D-007, in K.A. Fields and G.B. Wickramanayake (Chairs), *Remediation of Chlorinated and Recalcitrant Compounds—2010.*
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pH Effect on EDTA/Ferric Ion-Activated Persulfate Oxidation of Trichloroethylene in Batch Studies

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The ability of free ferrous ion-activated persulfate ($S_2O_8^{2-}$) to generate sulfate radicals ($SO_4^{-\cdot}$) for the oxidation of trichloroethylene (TCE) is limited by the scavenging of $SO_4^{-\cdot}$ with excess Fe^{2+} and a quick conversion of Fe^{2+} to Fe^{3+}. This study investigated the applicability of ethylene-diamine-tetra-acetic acid (EDTA) chelated Fe^{3+} in activating persulfate for the destruction of TCE in aqueous phase under pH 3, 7 and 10. Fe^{3+} and EDTA alone did not appreciably degrade persulfate. The presence of TCE in the EDTA/Fe^{3+} activated persulfate system can induce faster persulfate and EDTA degradation due to iron recycling to activate persulfate under a higher pH condition. Increasing the pH leads to increases in pseudo-first-rate constants for TCE, $S_2O_8^{2-}$ and EDTA degradations, and Cl generation. Accordingly, the experiments at pH 10 with different EDTA/Fe^{3+} molar ratios indicated that a 1/1 ratio resulted in a remarkably higher degradation rate at the early stage of reaction as compared to results by other ratios. Higher persulfate dosage under the EDTA/Fe^{3+} molar ratio of 1/1 resulted in greater TCE degradation rates. However, increases in persulfate concentration may also lead to an increase in the rate of persulfate consumption.

pH Effect on EDTA/Fe^{3+}-Activated Persulfate Oxidation of TCE in Batch Studies

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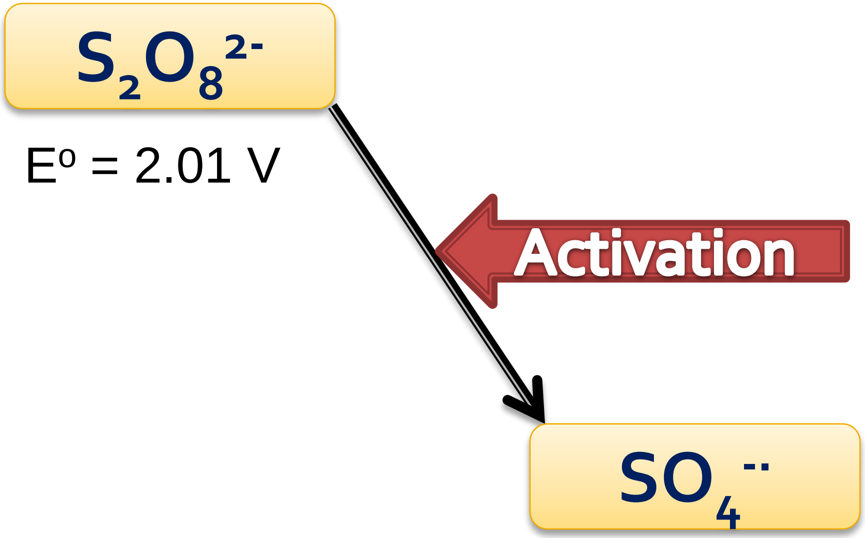
Introduction

- Persulfate $S_2O_8^{2-}$



$S_2O_8^{2-}$

$E^o = 2.01$ V

Activation

$SO_4^{\cdot -}$

$E^o = 2.4 \sim 2.6$ V

Homogeneous Fe^{2+} activation **Ea = 14.8 kcal/mol**

Thermal activation **Ea = 33.5 kcal/mol**

Introduction (cont.)

- **$SO_4^{\cdot -}$ scavenging due to the presence of excess Fe^{2+}**

$$Fe^{2+} + S_2O_8^{2-} \longrightarrow Fe^{3+} + SO_4^{\cdot -} + SO_4^{2-}$$

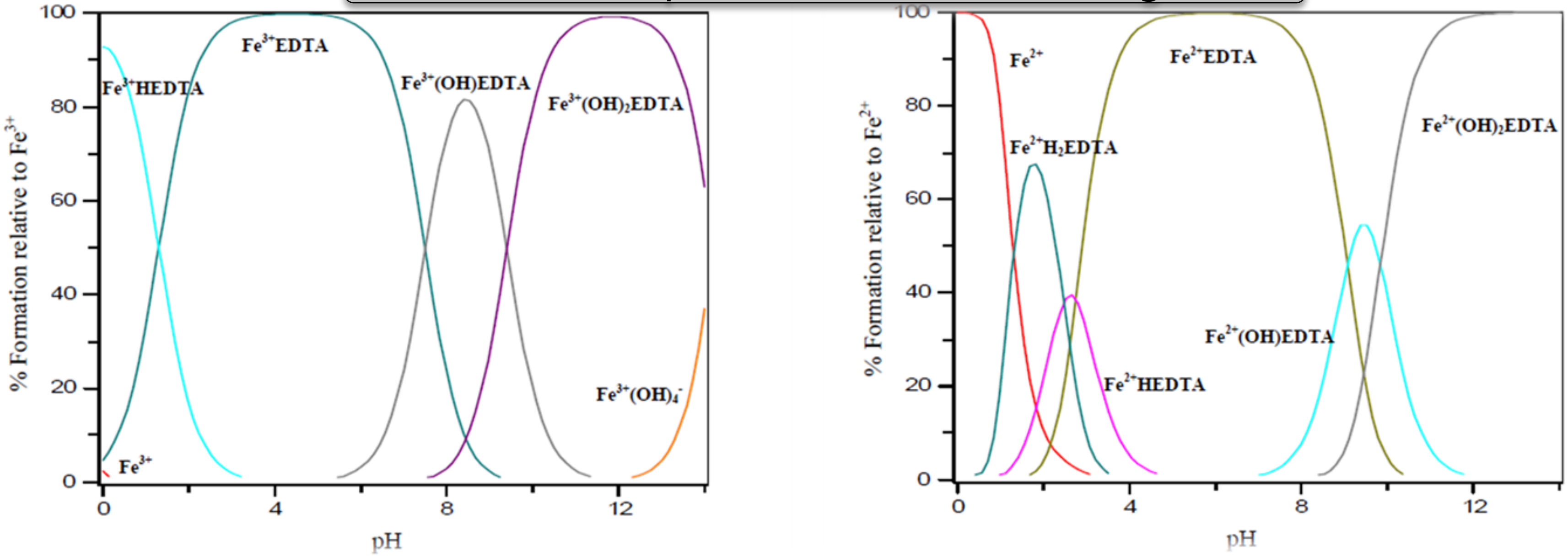
$$k = (1.2 \times 10^1 + 5.5 \times 10^1\,[H^+])\ M^{-1}s^{-1}$$

