Catalytically Facilitated Sequestration and Transformation of Persistent Organic Pollutants in Soils and Sediments

Walter J. Weber, Jr.

Energy and Environment Program
Department of Chemical Engineering
The University of Michigan, Ann Arbor

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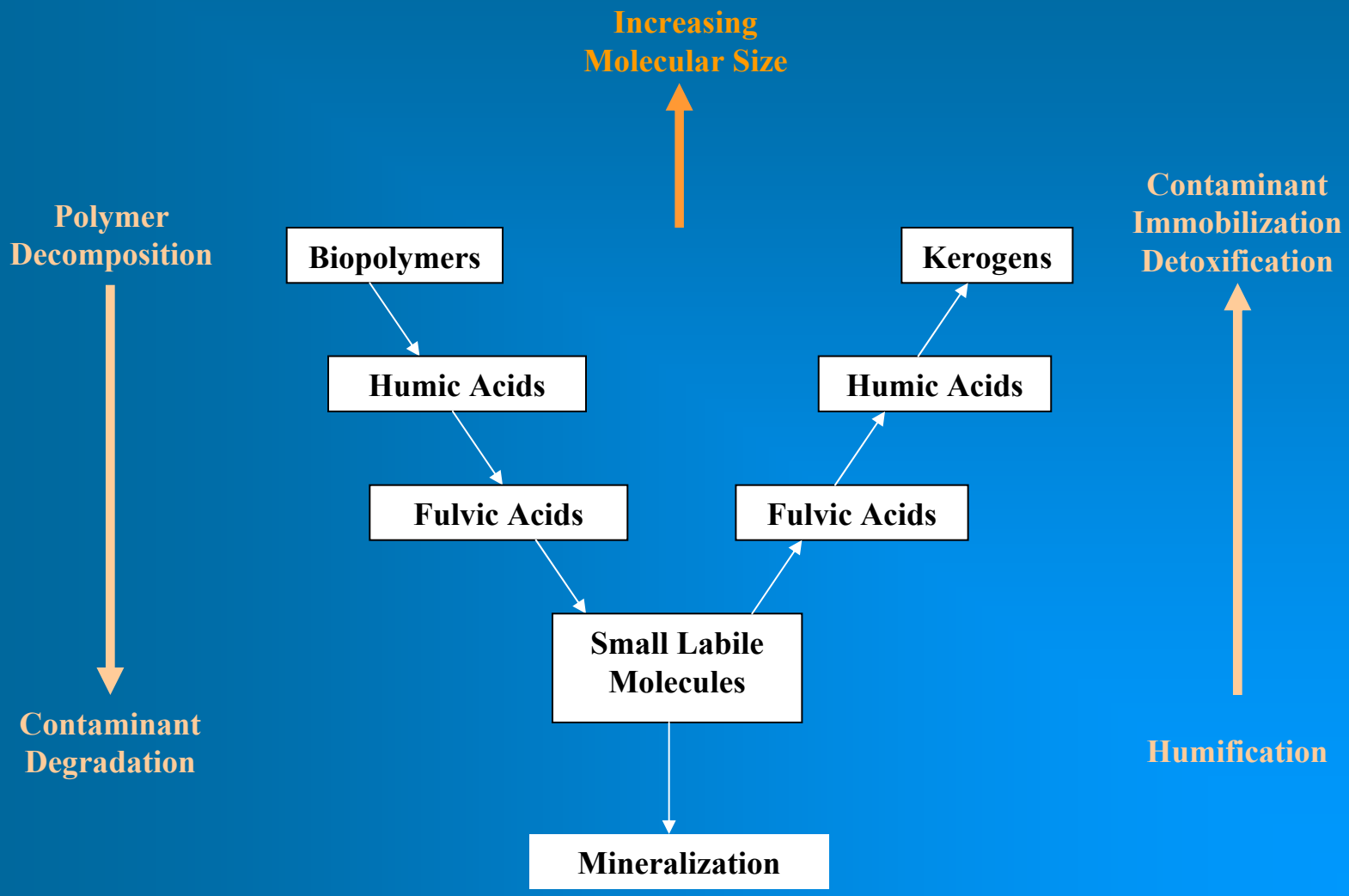
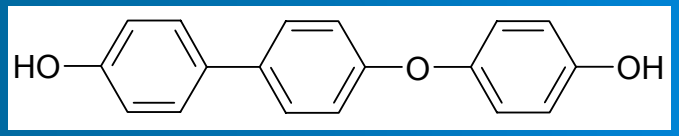
Natural Organic Matter Transformation



