

Sulfate Radical Oxidation of 2,4-D using Iron Activation of Persulfate and Peroxymonosulfate

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Introduction

- Compounds such as pesticides are persistent and toxic in the environment.
- Advanced oxidation are used to degrade these compounds.
- Sulfate radicals ($\text{SO}_4^{\cdot-}$) are stable with high oxidizing power.
- Sulfate radicals can be generated from
 - Persulfate ($\text{S}_2\text{O}_8^{2-}$)
 - Peroxymonosulfate (HSO_5^-)
- Various activation methods are used:
 - Heat
 - Transition metal
 - UV light
 - Ultrasound
- Reactions:
 - Activator + $\text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{\cdot-} + \text{SO}_4^{2-}$
 - Activator + $\text{HSO}_5^- \rightarrow \text{SO}_4^{\cdot-} + \text{OH}^-$

Objectives

- Overall goal is to evaluate iron as an activator for the generation of sulfate radicals in the oxidation of 2,4-dichlorophenoxyacetic (2, 4-D), a common pesticide.
- Specific objectives are:
- Evaluate different molar concentration of iron and persulfate or peroxymonosulfate on 2,4-D oxidation.
 - Investigate the kinetics of 2,4-D oxidation.

Methods and Materials

- 2,4-D concentration fixed at 0.045 mM
- Oxidants and Fe^{2+} concentrations ranged between 0 to 0.9 mM
- Reaction time = 2 hours at ambient temperature
- Samples collected at different time for kinetics study
- Collected samples quenched immediately with methanol
- 2,4-D analyzed with an HPLC-UV

Results and Discussions

Molar Ratios Study

- Figure 1 provides examples of 2,4-D oxidation with different molar concentrations.
- Optimal molar concentration ratio of oxidants and Fe^{2+} for 2,4-D degradation was 1:1.
- Higher molar ratio of Fe^{2+} added all at once was found to decrease degradation efficiency.

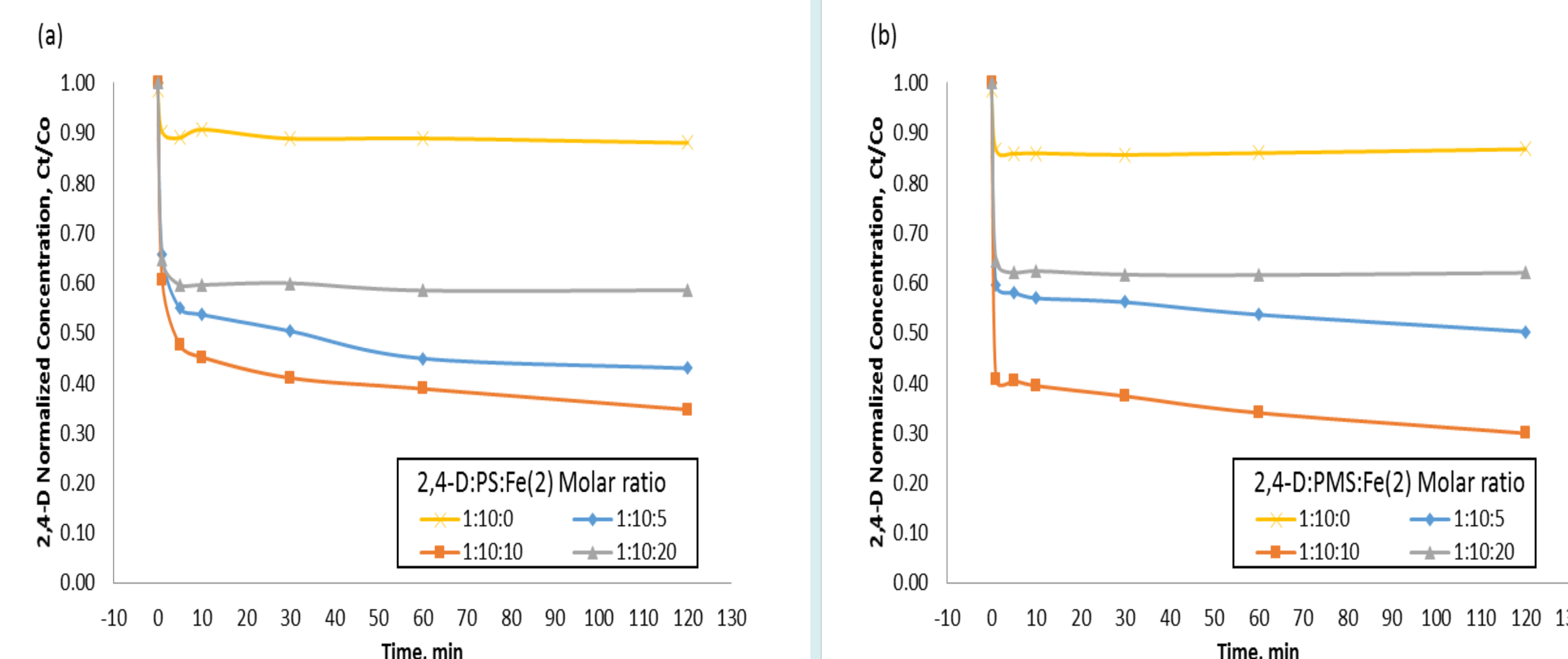


Figure 1 Examples of 2,4-D oxidation (a) persulfate and (b) peroxymonosulfate

- Sequential additions of Fe^{2+} showed further degradation of 2,4-D - implying Fe^{2+} was rapidly deactivated even though persulfate or peroxymonosulfate continue to be present (see Fig. 2).