$$SO_4^{\cdot -} + Fe^{2+} \longrightarrow Fe^{3+} + SO_4^{2-}$$

$$k = 4.6 \times 10^9\ M^{-1}s^{-1}$$

Introduction (cont.) EDTA

Fe^{2+} and Fe^{3+} speciation distribution diagrams



Equi-molar EDTA/iron, using Hyperquad speciation and simulation software and formation constants provided by Shimizu et al. 2007

- <u>The Potential Capability:</u>

The ligand-to-charge-transfer reduction of EDTA in simultaneously complexing Fe^{2+} and Fe^{3+} in solution for persulfate activation.

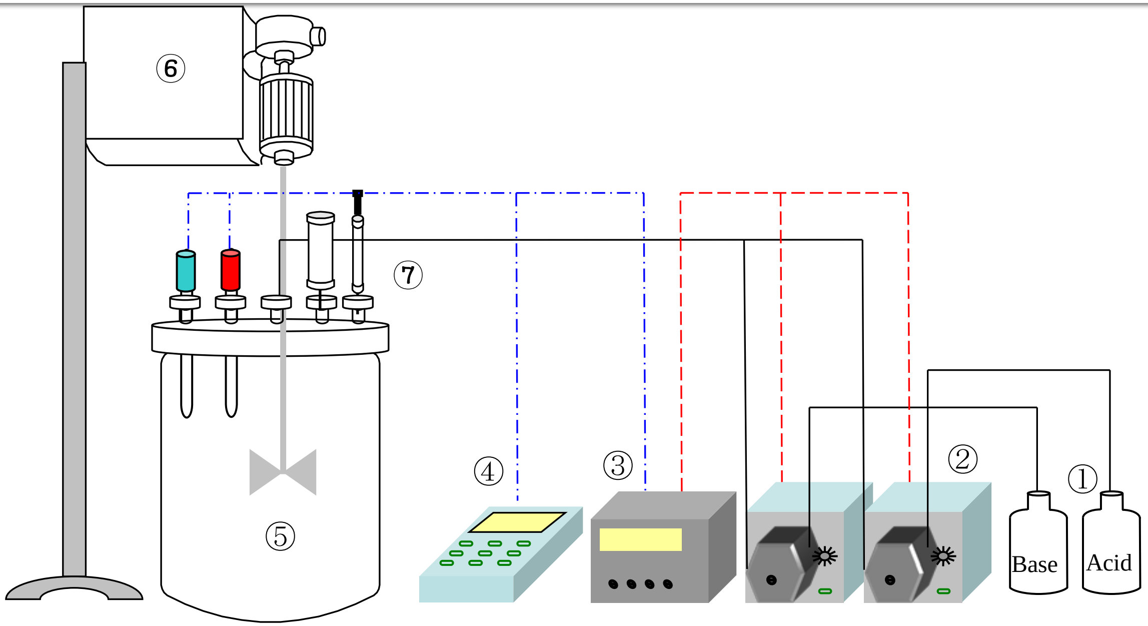
Objectives

1. The effects of Fe^{3+}, EDTA, and EDTA/Fe^{3+} on persulfate

2. EDTA/Fe^{3+} activated persulfate oxidation of TCE at differing pH

3. The effects of EDTA/Fe^{3+} molar ratios and persulfate concentrations on the TCE degradation
(at an optimum pH condition as determined in objective 2)

Metholodgy



Analysis:
- TCE
- TOC
- Persulfate
- ORP
- pH

① 0.5 N NaOH or 0.5 N H_2SO_4

② Cole-Parmer Masterflex C/L variable-speed tubing pump, 50 to 300 rpm, 115 VAC

③ pH/ORP control (SUNTEX pH/ORP controller, PC-310)

④ pH meter (Thermo Orion^R Advanced Multichannel Benchtop ISE/pH/mV/ORP Meters, Orion 720A+)

⑤ Reactor (IWAKI, 1.36L)

⑥ Mixer (SHIN KWANG DC-15, 80 to 1150 rpm)