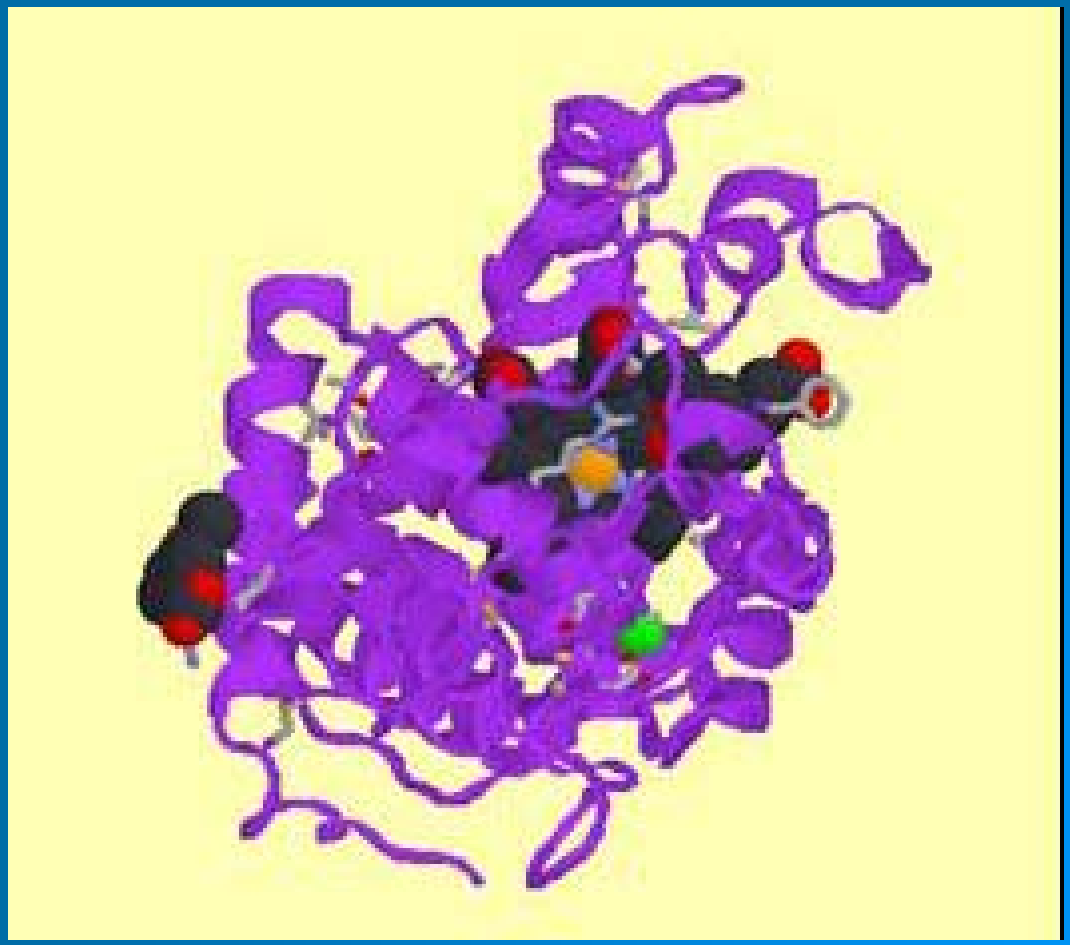
Catalyzed Oxidative Coupling

- **Oxidative coupling**
  - **Substrates**
    - Phenols, anilines
    - NOM building blocks
  - **Mediated by a variety of naturally occurring catalysts**
    - Peroxidases, laccases, tyrosinases (plants, bacteria, fungi)
    - Certain crystalline forms of manganese and iron oxides and hydroxides
  - **Mechanisms**
    - Enzyme-mediated oxidation followed by coupling

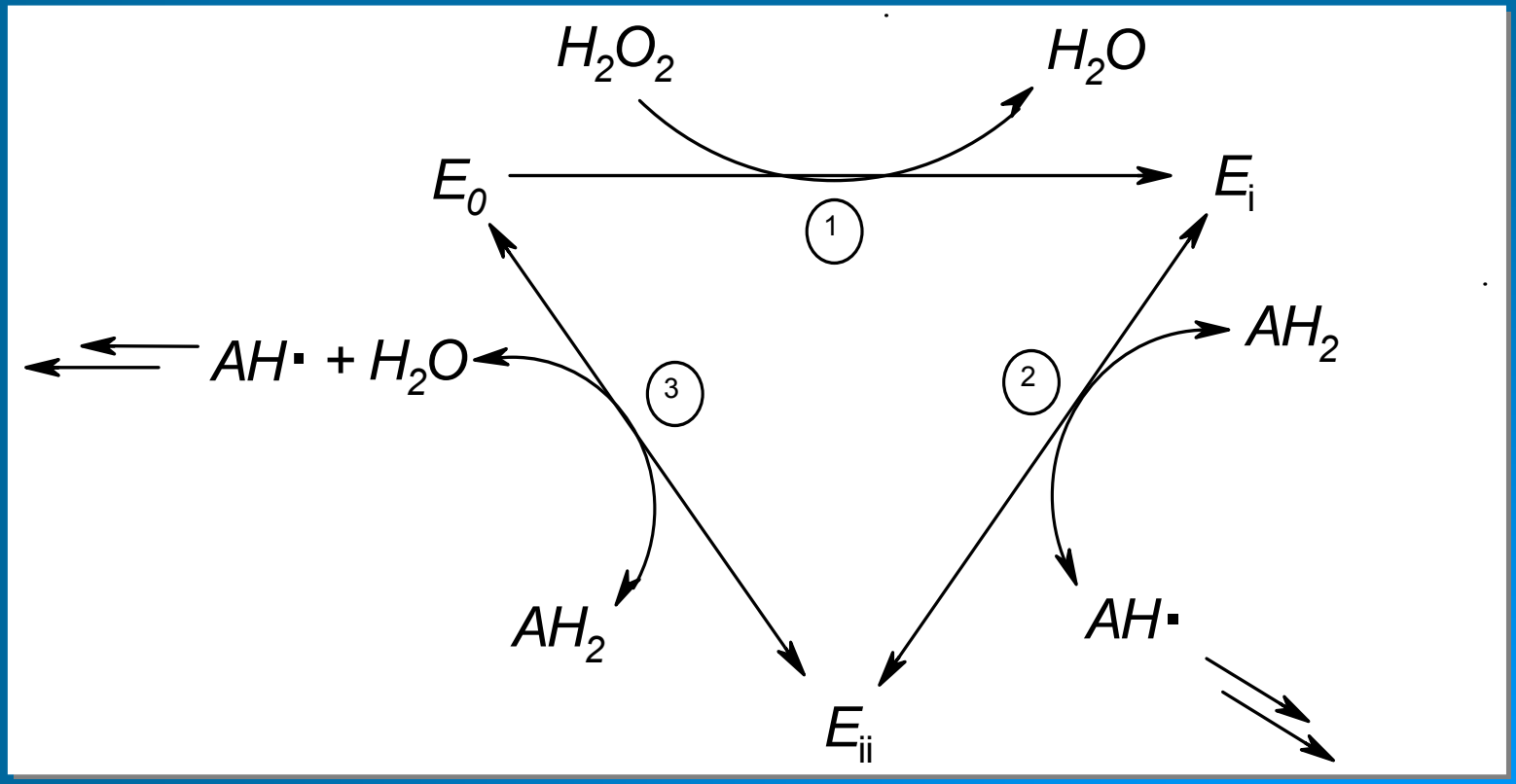


    - Leads to polymerization
- **Applications being researched**
  - **Water treatment**
  - **Soil and sediment decontamination**

