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# **Retrospective on Twenty Years of Peroxygen ISCO Research**

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# Peroxygens Used for ISCO

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- Hydrogen Peroxide
  - H-O-O-H
- Persulfate
  - $^{-}\text{SO}_3\text{-O-O-SO}_3^{-}$

# Presentation Outline

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- Hydrogen Peroxide
  - Introduction
  - Activation
  - Stabilization
  - Degradation of Carbon Tetrachloride
- Persulfate
  - Introduction
  - Activation by Minerals
  - Activation by Hydrogen Peroxide
  - Activation by Organic Compounds

# Hydrogen Peroxide ISCO: Fenton's Reagent

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# Reactivity of Hydroxyl Radical

- Reactive with Most Contaminants of Concern
  - TCE, PCE
  - Chlorophenols and Chlorobenzenes
  - PCBs and PCDDs
- Not Reactive with Highly Chlorinated Alkanes
  - Carbon Tetrachloride
  - Freons

# Catalyzed H<sub>2</sub>O<sub>2</sub> Propagations (CHP) (Modified Fenton's Reagent)

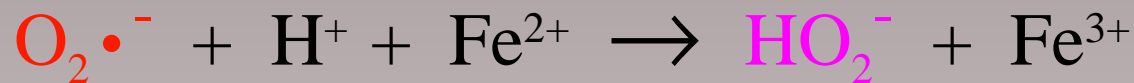
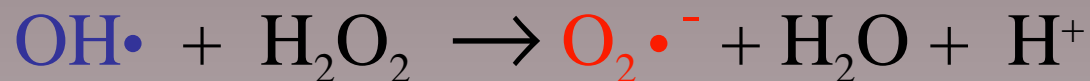
- Based on Fenton's reagent



- High H<sub>2</sub>O<sub>2</sub> concentrations (2–15%)
- Alternative activators

It's all about speed and propagations.

# Catalyzed H<sub>2</sub>O<sub>2</sub> Propagation Reactions

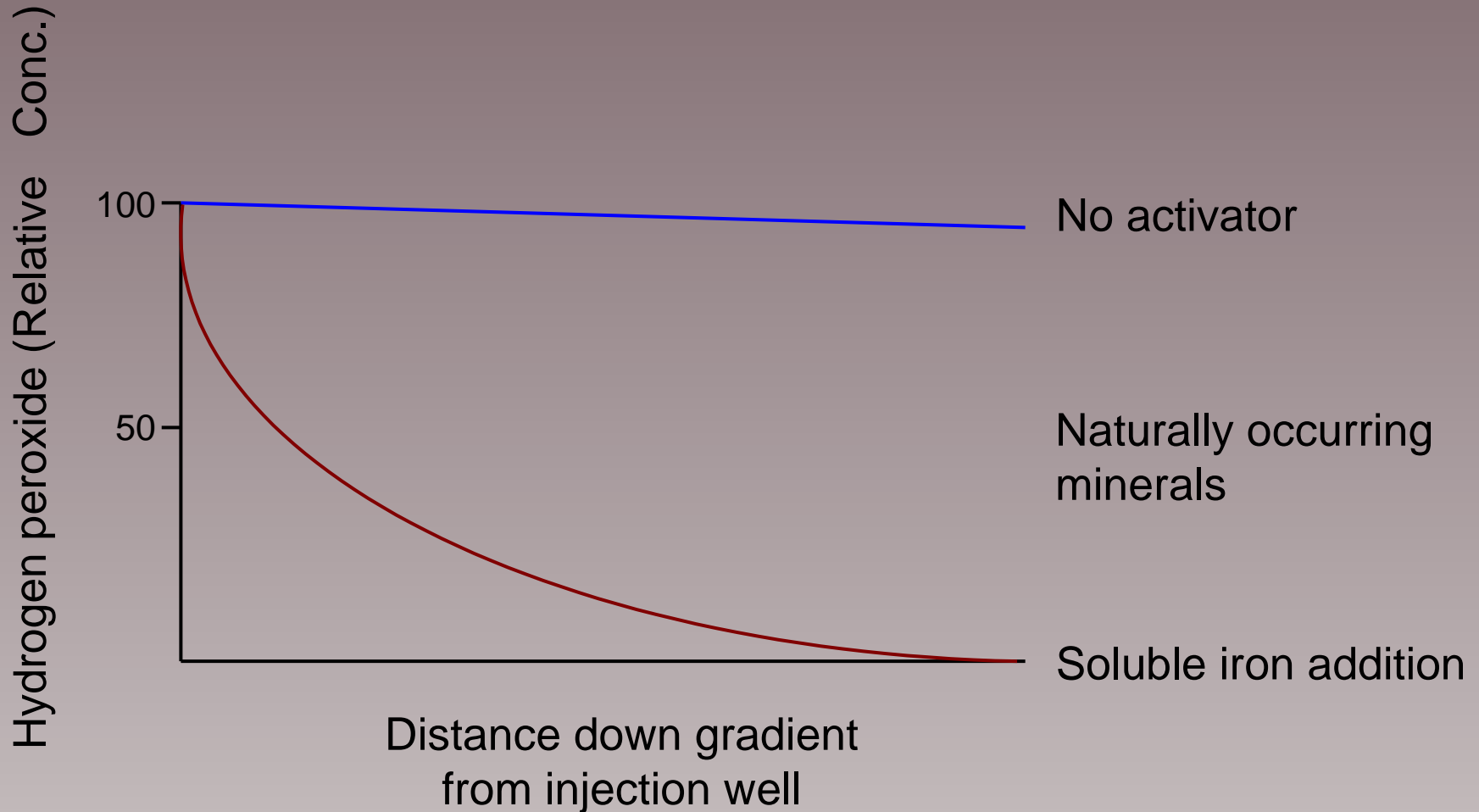


# CHP Activators



- Iron (II)
- Iron (III): Superoxide-driven reaction
- Iron chelates
- Iron oxide minerals
  - Goethite
  - Hematite
  - Ferrihydrite
- Manganese oxide minerals