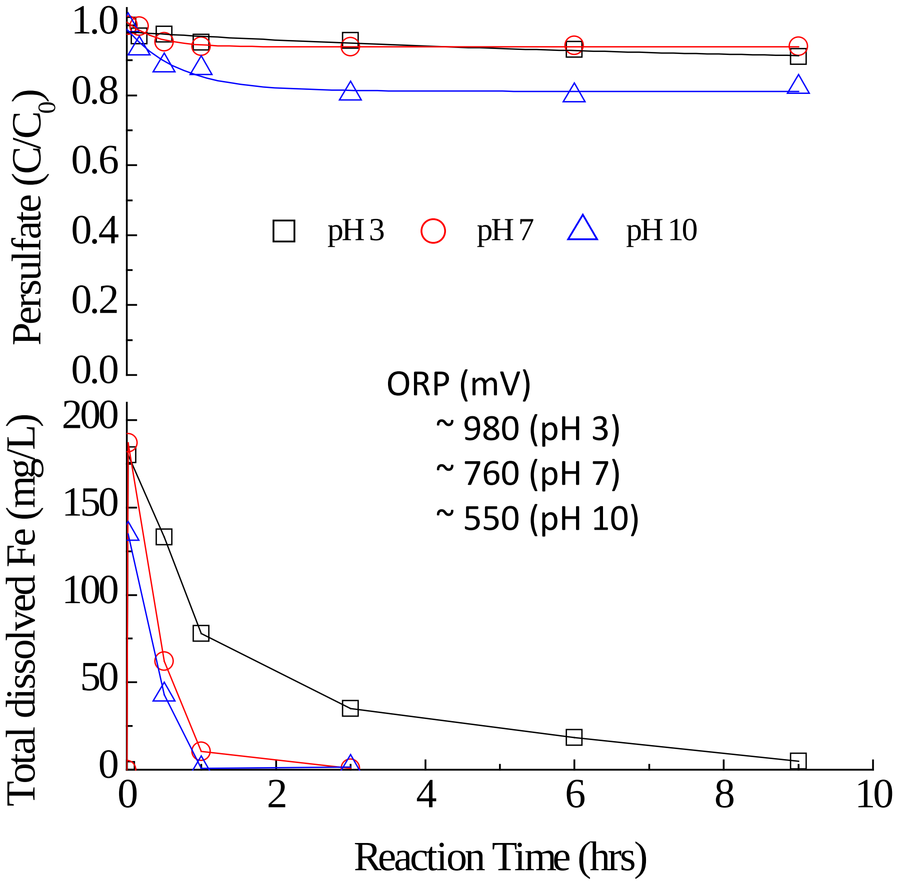
⑦ Gas-tight syringe, fitted with push-button luer lock valve 5 ml) and plastic syringe (60 ml)

Results and Discussion

- ***Objective 1***

  Fe^{3+}, EDTA and EDTA/Fe^{3+} impacts on the persulfate decomposition

The $S_2O_8^{2-}/Fe^{3+}$ system



ORP (mV)
~ 980 (pH 3)
~ 760 (pH 7)
~ 550 (pH 10)

$[S_2O_8^{2-}]_o$ = 20 mM; $[Fe^{3+}]_o$ = 3.58 mM.

- Persulfate reduction (i.e., < 20%) occurred under three pH conditions where iron precipitated out quickly, within 1 hr for pH 7 and 10 tests.
- Fe^{3+} alone did not appear to appreciably reduce the persulfate concentration.

Note

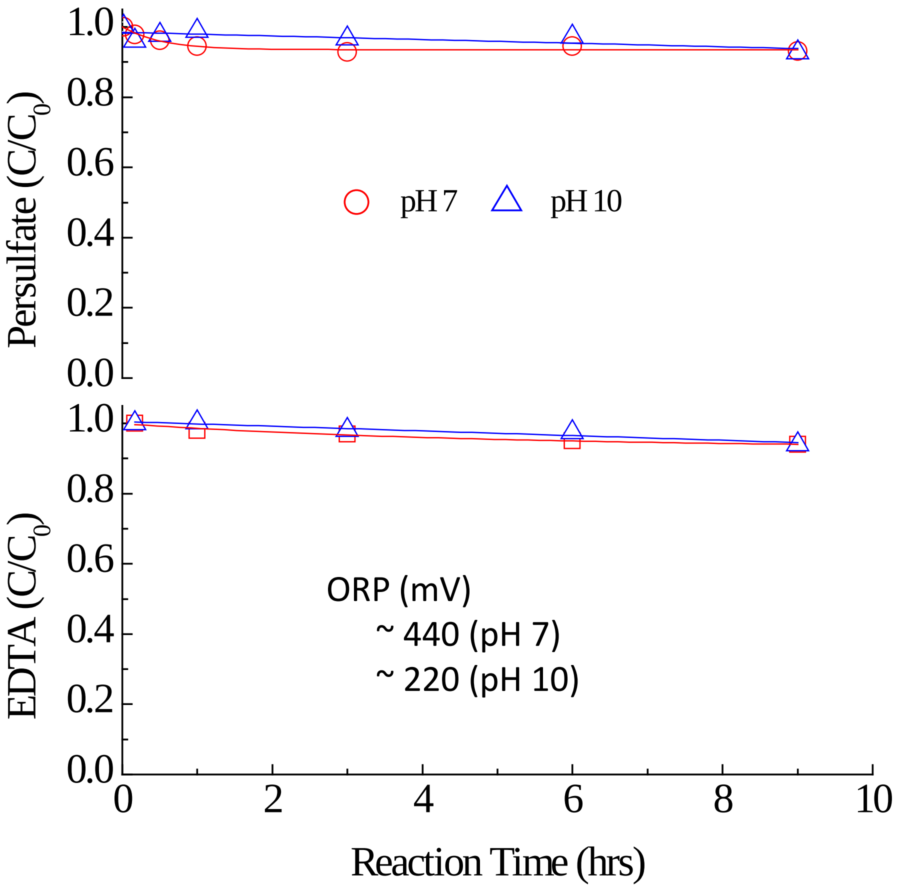
$SO_4^{-\cdot} + OH^- \rightarrow SO_4^{2-} + HO^\cdot$ $k = (6.5 \pm 1.0) \times 10^7\ M^{-1}s^{-1}$ *(Hayon et al., 1972)*