Peroxidases

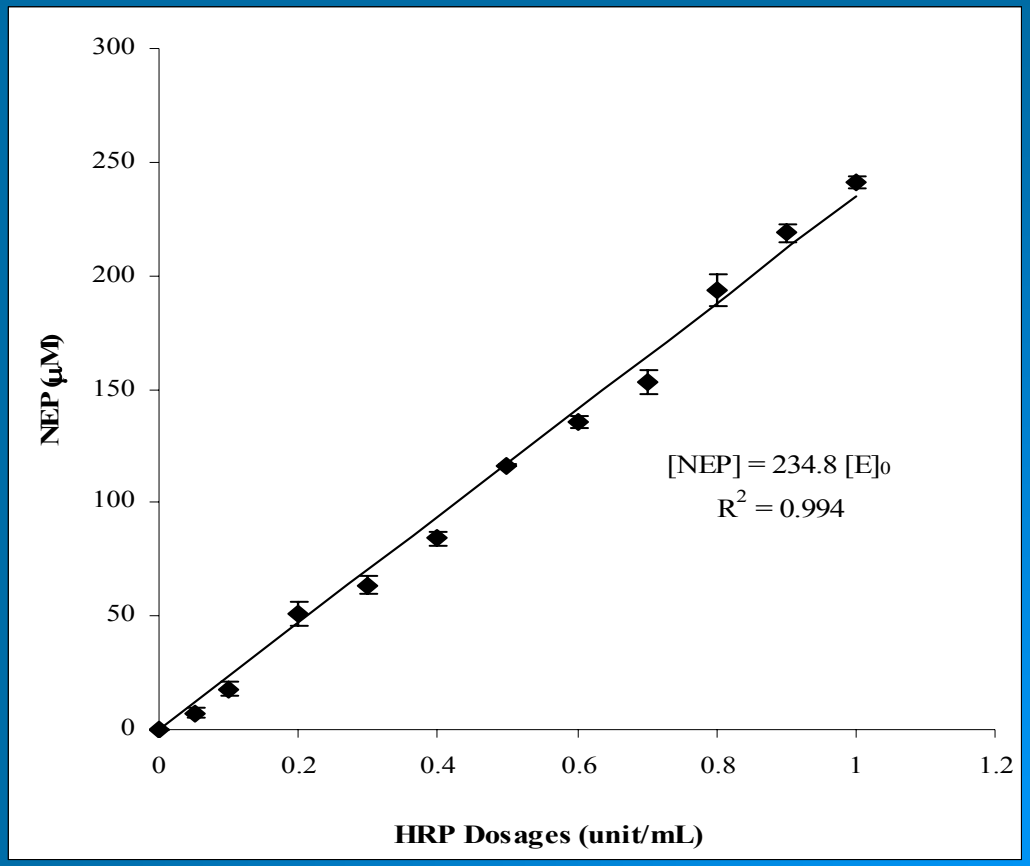


HRP-Mediated Catalytic Cycle



(Huang Q., Selig H., Weber W.J.Jr., ES&T, 36, 19, 2002)

Phenol Conversion via HRP-Mediated Coupling



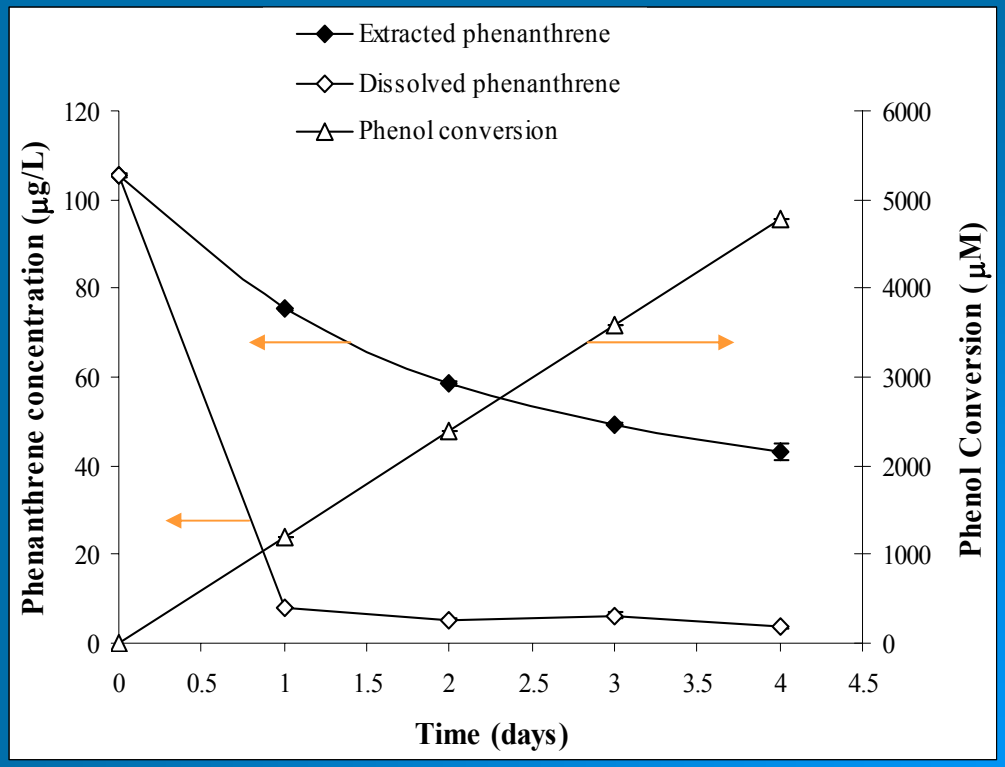
Formation of Non-extractable Products in HRP-mediated Aqueous Systems