# Effect of Iron Addition on Hydrogen Peroxide Decomposition Rate

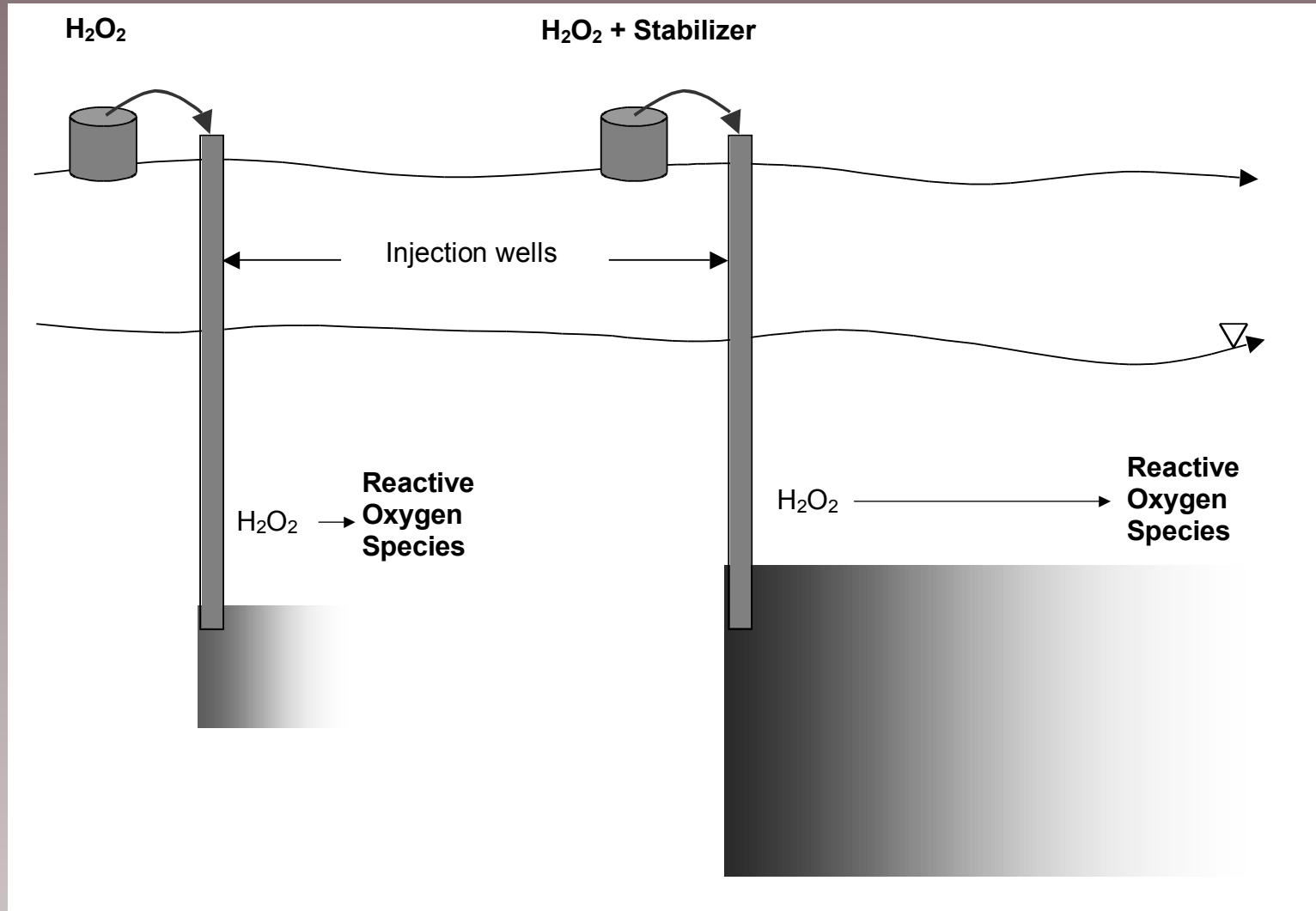


# Primary Limitation of CHP ISCO: Delivery

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- Hydrogen peroxide is short lived.
- It is difficult to deliver hydrogen peroxide beyond a few meters down gradient.
- It is nearly impossible to deliver hydrogen peroxide to low permeability regions of the subsurface.

# Increased Hydrogen Peroxide Stability

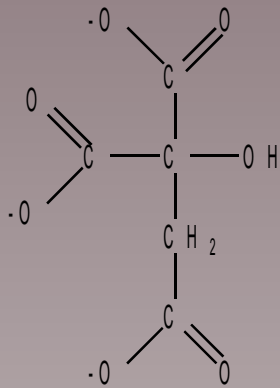


# Traditional Mechanisms for Stabilizing Hydrogen Peroxide

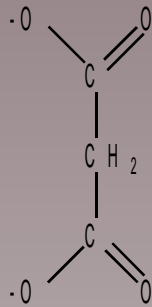
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- Phosphate addition
- Acidification