$SO_4^{-\cdot} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{-\cdot}$ $k = 6.1 \times 10^5\ M^{-1}s^{-1}$ *(Buxton et al., 1999)*

$HO^\cdot + S_2O_8^{2-} \rightarrow OH^- + S_2O_8^{-\cdot}$ $k = 1.2 \times 10^7\ M^{-1}s^{-1}$ *(Das, 2001)*

- At pH 10, persulfate was reduced to a slightly greater extent than those under pH 3 and 7.
- Sulfate radicals formed upon persulfate activation can be converted to $HO^\cdot$, which may attack persulfate anion at a faster rate than attacked by SO_4^-.

The $S_2O_8^{2-}$/EDTA system

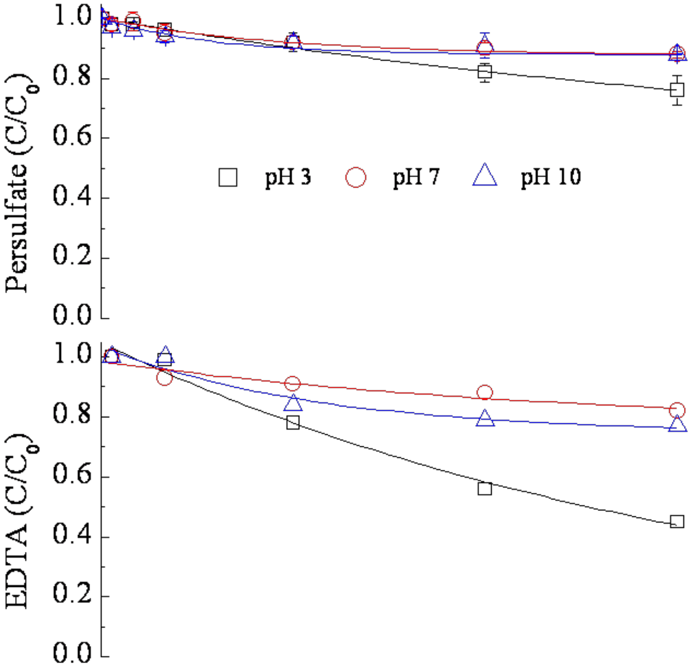


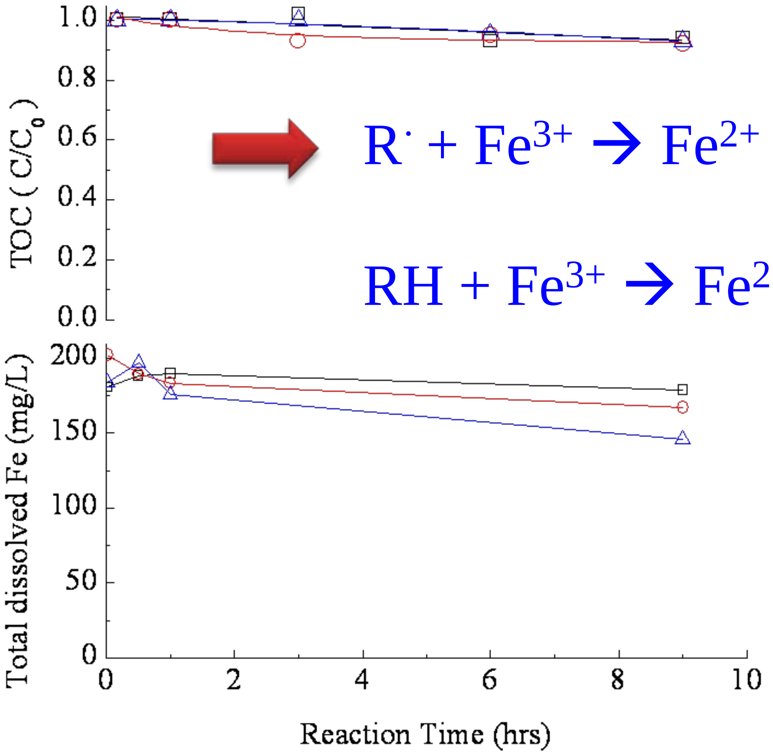
ORP (mV)
~ 440 (pH 7)
~ 220 (pH 10)

- EDTA did not yield a remarkable difference in the degradation of EDTA and persulfate at different pH.
- Direct oxidation of EDTA by persulfate anion is insignificant.

The $S_2O_8^{2-}$/EDTA/Fe^{3+} system

- Less than 5% of TOC is removed.
- Two types of radical chain mechanisms may be involved for recycling Fe^{2+}.





$R^{\cdot} + Fe^{3+} \rightarrow Fe^{2+} + \text{products}$

$RH + Fe^{3+} \rightarrow Fe^{2+} + RH^{+\cdot}$

- More persulfate degradation occurred when more EDTA degradation occurred.