(Initial phenol concentration = 0.5 mM , H_2O_2 concentration = 2 mM)

(Huang Q. and Weber W.J.Jr., ES&T, in review)

Catalytically Facilitated Sequestration and Transformation (CFaST) of POPs in Phenol-Based Oxidative Coupling Systems

- **Phenanthrene transformation in semi-batch reactors**



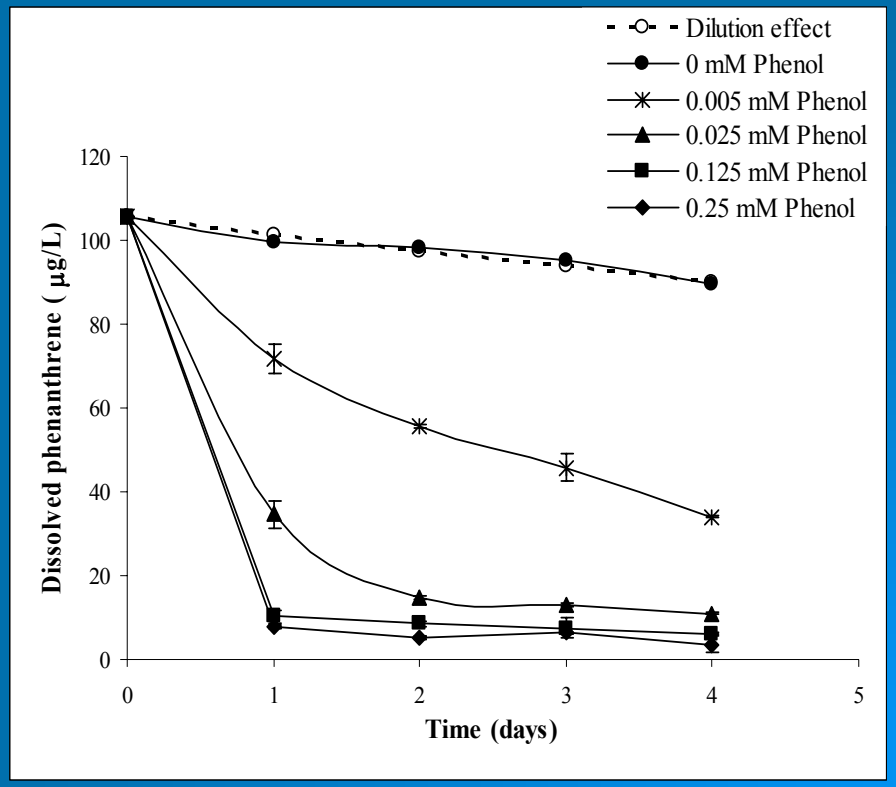
Phenanthrene Disappearance in Solution and in 50% Methanol Extractions and Phenol Conversion

(0.25mM phenol, 0.25mM H_2O_2, and 1unit/mL HRP were added repeatedly five times a day)

(Weber W.J.Jr. and Huang Q., ES&T, 37,18, 2003)

CFaST of POPs in Phenol-Based Oxidative Coupling Systems

- **Phenanthrene transformation in CFaST systems of different reaction strength**



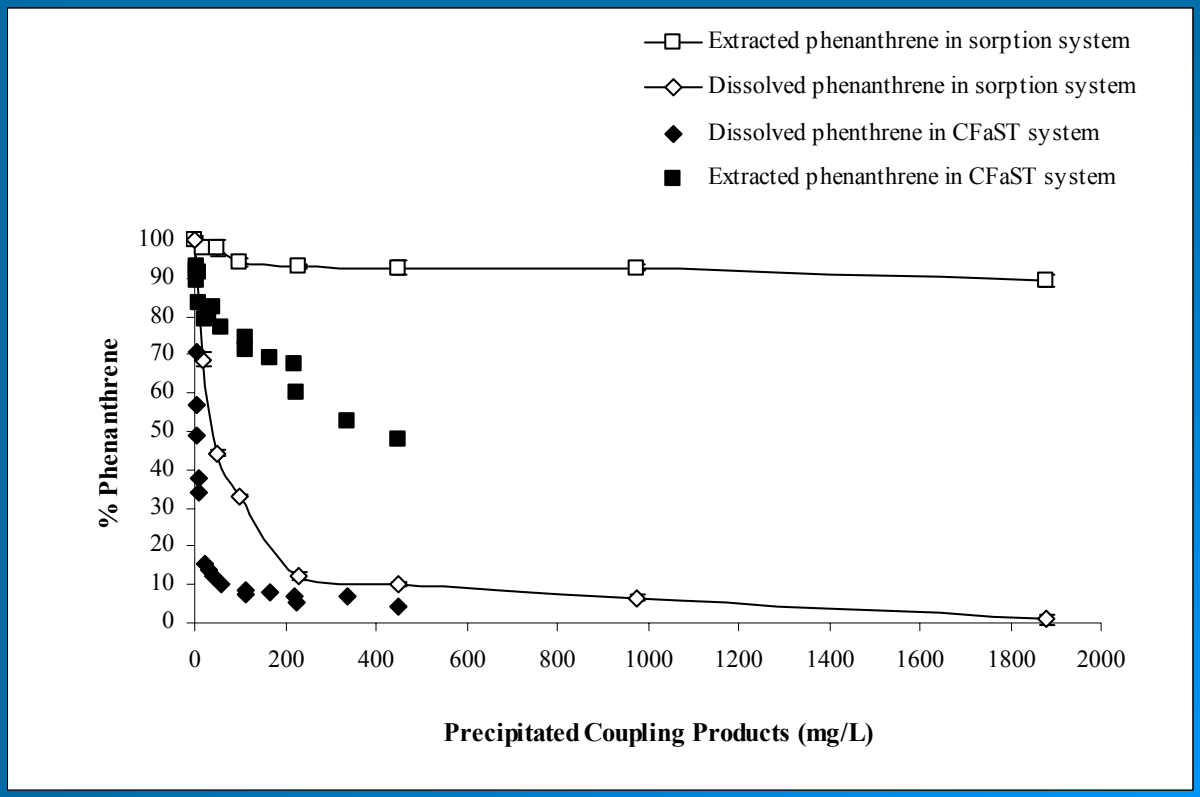
Phenanthrene Disappearance in Solution under Varying Reaction Conditions