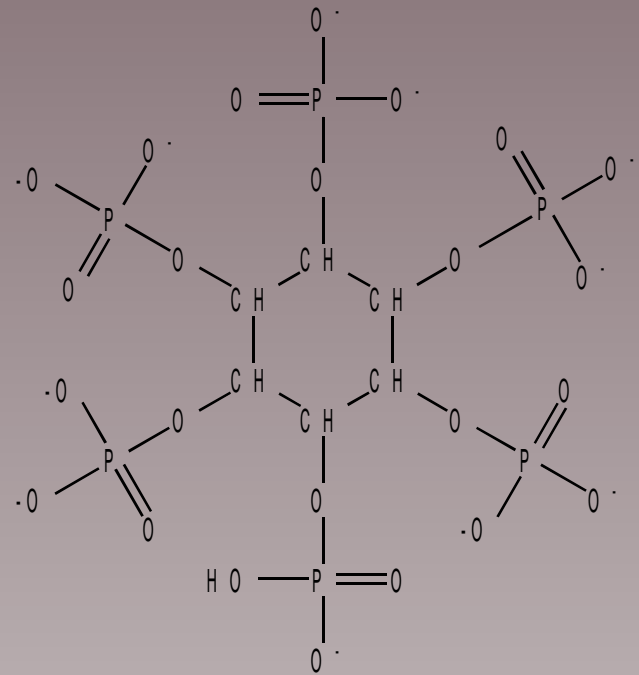
# Most Effective Stabilizers



Citrate

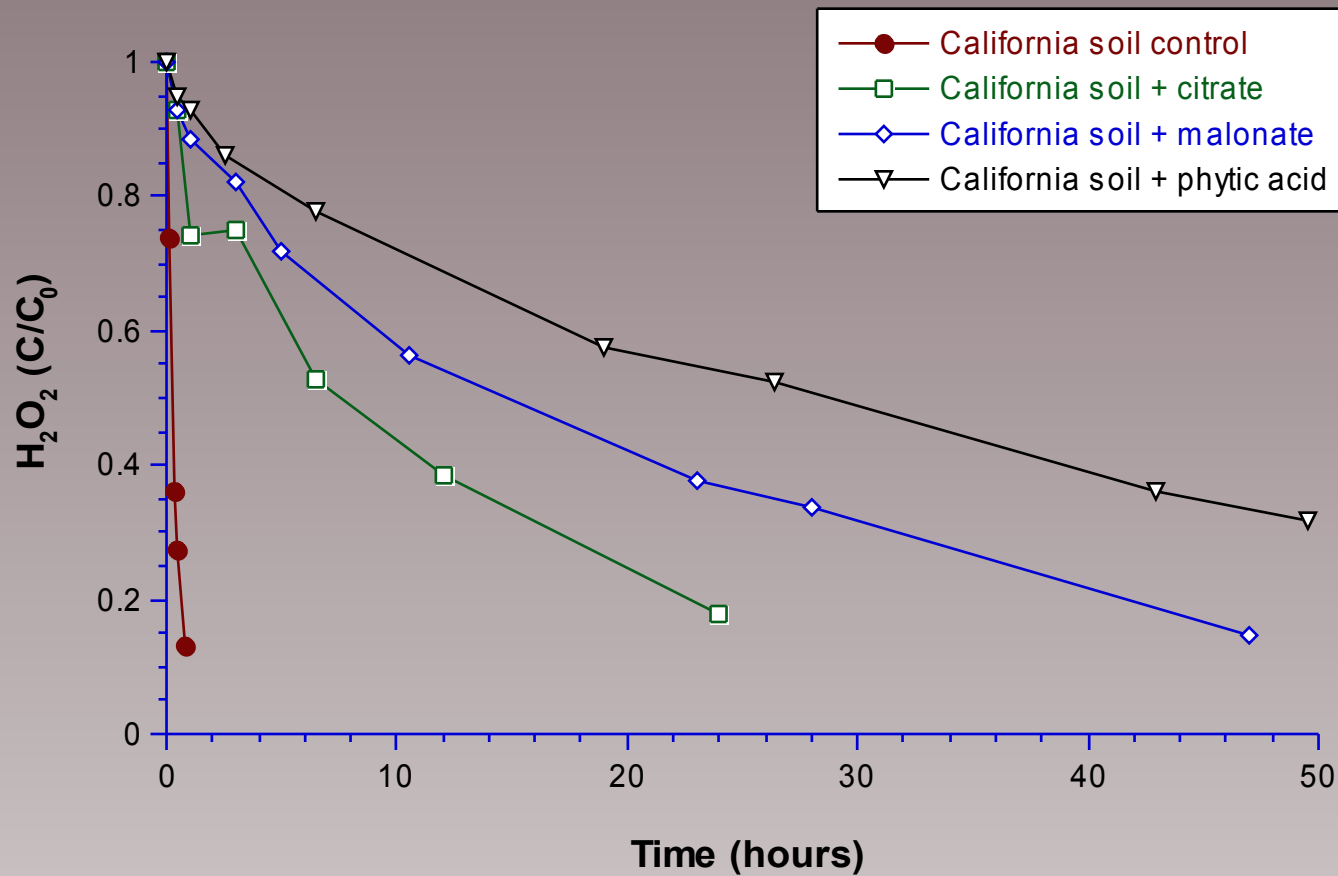


Malonate

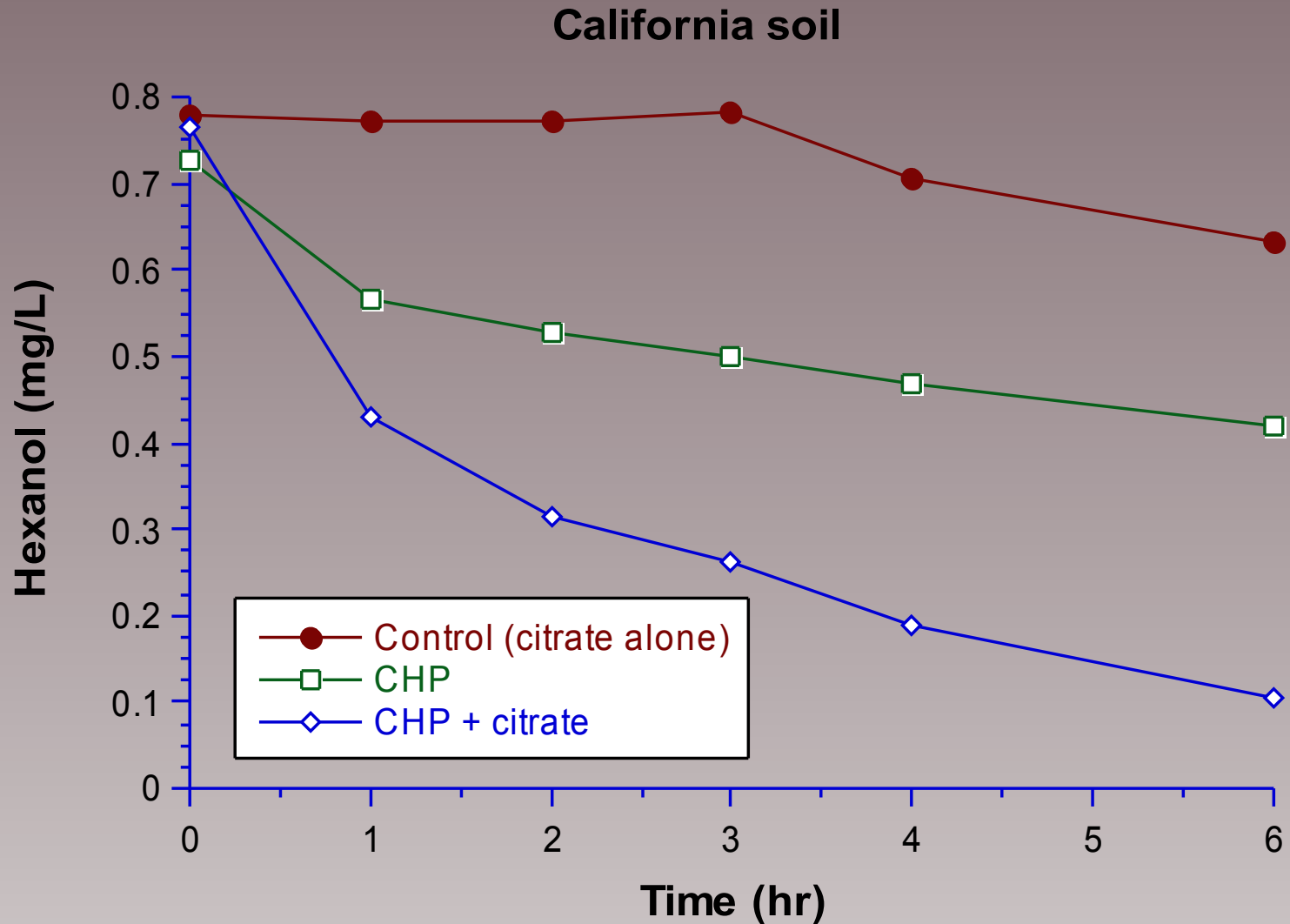


Phytate

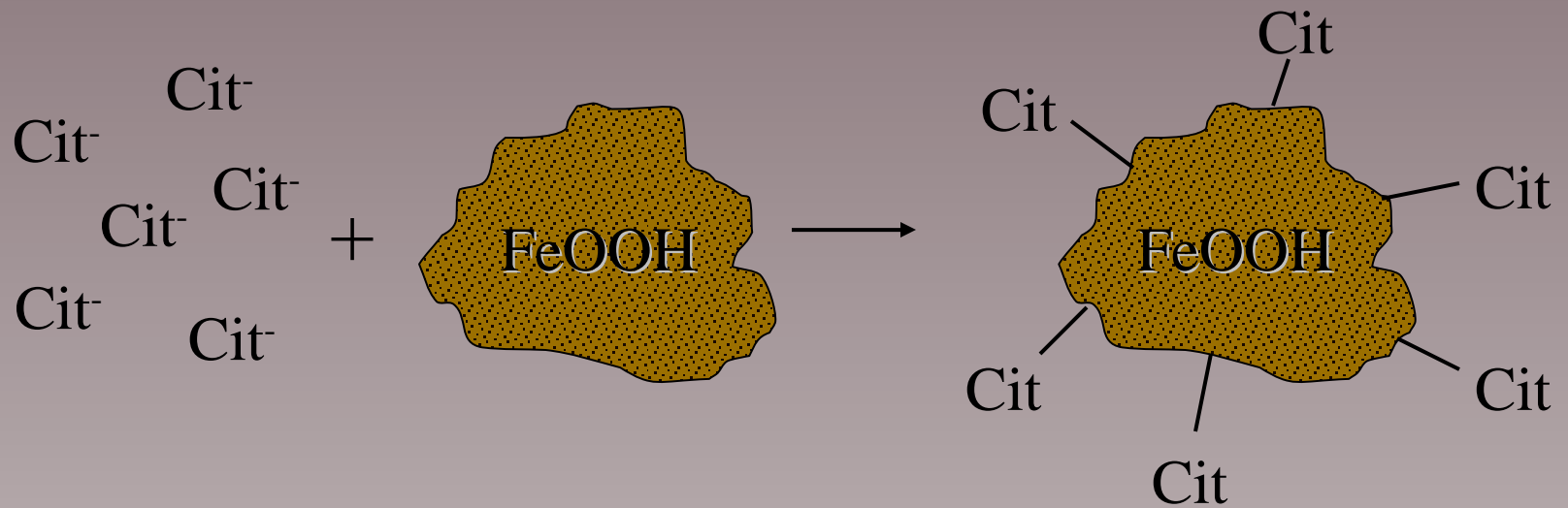
# H<sub>2</sub>O<sub>2</sub> Stabilization in the Presence of Subsurface Solids Collected from California



# Effect of Stabilizer on $\text{OH}\cdot$ Generation



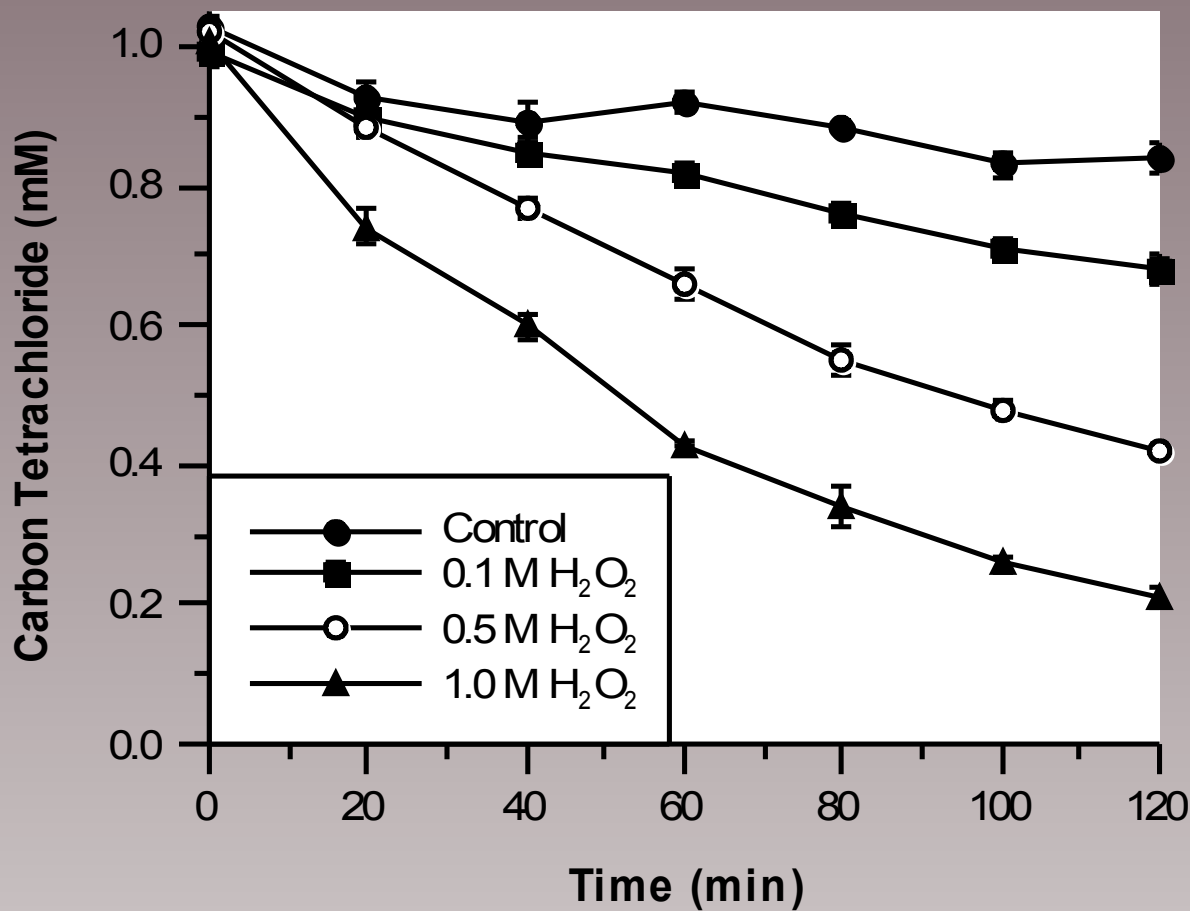
# Possible Stabilization Mechanism: Binding to Mineral Surfaces