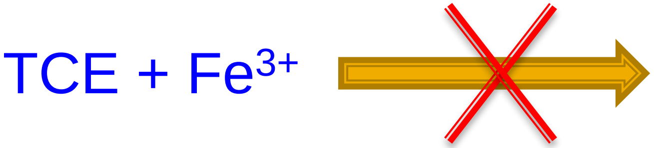
Results and Discussion

- ***Objective 2***

  Influence of pH on EDTA/Fe^{3+} activated persulfate oxidation of TCE

The EDTA/TCE, EDTA/Fe^{3+}/TCE or Fe^{3+}/TCE systems

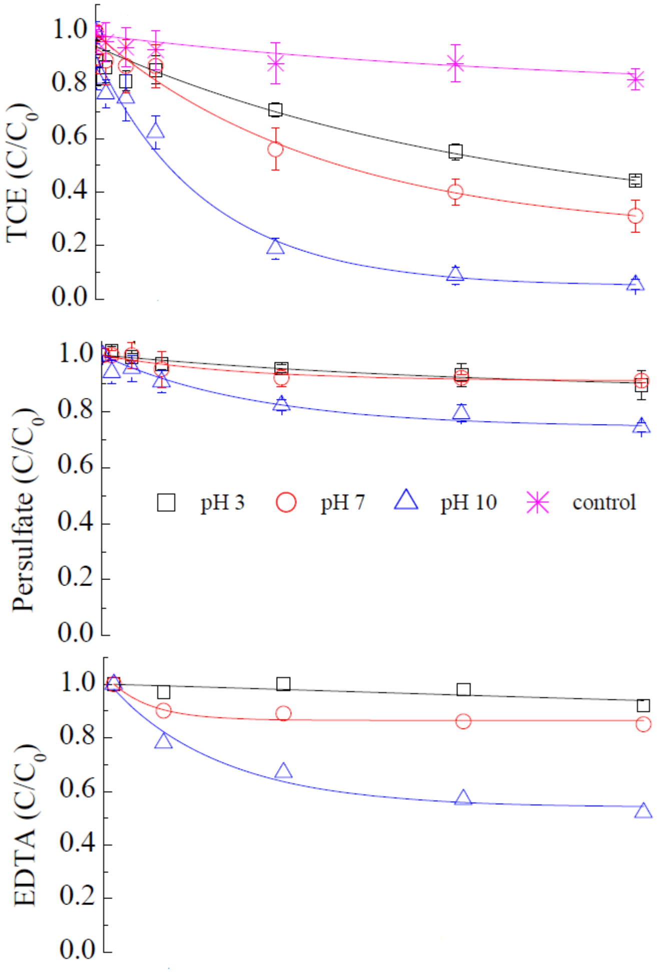
- TCE degradation (< 10%) was observed in the presence of EDTA/Fe^{3+} or Fe^{3+} without $S_2O_8^{2-}$ at pH 3, 7 and 10.
- An additional control test investigating the effect of Fe^{3+} alone at pH 10 on TCE exhibited no reduction of TCE in solution and demonstrated that no TCE was adsorbed by insoluble ferric oxide precipitates.