The ratio of inputs (Phenol: H_2O_2:HRP) are maintained constant for different CFaST systems

(Weber W.J.Jr. and Huang Q., ES&T 37,18, 2003)

CFaST of POPs in Phenol-Based Oxidative Coupling Systems

- **Phenanthrene removed and extractability in sorption and CFaST systems**



- **Points of note**
  - **Greater sorption in the CFaST system**
  - **Lower extractability in the CFaST system**

CFaST of POPs in Phenol-Based Oxidative Coupling Systems

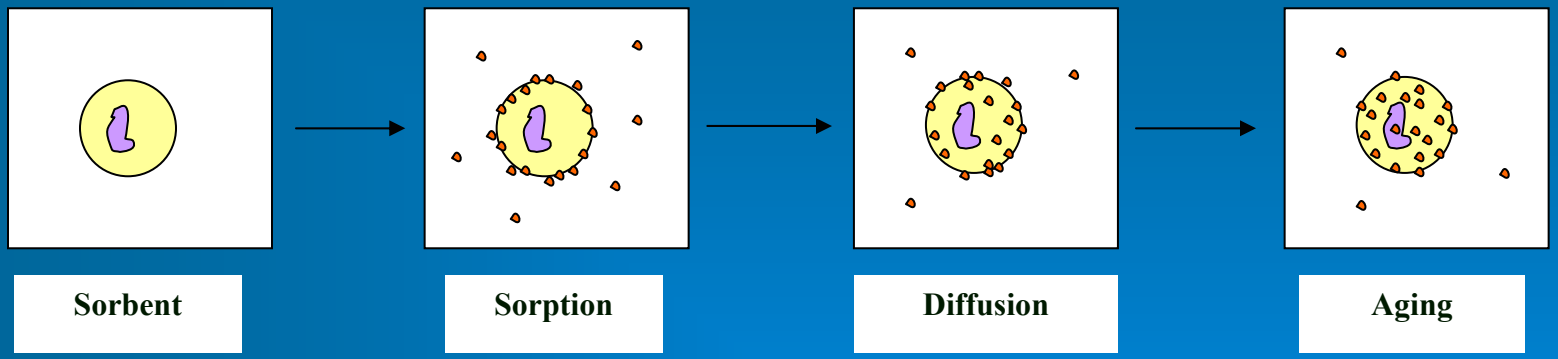
- **Analysis of precipitated products**

System	Phenanthrene Concentration	Total radioactivity before MSE	MSE Extracts		Remained radioactivity after MSE
			Radioactivity	HPLC	
	(μg/g)	102.1	88.87	69.23	5.74
	Std	1	1.59	1.29	0.13
CFaST	%	**100**	**87.04**	**67.81**	**5.62**
	% std	0.98	1.56	1.26	0.12
	(μg/g)	19.64	18.5	18.74	6.93E-04
Sorption	std	0.55	0.38	0.69	5.20E-03
	%	**100**	**94.21**	**95.44**	**0**
	% std	2.78	1.93	3.49	0.03

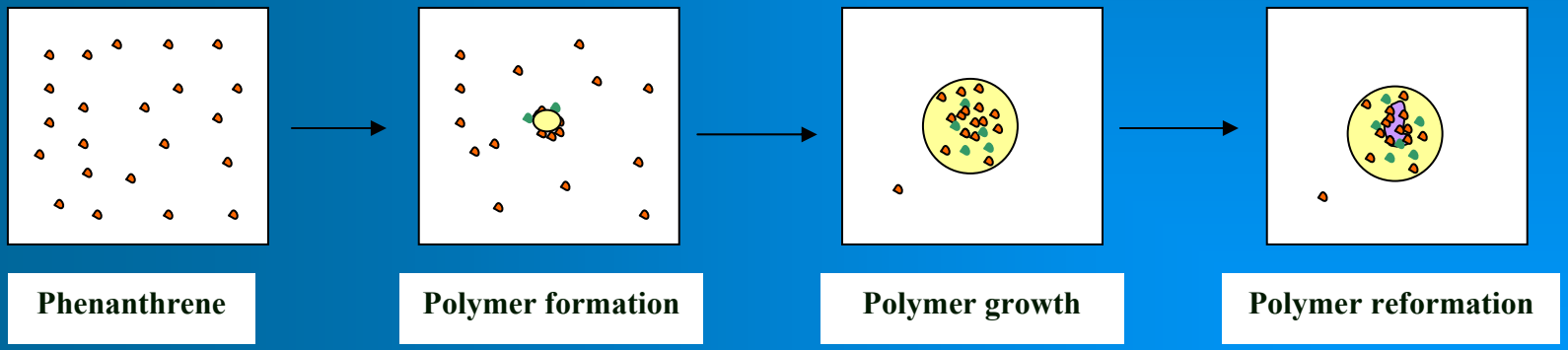
- **Points of note**
  - **Chemical binding occurs; phenanthrene apparently activated by radical transfer mechanisms**
  - **Physical sequestration still plays an important role, but is enhanced**