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# Destruction of Carbon Tetrachloride by CHP

# Carbon Tetrachloride Degradation with Increasing Hydrogen Peroxide Concentrations in CHP Reactions



# Generation of Superoxide



- Superoxide:
  - Weak nucleophile and reductant
  - Highly reactive with carbon tetrachloride when dissolved in organic solvents
  - Minimal reactivity in water

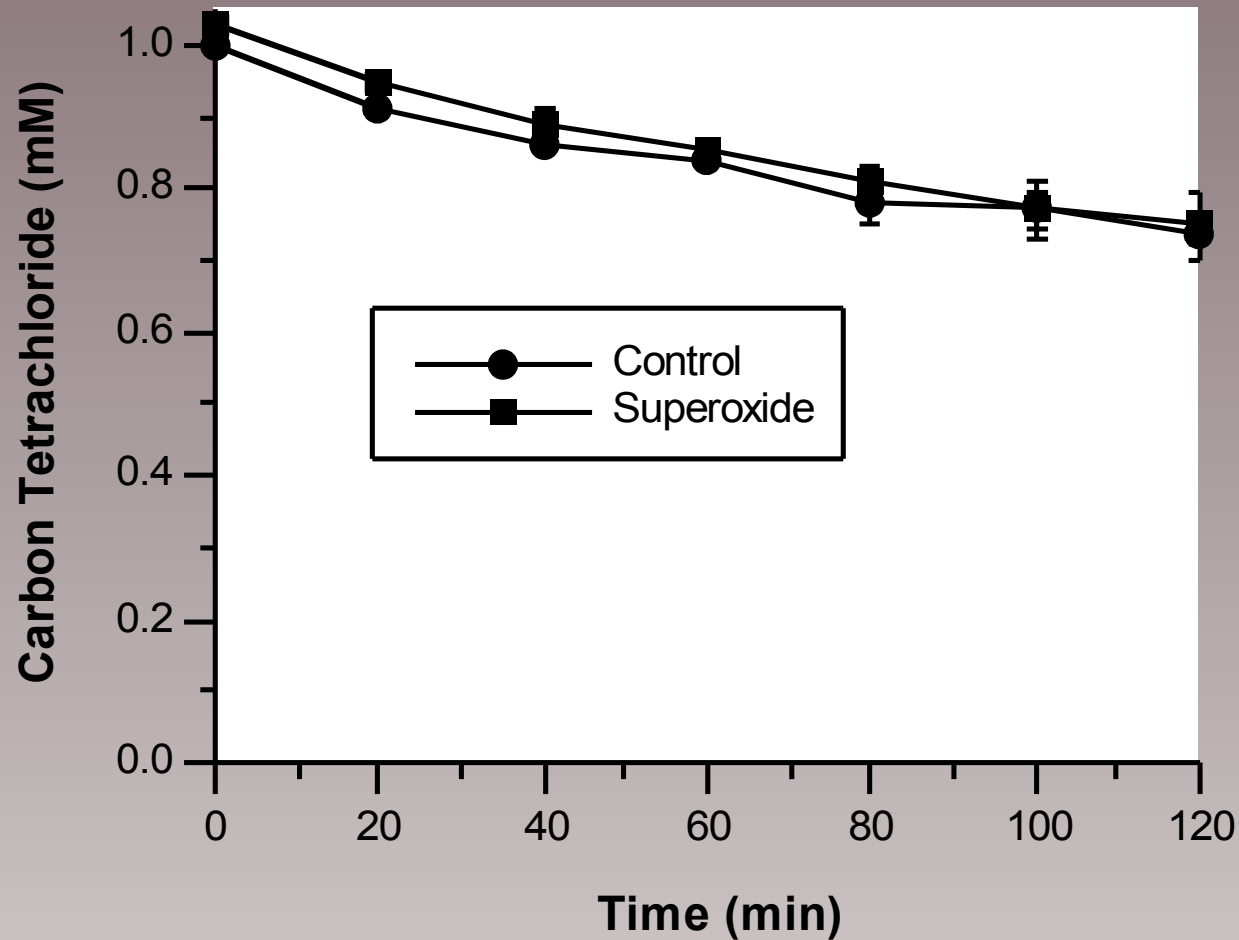
# Consensus on Superoxide Reactivity in Water

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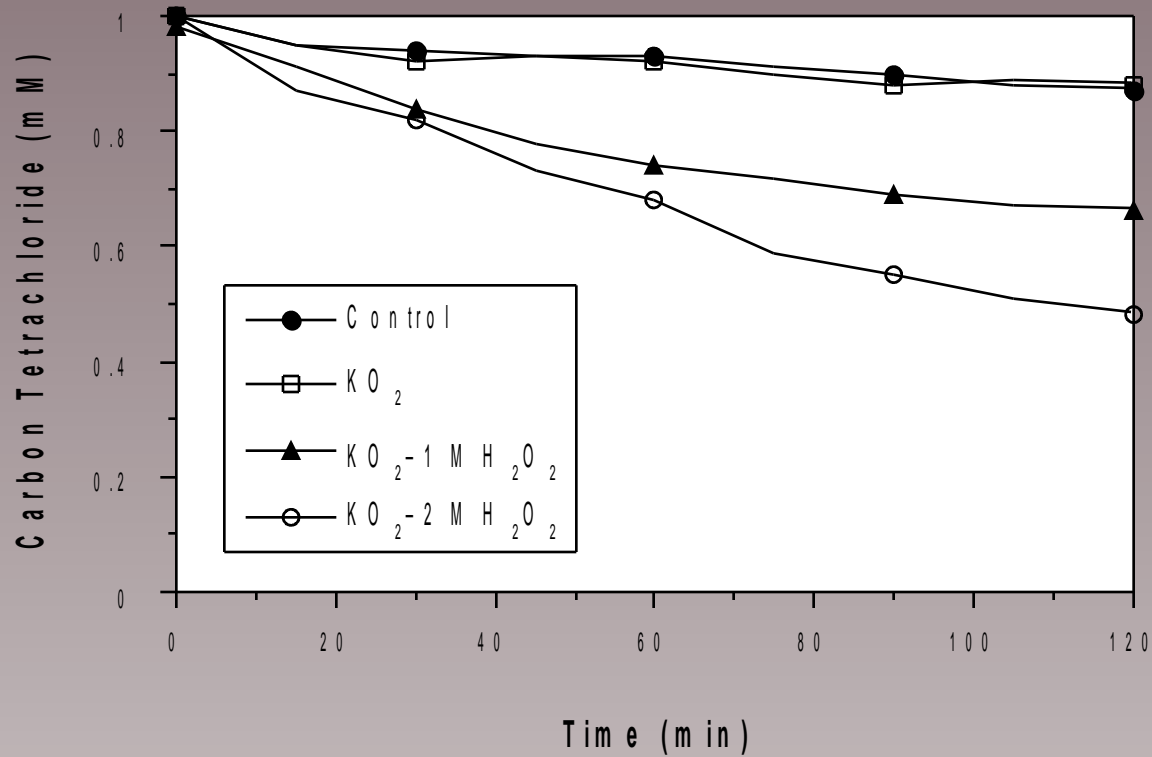
“An intellectually curious species which is characterized by minimal reactivity in aqueous systems”

Sawyer, D.T., and J.S. Sullivan. 1973. How Super is Superoxide? *Acc. Chem. Res.* 14:393-400.