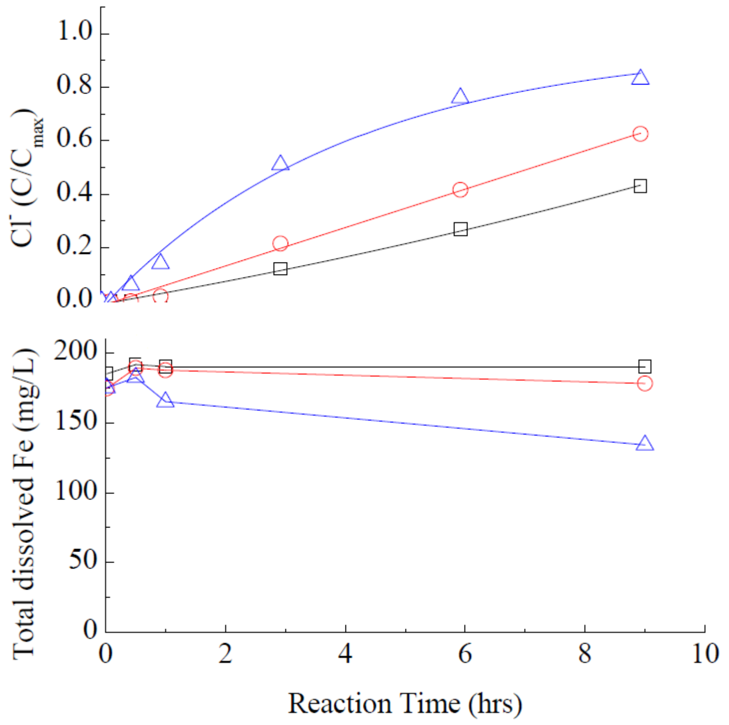
TCE + Fe^{3+}

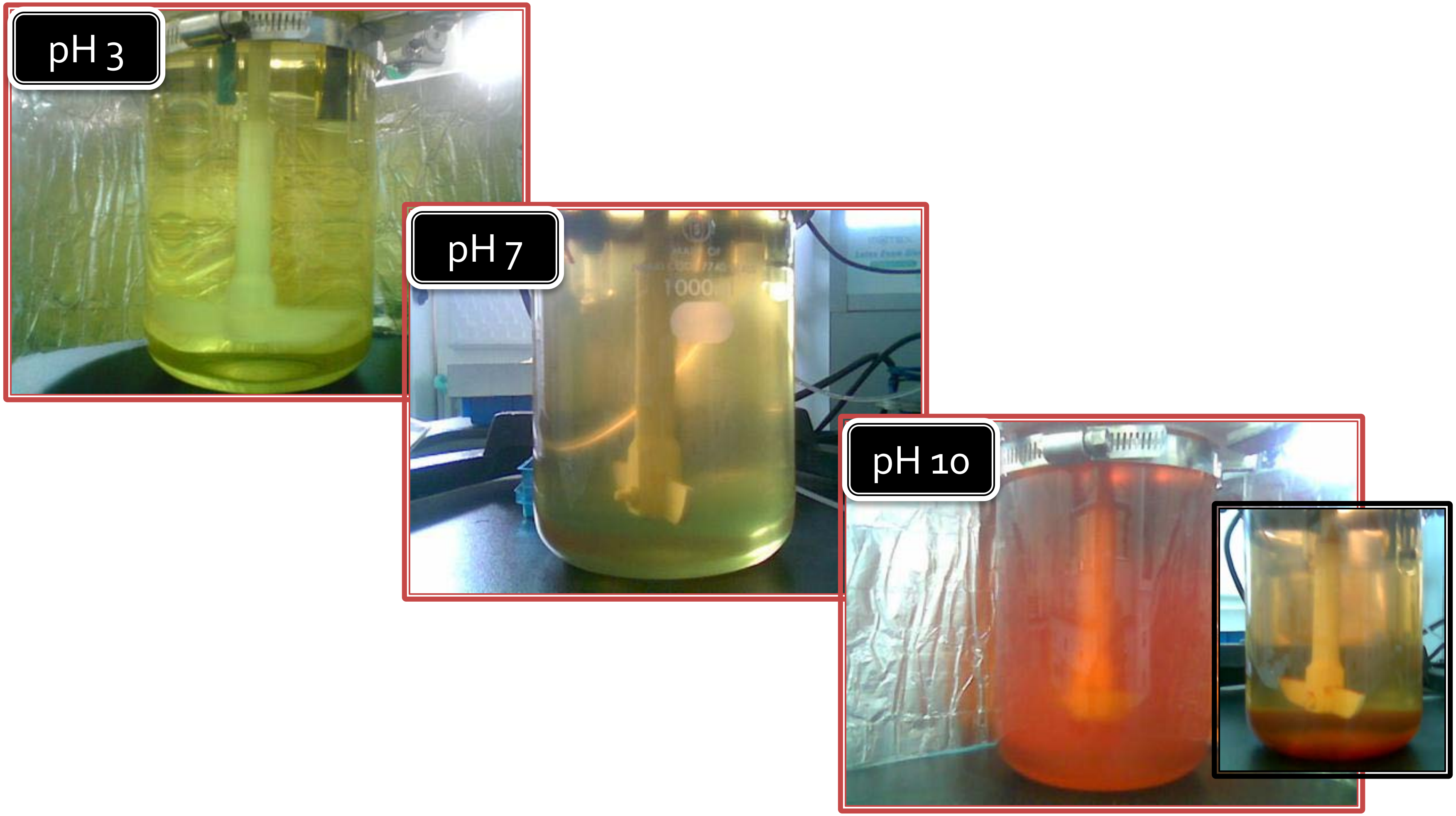
$$RH + Fe^{3+} \rightarrow Fe^{2+} + RH^{+\cdot}$$

The $S_2O_8^{2-}$/EDTA/Fe^{3+}/TCE system



In general, increasing the pH leads to increases in k_{obs} for TCE, PS, Cl and EDTA.




pH 3
pH 7
pH 10

Note

- As opposed to acidic and neutral conditions, the EDTA/Fe complexes exist predominately in their protonated forms at pH 10 (e.g., $Fe^{3+}(OH)_2EDTA$ or $Fe^{2+}(OH)_2EDTA$) which have relatively lower values of formation constants (i.e., log β) and exhibit thermodynamically unstable characteristics.

- For example, $Fe^{3+}EDTA$ and $Fe^{3+}(OH)_2EDTA$, as major species at pH 3 and 10, respectively, have formation constant values (log β) of **37.4** and **8.2**.

Note (cont.)

- As soon as $SO_4^{-\cdot}$ is generated **at pH 10**, the sulfate radical can attack TCE and also undergo radical interconversion to form $HO^{\cdot}$.

$$>C{=}C< + HO^{\cdot} \rightarrow\ >(OH)C{-}C<^{\cdot}\ (R^{\cdot})$$

$$R^{\cdot} + Fe^{3+} \rightarrow Fe^{2+} + \text{products}$$

$$>C{=}C< + SO_4^{-\cdot} \rightarrow\ >{\cdot}C{-}C<^{+} + SO_4^{2-}$$

$$>{\cdot}C{-}C<^{+} + H_2O \rightarrow\ >(OH)C{-}C<^{\cdot}\ (R^{\cdot}) + H^{+}$$

- The presence of TCE in the EDTA/Fe^{3+} activated persulfate system can induce faster persulfate and EDTA degradations.

Pseudo-first-order kinetic kobs of TCE, persulfate, chloride and EDTA in the persulfate oxidation system