CFaST of POPs in Phenol-Based Oxidative Coupling Systems

- **Processes in simple sorption systems**

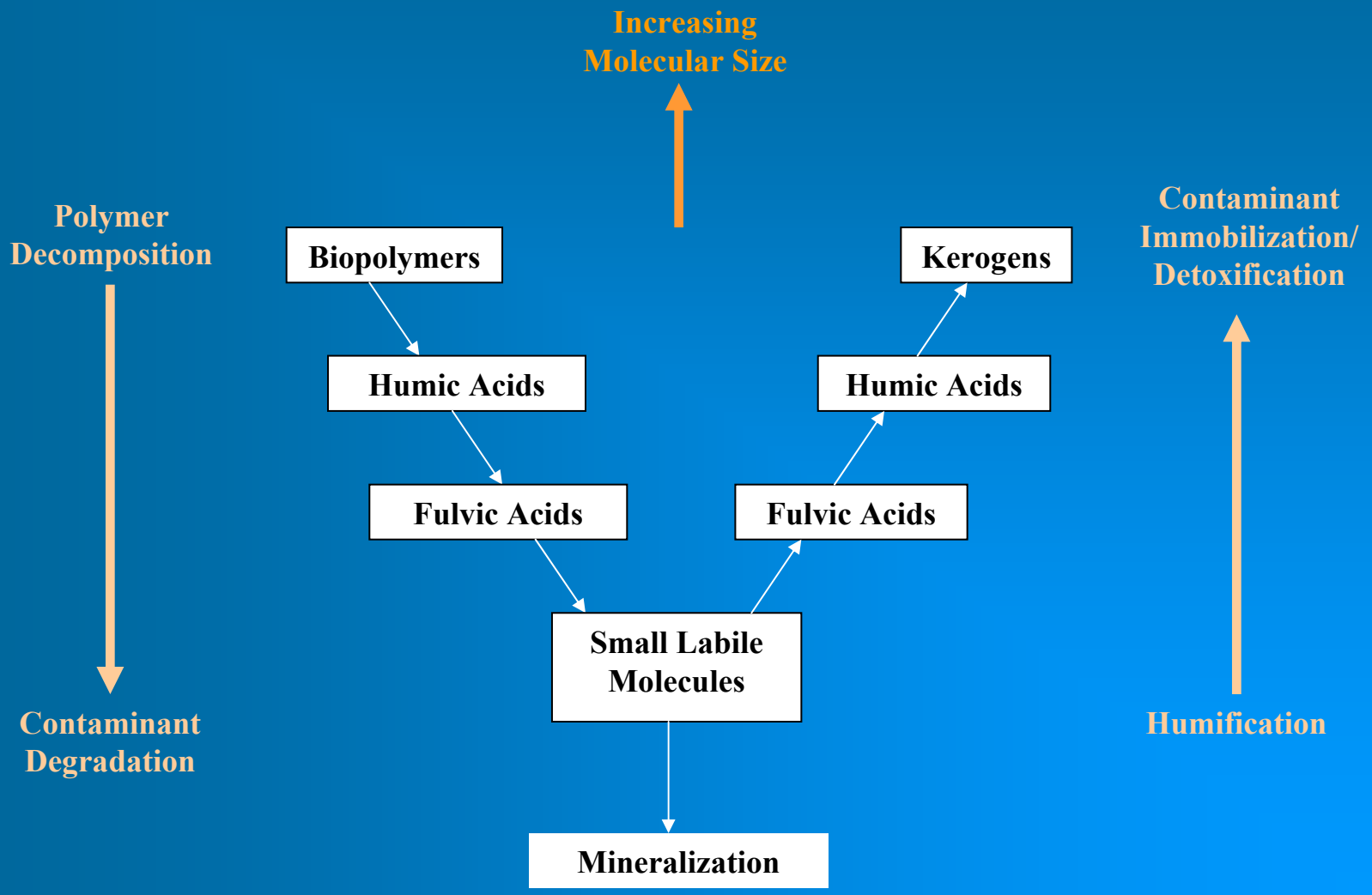


- **Processes in CFaST systems**



- **Points of note**
  - **CFaST process is mechanistically different than physical sequestration**
  - **Higher capacity, lower leachability, loss of chemical identity, dynamic processes having potential for further transformation**

Sorbent Effects on CFaST with Phenol as a Surrogate "POP"



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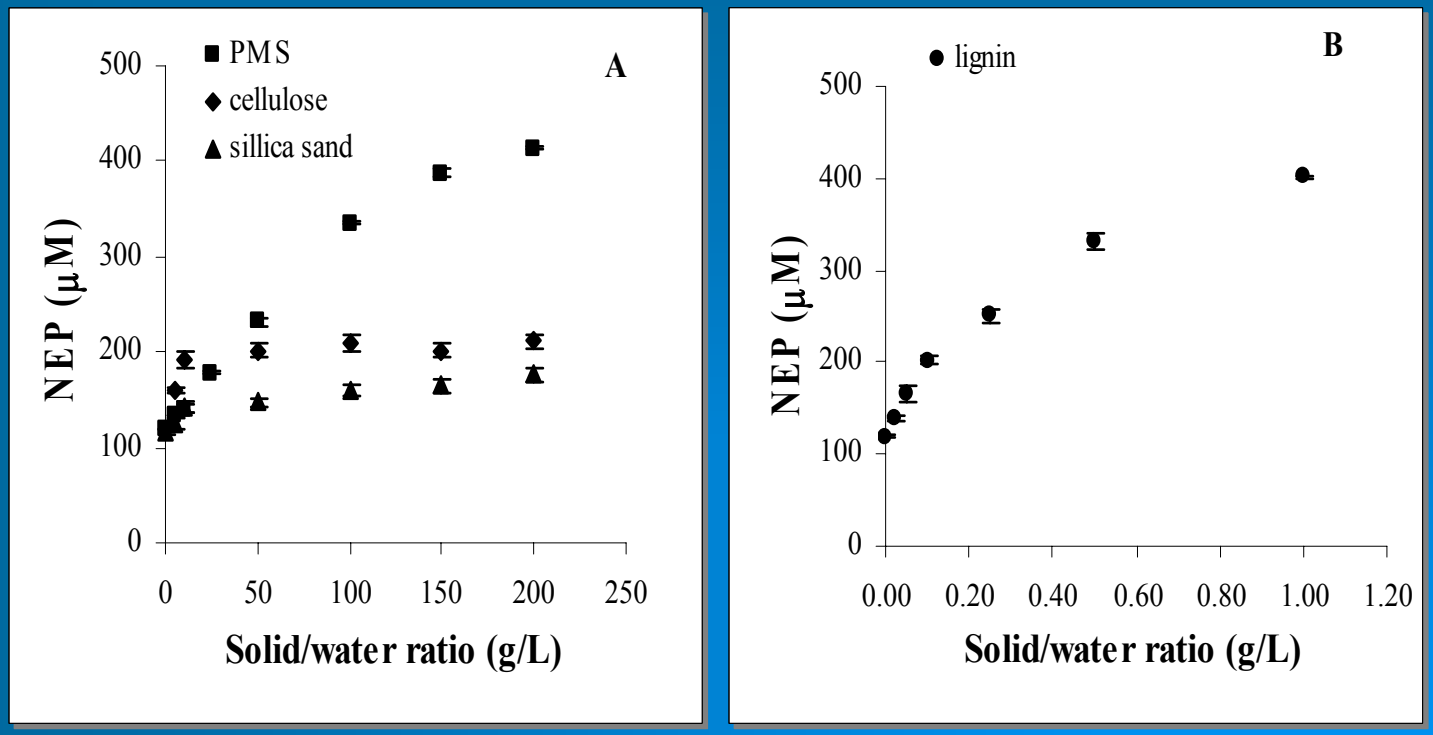