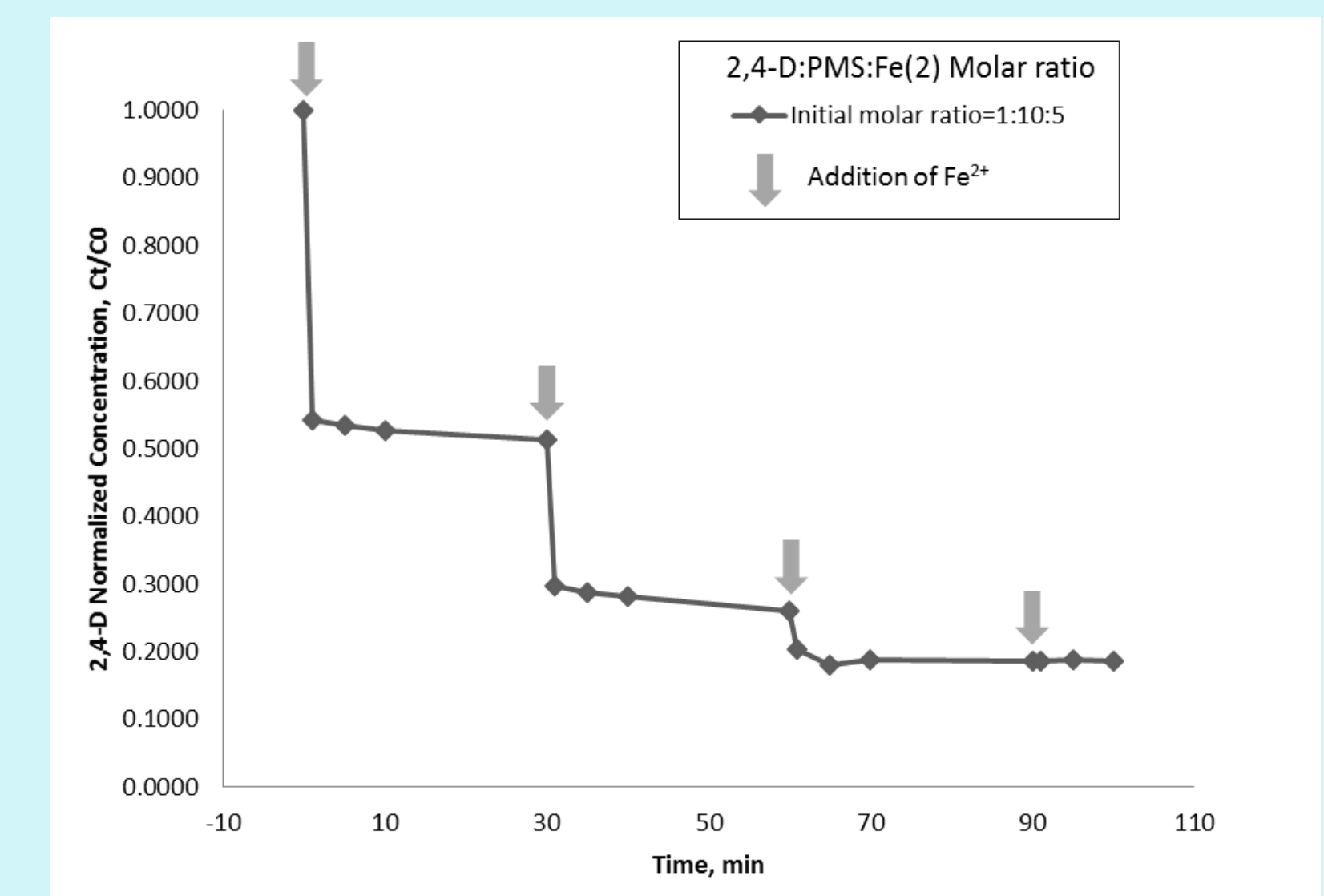


Figure 2 Sequential addition of Fe^{2+}

Kinetic Study

- Three kinetic models were used:
 - Model 1: First-order
 - Model 2: Bi-exponential first-order model
 - Model 3: Availability-adjusted first-order model
- Model 2 gave the best fit of the data ($R^2 = 0.99$)

$$C(t) = C_{01} \exp(-k_1 \cdot t) + C_{02} \exp(-k_2 \cdot t)$$
 where C_{01} and C_{02} represent concentrations initially distributed between the two pools
- Results showed a bi-modal reaction where Fe^{2+} was rapidly exhausted in initial part of the reaction in comparison to the decomposition of persulfate or peroxymonosulfate to sulfate radicals.

Conclusions

- A low cost material such as Fe^{2+} can be applied to activate persulfate or peroxymonosulfate for oxidation of 2,4-D in contaminated groundwater and drinking water.
- A disadvantage with using Fe^{2+} was that it was consumed rapidly and addition of higher concentrations has no advantage. Fe^{2+} has to be added sequentially.