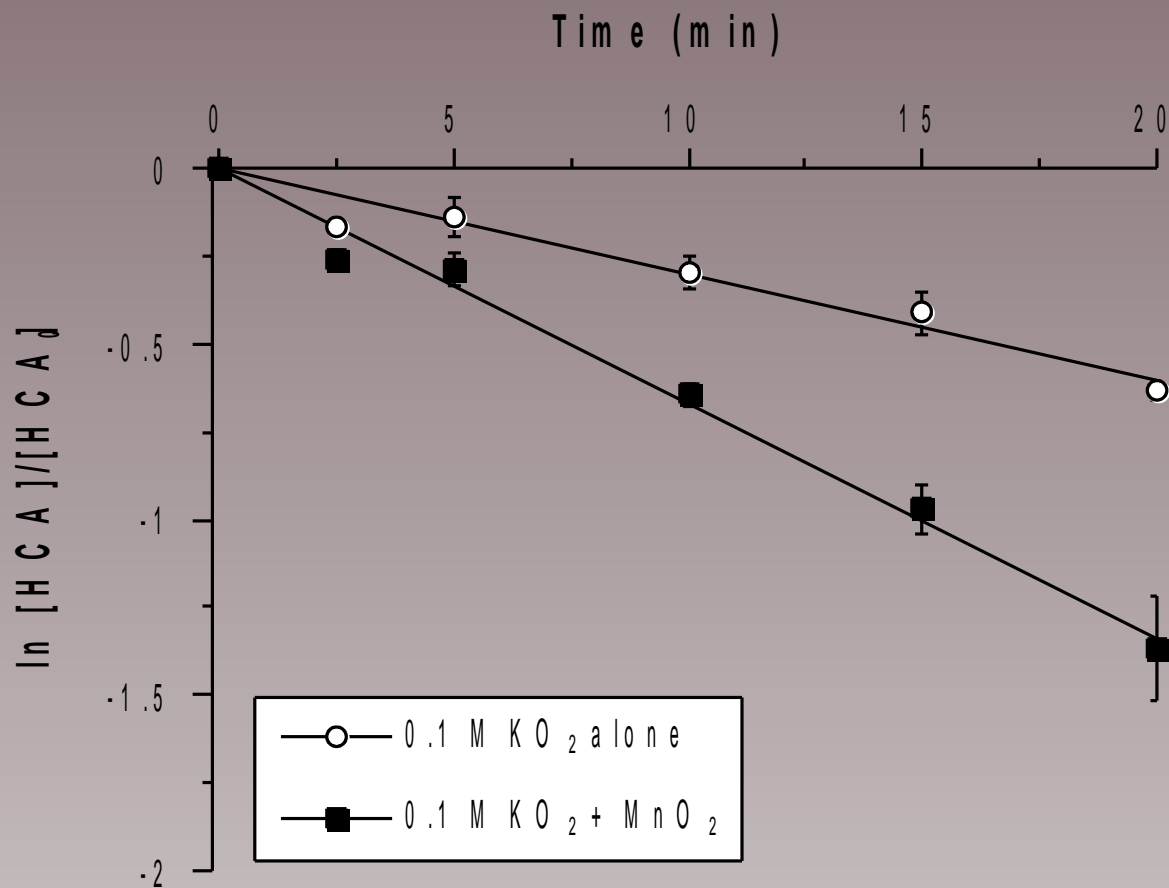
# Degradation of Carbon Tetrachloride in $\text{KO}_2$ Systems



# Effect of $H_2O_2$ on Superoxide Reactivity



# Effect of Mineral Surfaces on Superoxide Reactivity



# Components of CHP Systems That Enhance the Reactivity of Superoxide

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- Hydrogen Peroxide
- Hydrocarbons
- Solid Surfaces
- Soil Organic Matter (?)

# Summary: Hydrogen Peroxide

- Almost all minerals will decompose hydrogen peroxide, so it is short lived in the subsurface.
- Hydrogen peroxide stability can be enhanced by the addition of citrate, malonate, or phytate.
- Superoxide is unreactive with halogenated organic contaminants in deionized water.
- Perhalogenated alkanes, which are not reactive with hydroxyl radicals, can be degraded by superoxide if hydrogen peroxide, hydrocarbons, or surfaces are present to increase superoxide reactivity.
- CHP will destroy just about everything.

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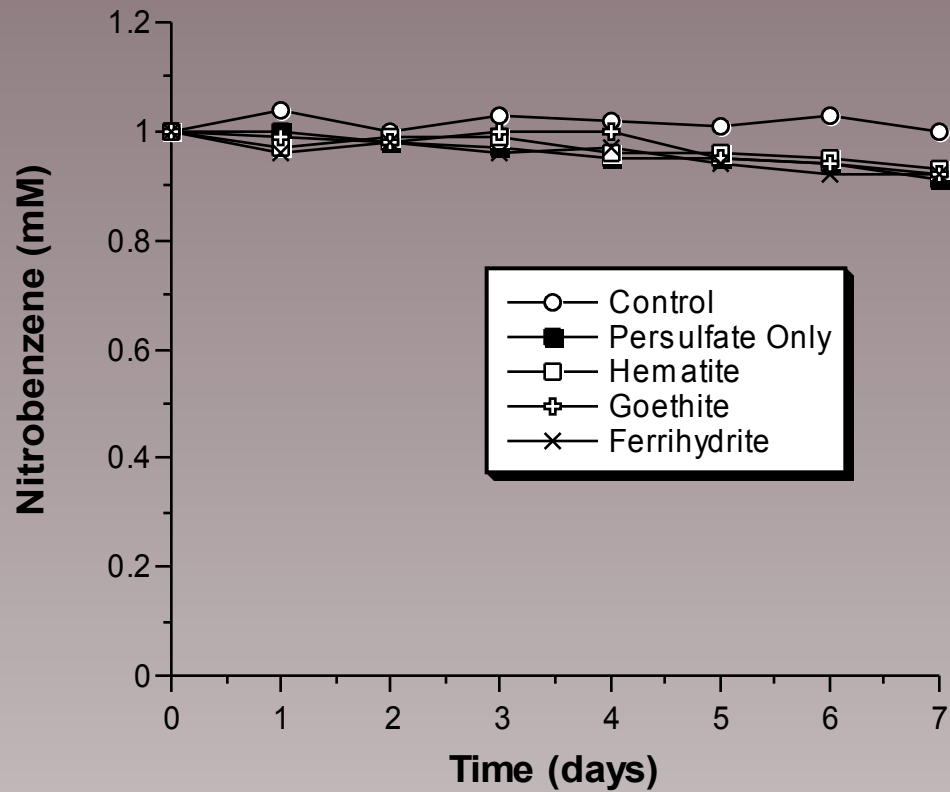
# Activated Persulfate

# Activators of Persulfate

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- Transition Metals
- Ultraviolet Light
- Heat
- Base
- Minerals (?)
- Hydrogen Peroxide (?)
- Some Organic Compounds

# Hydroxyl Radical Generation in Mineral-Persulfate Systems



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# Persulfate Activation by Hydrogen Peroxide

It's all about weak acid chemistry.