Formation of non-extractable products (NEP) in systems containing different solids

initial phenol concentration = 0.5 mM, H_2O_2 concentration = 2 mM, HRP = 0.5 unit/mL

(Huang Q. and Weber W.J.Jr., ES&T, in review)

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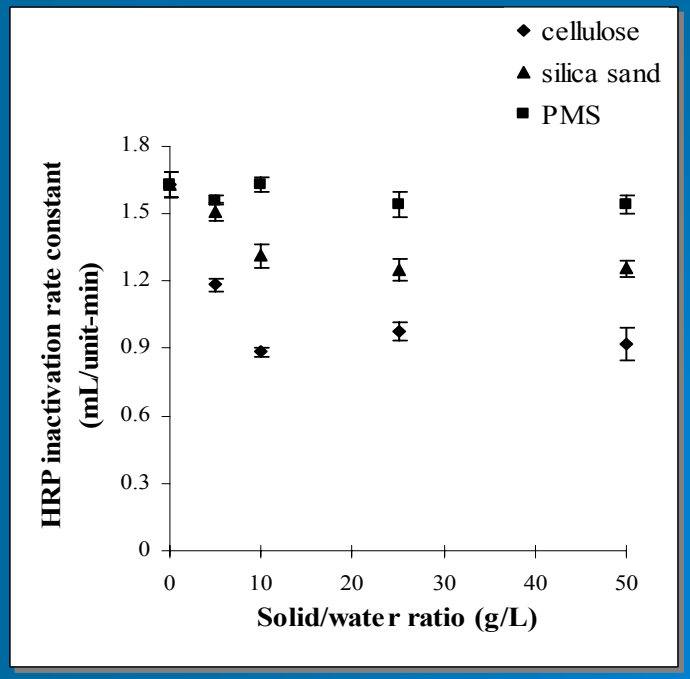
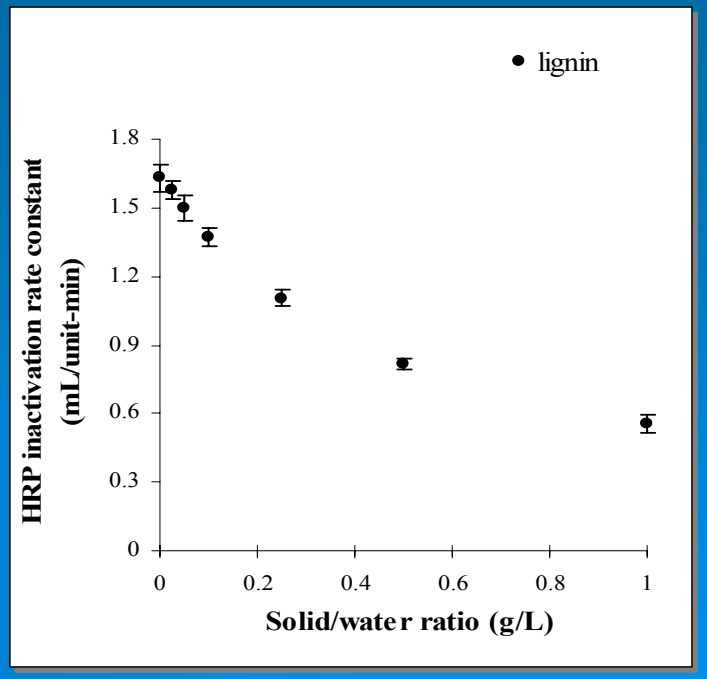