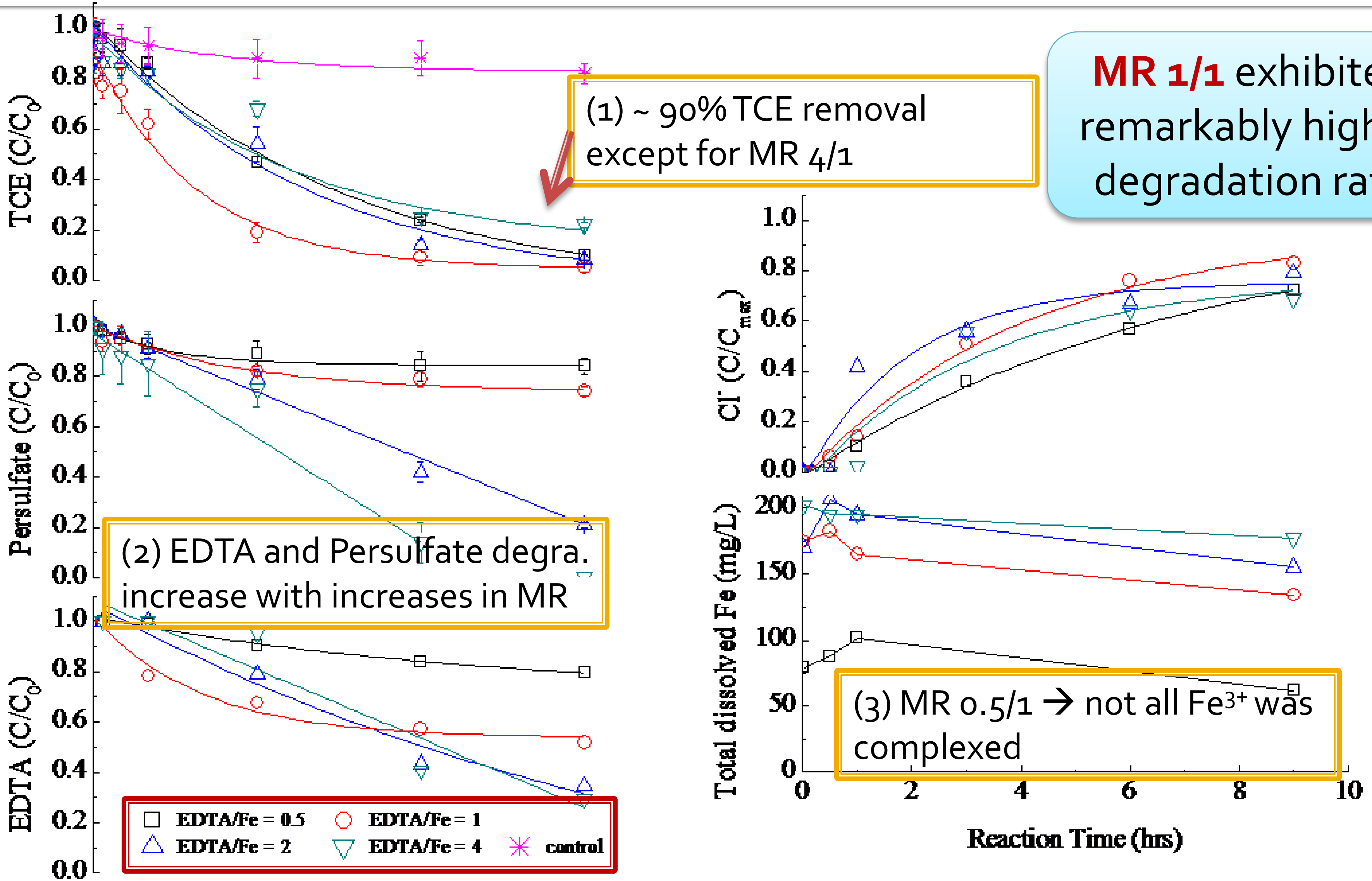
PS/EDTA/Fe^{3+}/TCE Molar Ratio	pH	$k_{obs,TCE}$ (h^{-1}) (R^2)	$k_{obs,PS}$ (h^{-1}) (R^2)	$k_{obs,Cl}$ (h^{-1}) (R^2)	$k_{obs,EDTA}$ (h^{-1}) (R^2)	$k_{obs,TCE}$/ $k_{obs,TCE\ (no\ act.\ pH\ 7)}$ (1)
20/3.58/3.58/0	3		0.031 (0.99)		0.089 (0.99)	
	7		0.016 (0.91)		0.036 (0.96)	
	10		0.017 (0.87)		0.034 (0.94)	
0/0/0/0.3	3	0.025 (0.67)				
	7	0.018 (0.95)				
	10	0.025 (0.56)				
0/3.58/3.58/0.3	3	0.033 (0.76)				
	7	0.021 (0.84)				
	10	0.020 (0.41)				
0/0/3.58/0.3	10	0.031 (0.58)				
20/0/0/0.3	3	0.039 (0.95)	0.016 (0.94)	0.019 (0.98)		0.4
	7	0.094 (0.99)	0.009 (0.96)	0.103 (0.99)		1.0
	10	0.075 (0.98)	0.011 (0.93)	0.074 (0.99)		0.8
20/3.58/3.58/0.3	3	0.096 (0.95)	0.013 (0.97)	0.058 (0.98)	0.007 (0.79)	1.0
	7	0.142 (0.98)	0.013 (0.84)	0.101 (0.98)	0.022 (0.86)	1.5
	10	0.502 (0.97)	0.038 (0.92)	0.210 (0.99)	0.084 (0.94)	5.3
20/1.79/3.58/0.3	10	0.251 (0.99)	0.025 (0.90)	0.141 (0.99)	0.027 (0.99)	2.7
20/7.16/3.58/0.3		0.291 (0.99)	0.157 (0.97)	0.186 (0.95)	0.120 (0.98)	3.1
20/14.32/3.58/0.3		0.184 (0.96)	0.591 (0.86)	0.151 (0.93)	0.130 (0.93)	2.0
10/3.58/3.58/0.3	10	0.301 (0.98)	0.037 (0.99)	0.105 (0.98)	0.049 (0.99)	3.2
40/3.58/3.58/0.3		0.671 (0.96)	0.021 (0.92)	0.165 (0.96)	0.067 (0.92)	7.1