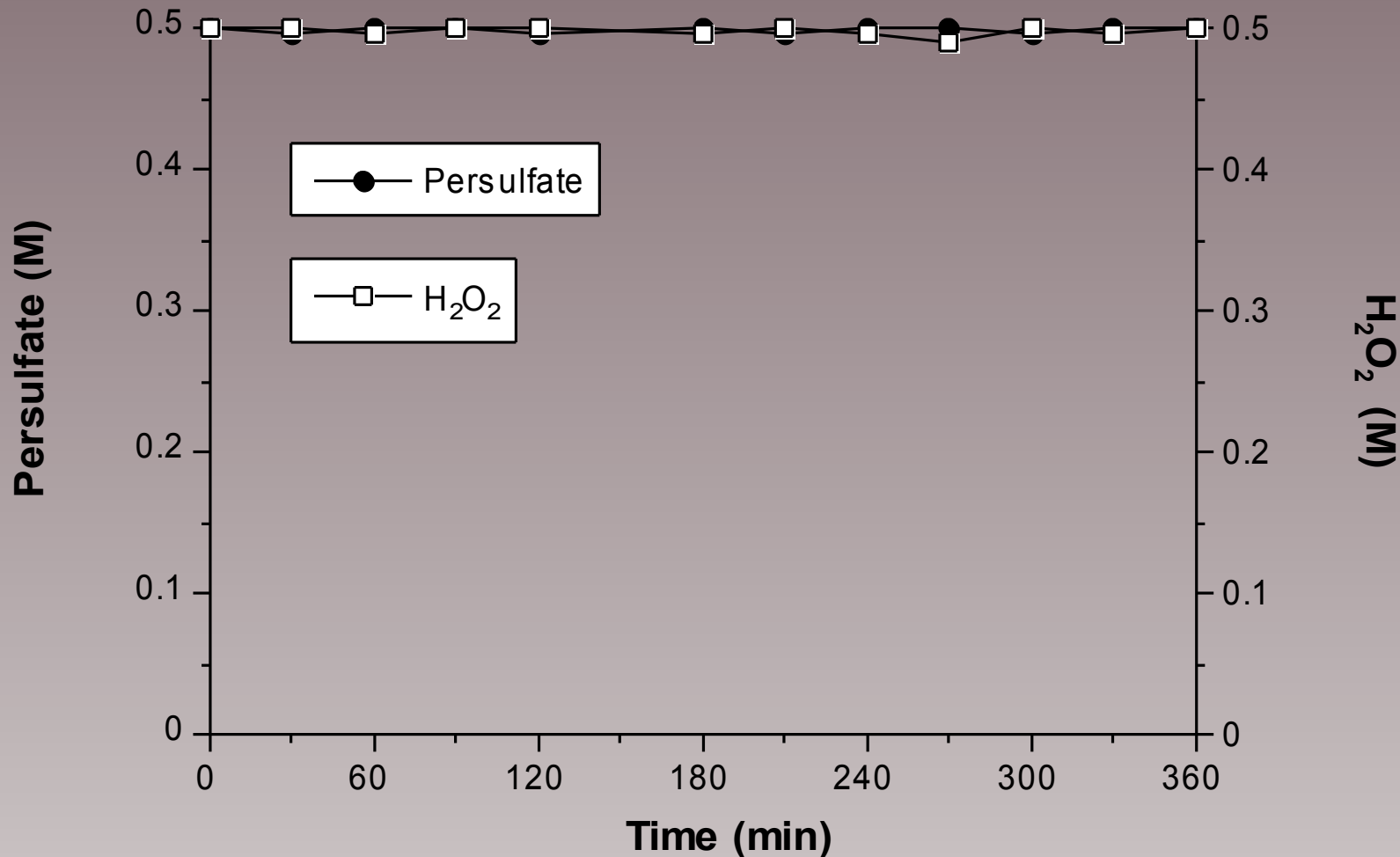
# Hydrogen Peroxide vs. Hydroperoxide Anion:

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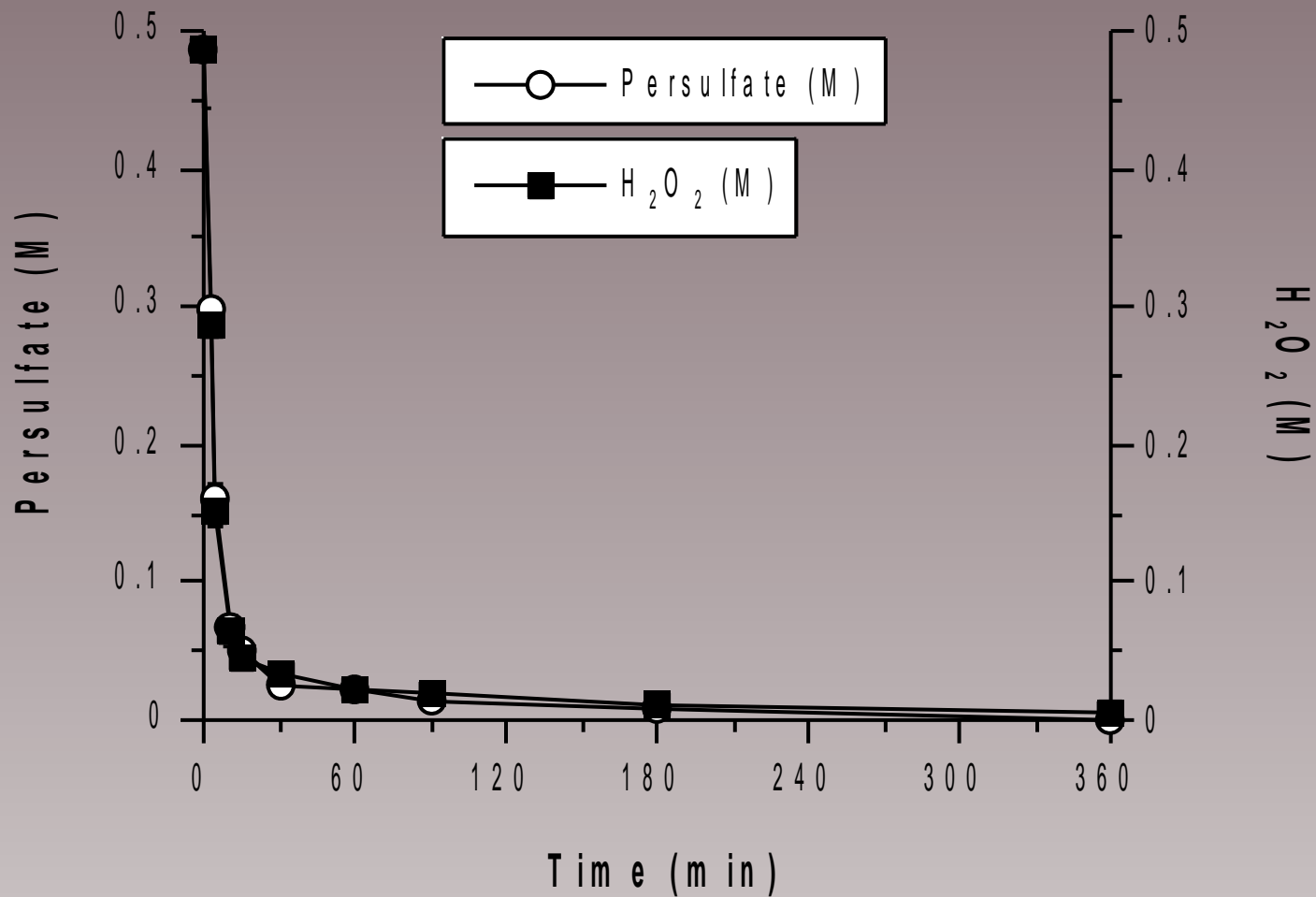
Hydrogen peroxide is a weak acid:



