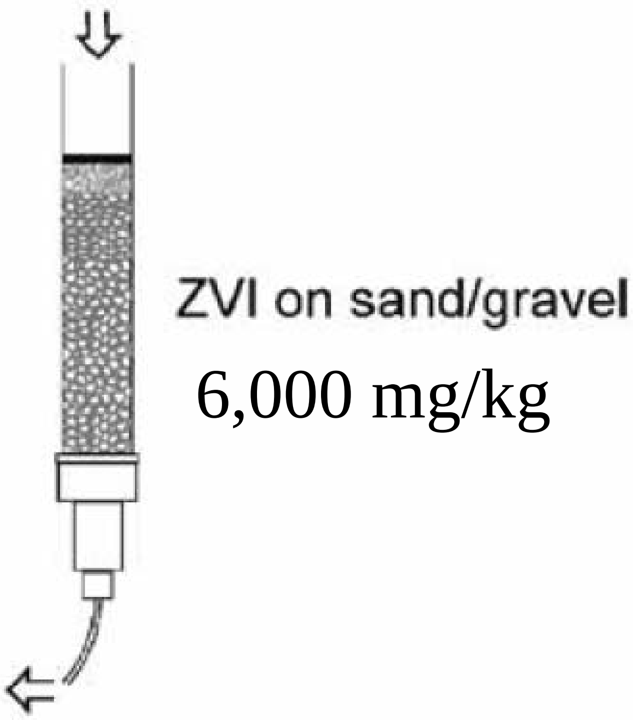
# Potential nZVI Applications

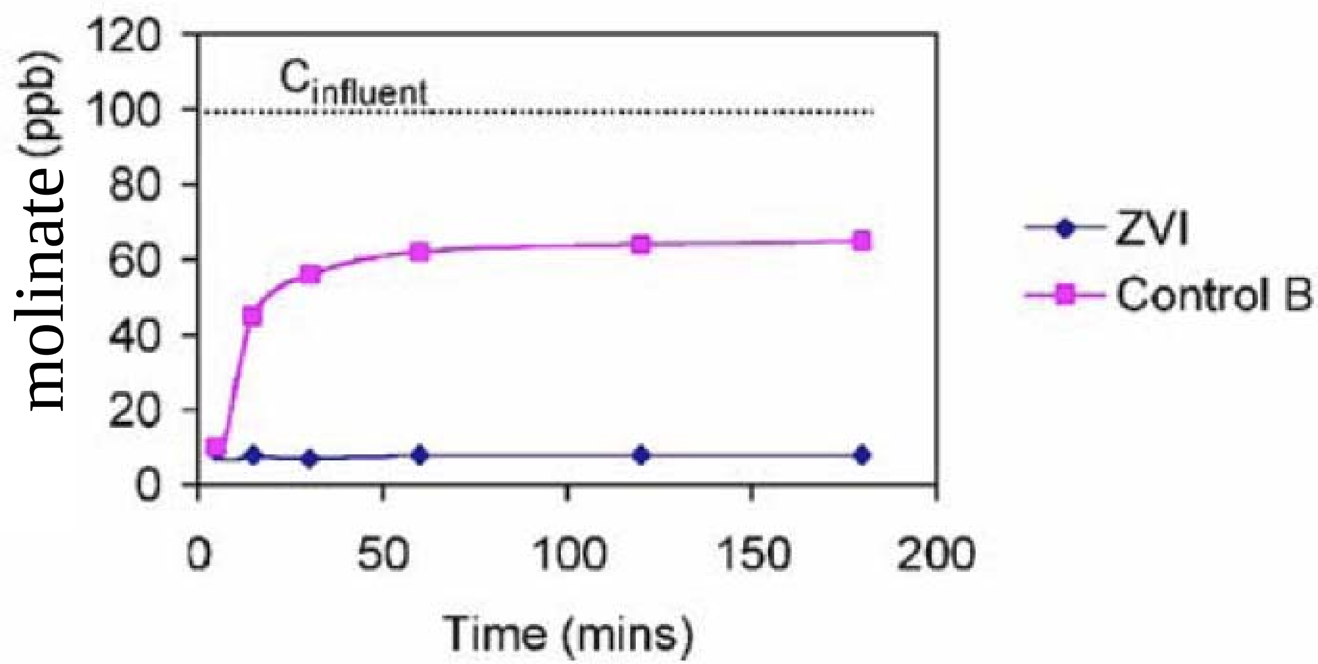
- As(III) removal (Kanel et al. 2005)



# Potential nZVI Applications

- Treatment of runoff (Feitz et al. 2005)



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

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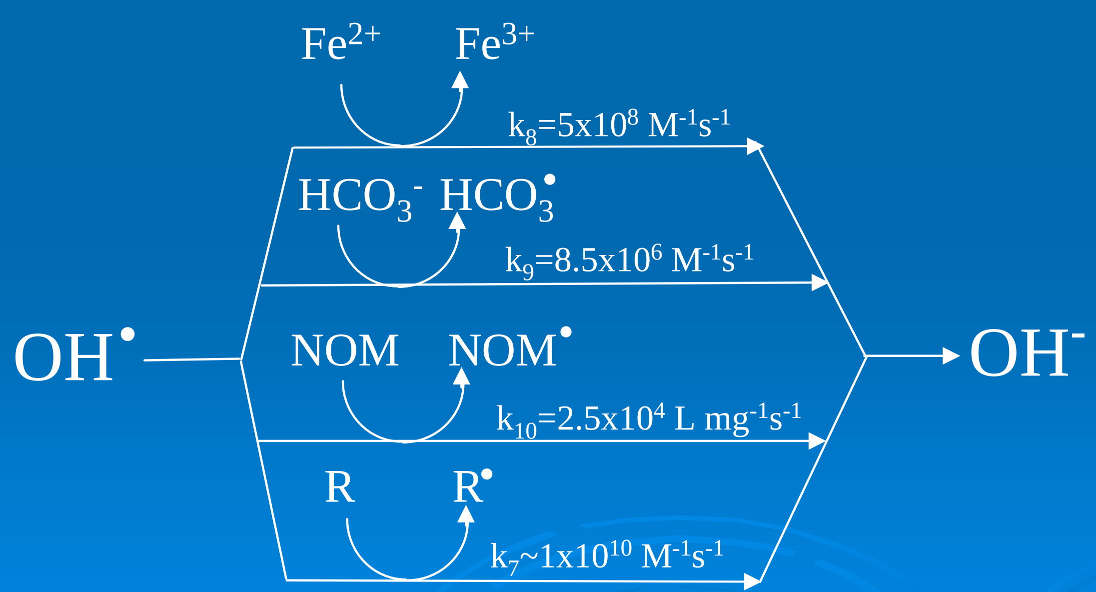
  $\Delta[O_2] = 0.25$ mM
  20% yield (2 $e^-$ pathway) = 50 $\mu$M $OH^{\bullet}$

# Potential nZVI Applications

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

  $\Delta[O_2] = 0.25$ 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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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.

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