Results and Discussion

- ***Objective 3***

  The effects of EDTA/Fe^{3+} molar ratios and persulfate concentrations on the TCE degradation at pH 10

EDTA/Fe^{3+} molar ratio



(1) ~ 90% TCE removal except for MR 4/1

MR 1/1 exhibited remarkably higher degradation rate

(2) EDTA and Persulfate degra. increase with increases in MR

(3) MR 0.5/1 → not all Fe^{3+} was complexed

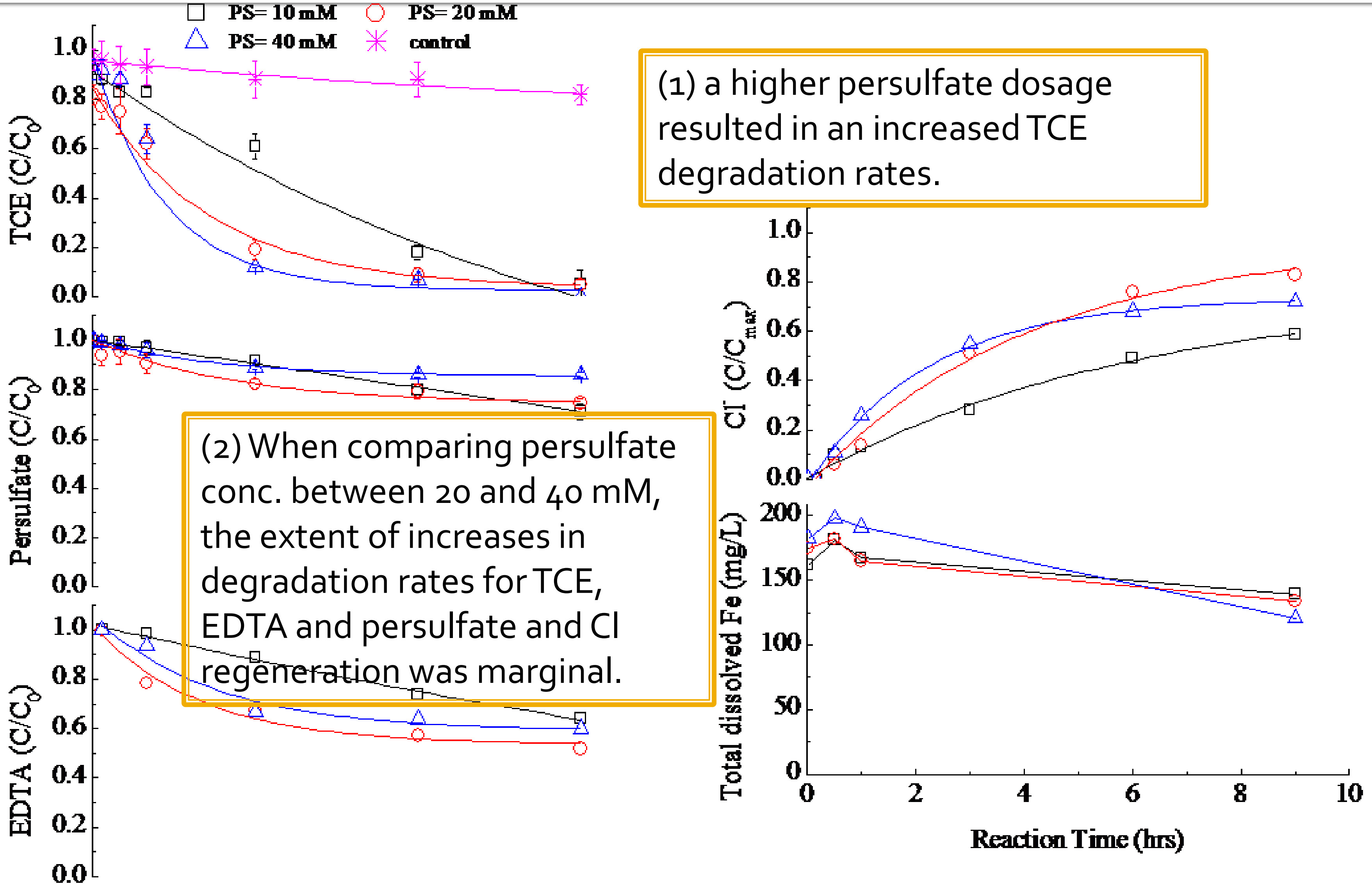
Note

EDTA/Fe^{3+} MR 0.5

EDTA/Fe^{3+} MR 2.0

EDTA/Fe^{3+} MR 4.0

Persulfate conc. (at MR 1/1)



(1) a higher persulfate dosage resulted in an increased TCE degradation rates.

(2) When comparing persulfate conc. between 20 and 40 mM, the extent of increases in degradation rates for TCE, EDTA and persulfate and Cl regeneration was marginal.

Conclusion

1. Application of an EDTA/Fe^{3+} mixture was successfully used to activate persulfate and degrade TCE in solution at various pH conditions.

2. EDTA is a promising chelating agent for the chelated iron activated persulfate system because it simultaneously complexes Fe^{2+} and Fe^{3+} via a redox-chain mechanism.

Conclusion (cont.)

3. It was theoretically demonstrated that an elevated pH could be a preferred pH condition in enhancing EDTA/Fe^{3+} activated persulfate oxidation of TCE.

4. The optimum pH of the EDTA/Fe^{3+} activated persulfate system was demonstrated to be alkaline conditions (pH 10), and an EDTA/Fe^{3+} molar ratio of 1/1 was observed to be an optimum ratio.

Thank You & Any Question?