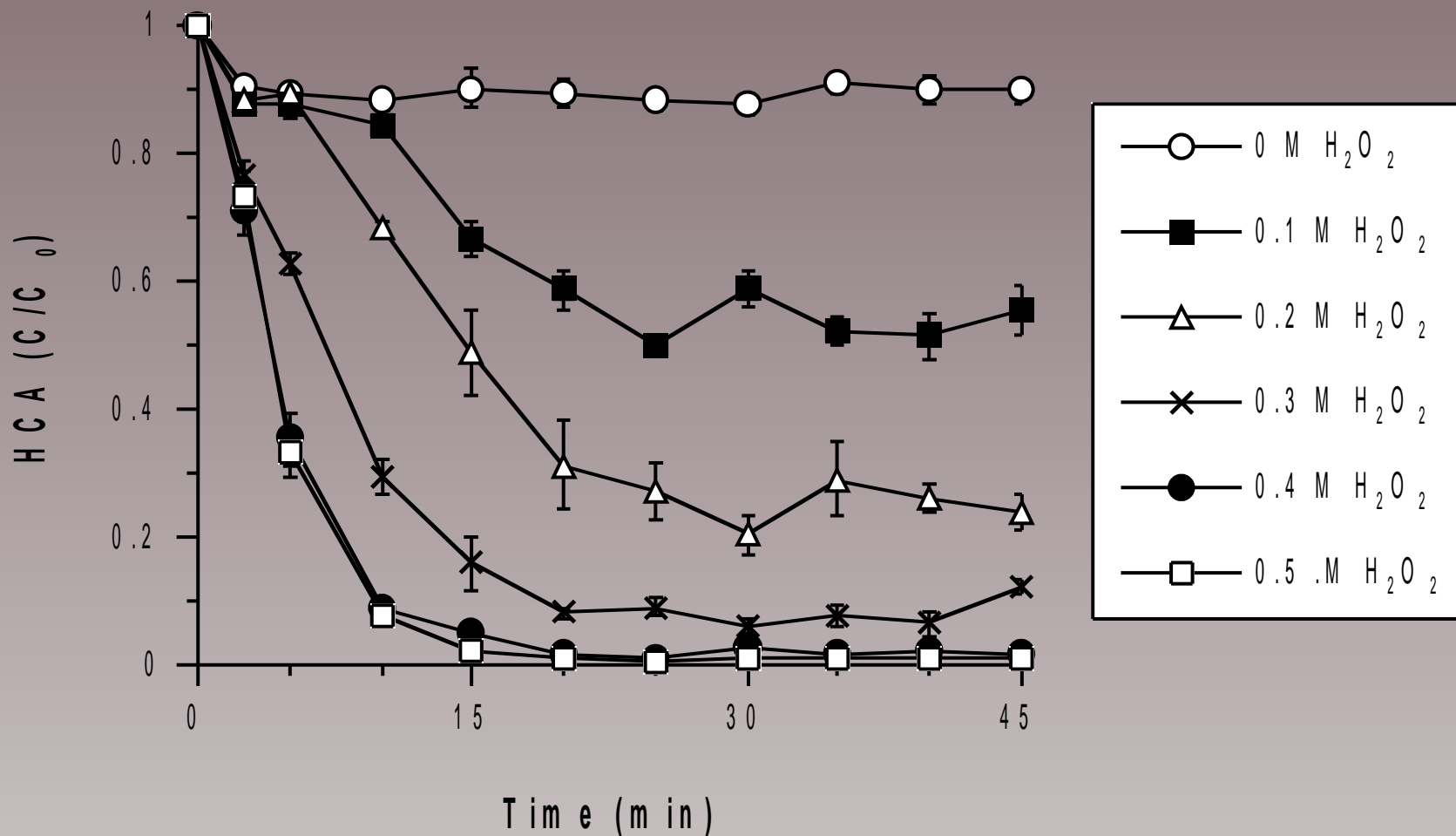
# Persulfate Decomposition in the Presence of Hydrogen Peroxide at Neutral pH



# Persulfate Decomposition in the Presence of Hydroperoxide at pH 12



# Degradation of Hexachloroethane in Persulfate Systems at pH 12 with Increasing Hydroperoxide Additions



# Activation of Persulfate by Hydroperoxide



# Activation of Persulfate by Hydrogen Peroxide at Neutral pH

Activator, Propagations



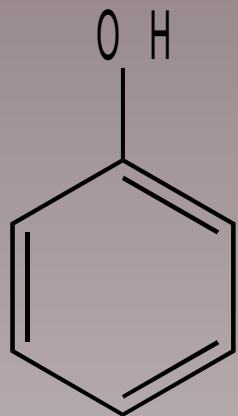
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# Persulfate Activation by Organic Compounds

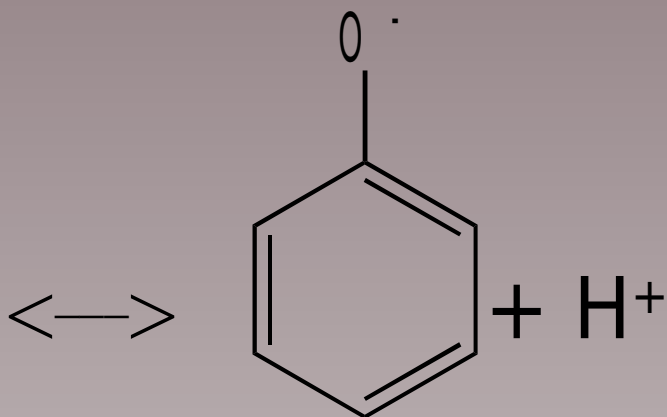
Also about weak acid chemistry

# Dissociation of Phenol to Phenoxide

Phenol

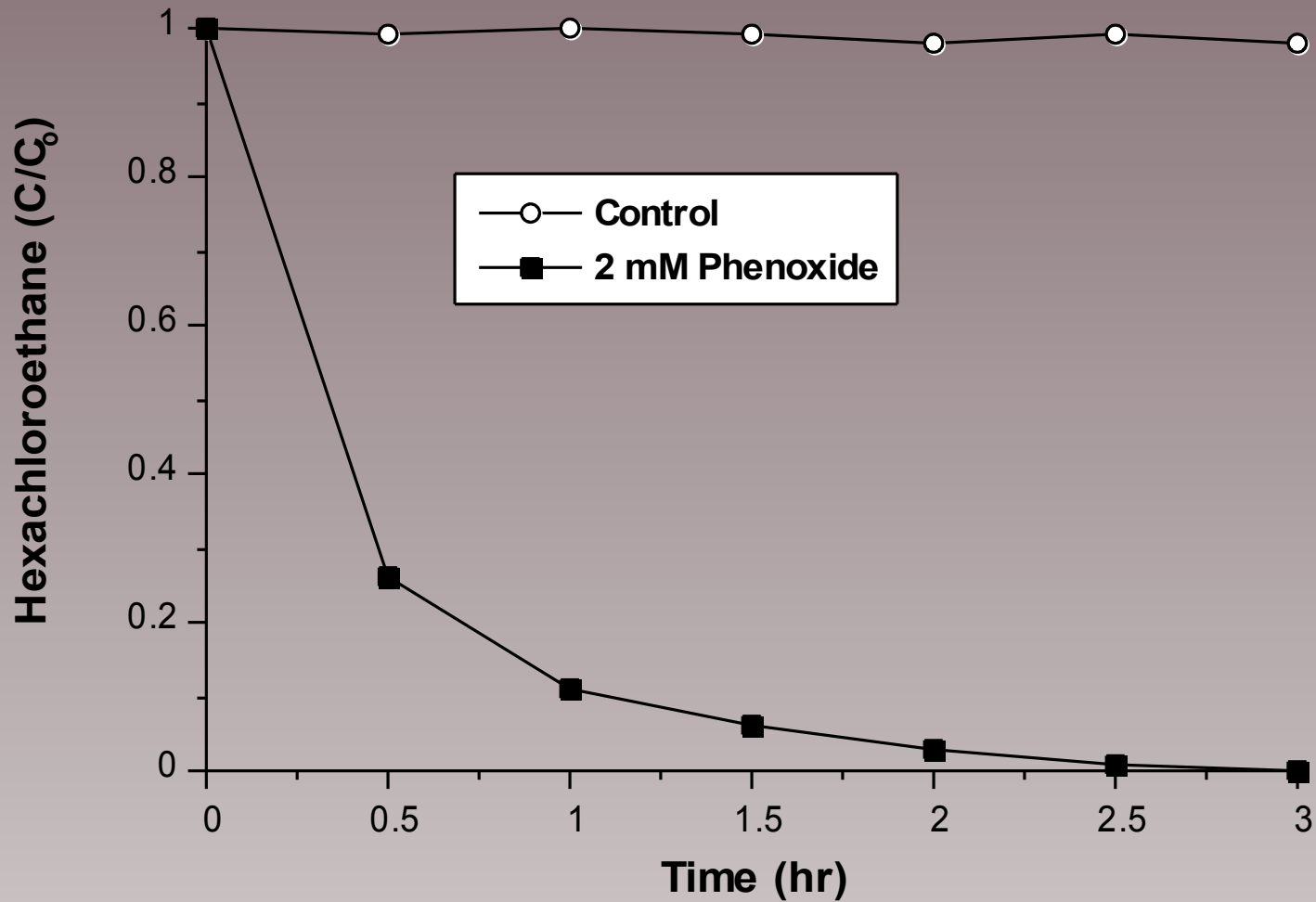


Phenoxide

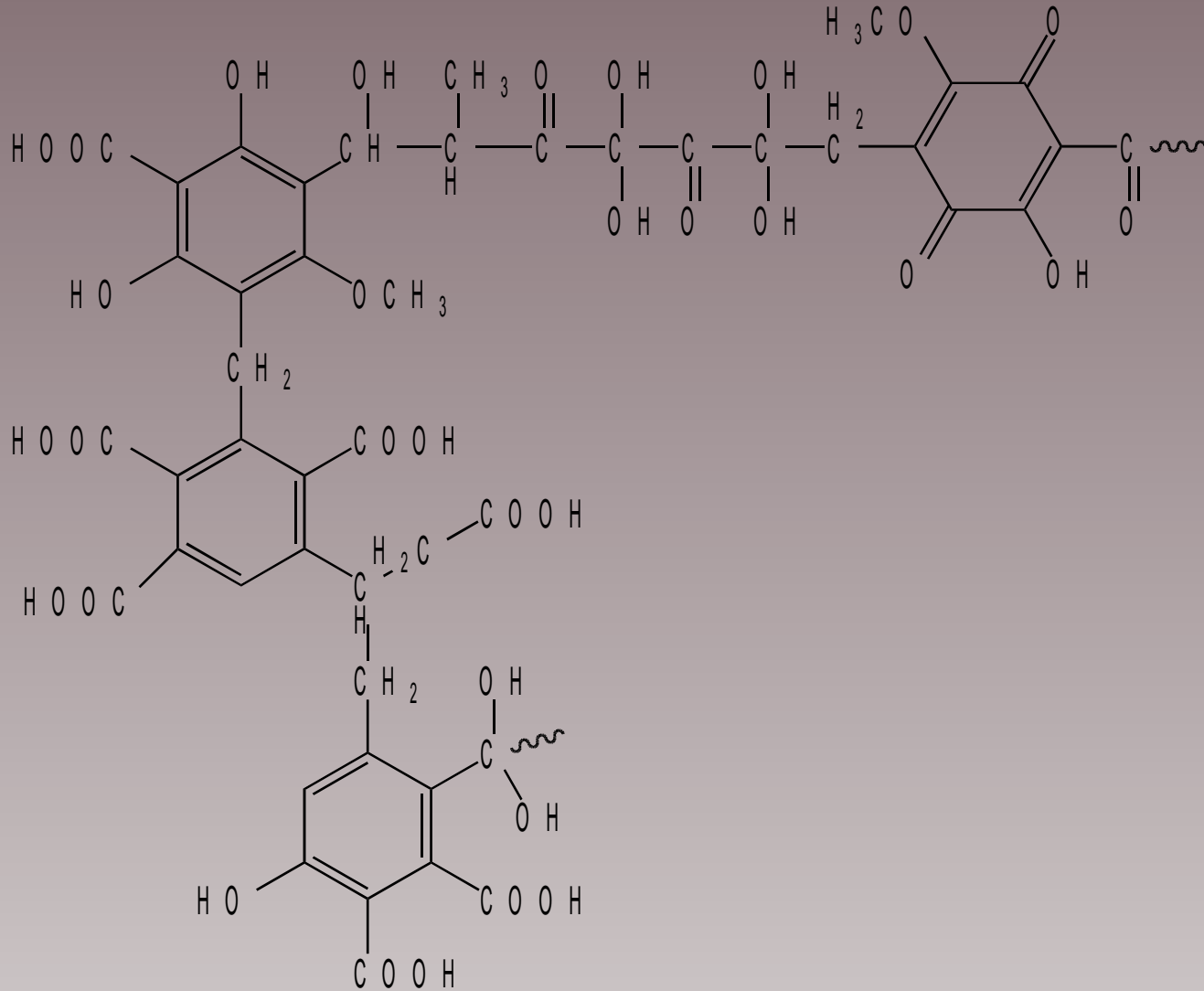


$$pK_a = 9.8$$

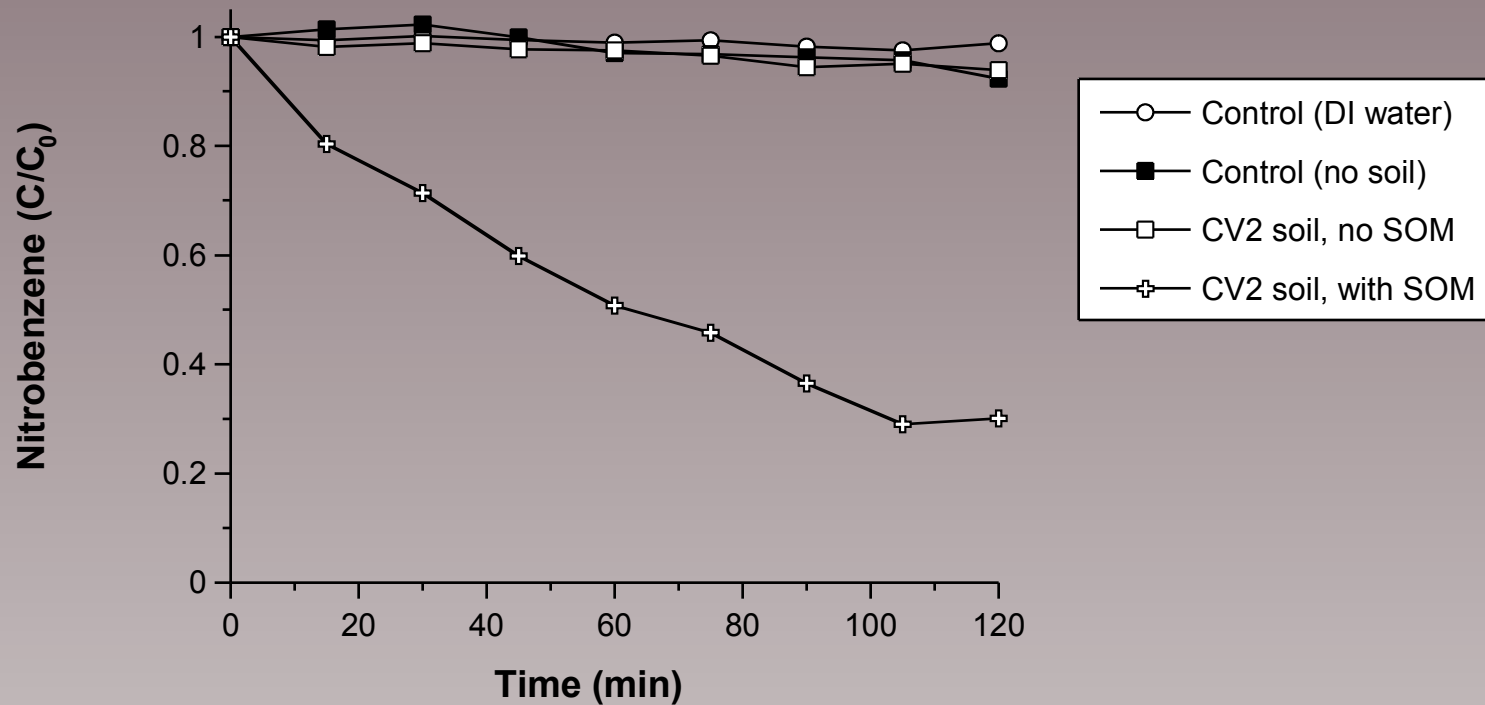
# Persulfate Activation by Phenoxide



# Soil Organic Matter



# Effect of SOM on Hydroxyl Radical Generation in Base-Activated Persulfate Systems



# Compounds that Activate Persulfate

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- Phenoxides
- Soil Organic Matter
- Ketones
- Some Krebs's Cycle Intermediates
- Glucose and Other Simple Sugars

# Summary: Persulfate

- Naturally occurring minerals exhibit a negligible role in activating persulfate.
- Hydrogen peroxide does not activate persulfate. Hydroperoxide activates persulfate by reducing it, producing sulfate radical and superoxide.
- Phenoxides activate persulfate.
- Soil organic matter activates persulfate at basic pH.

# Acknowledgments

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