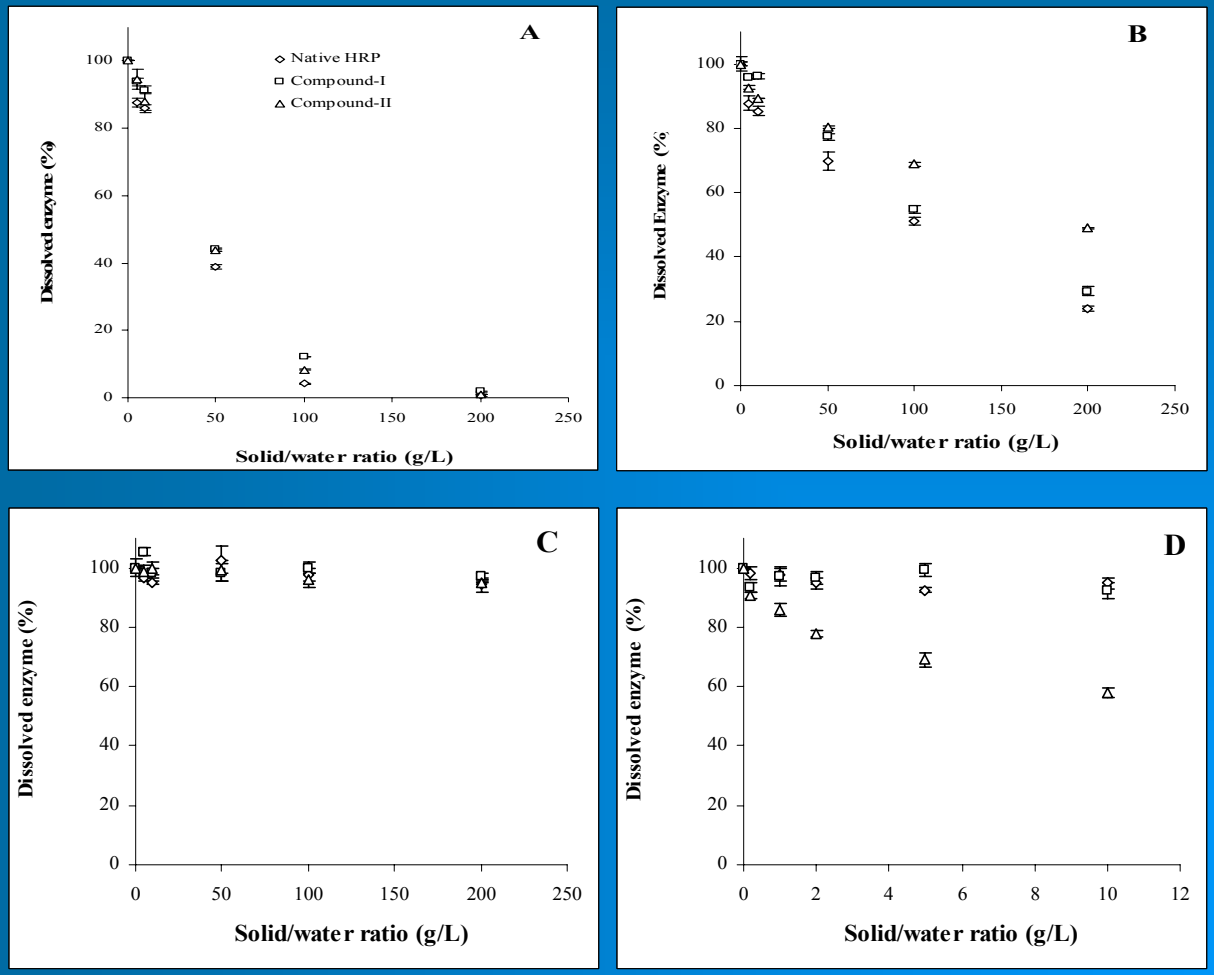
HRP inactivation rate constants in systems containing different solids

initial phenol concentration =500 μM, H_2O_2 concentration = 2 mM, HRP = 0.5 unit/mL

(Huang Q. and Weber W.J.Jr., ES&T, in review)

Sorbent Effects on CFaST with Phenol as a Surrogate "POP"

- **HRP sorption on different solids**



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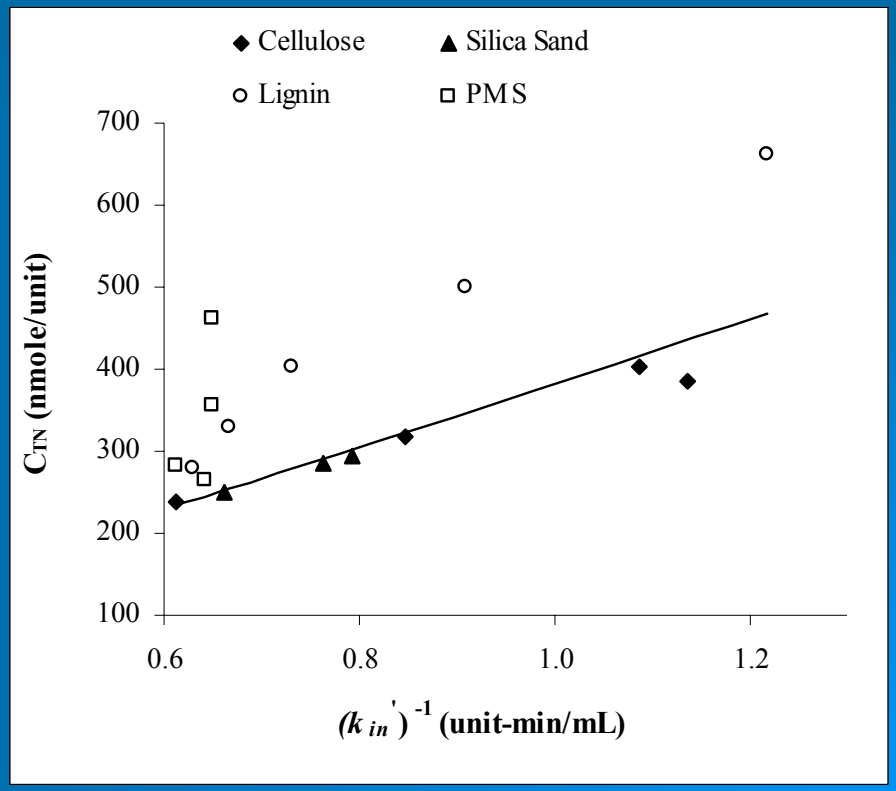


Relationship between turnover capacity (C_{TN}) and HRP inactivation rate constants (k_{in}')

(Huang Q. and Weber W.J.Jr., ES&T, in review)

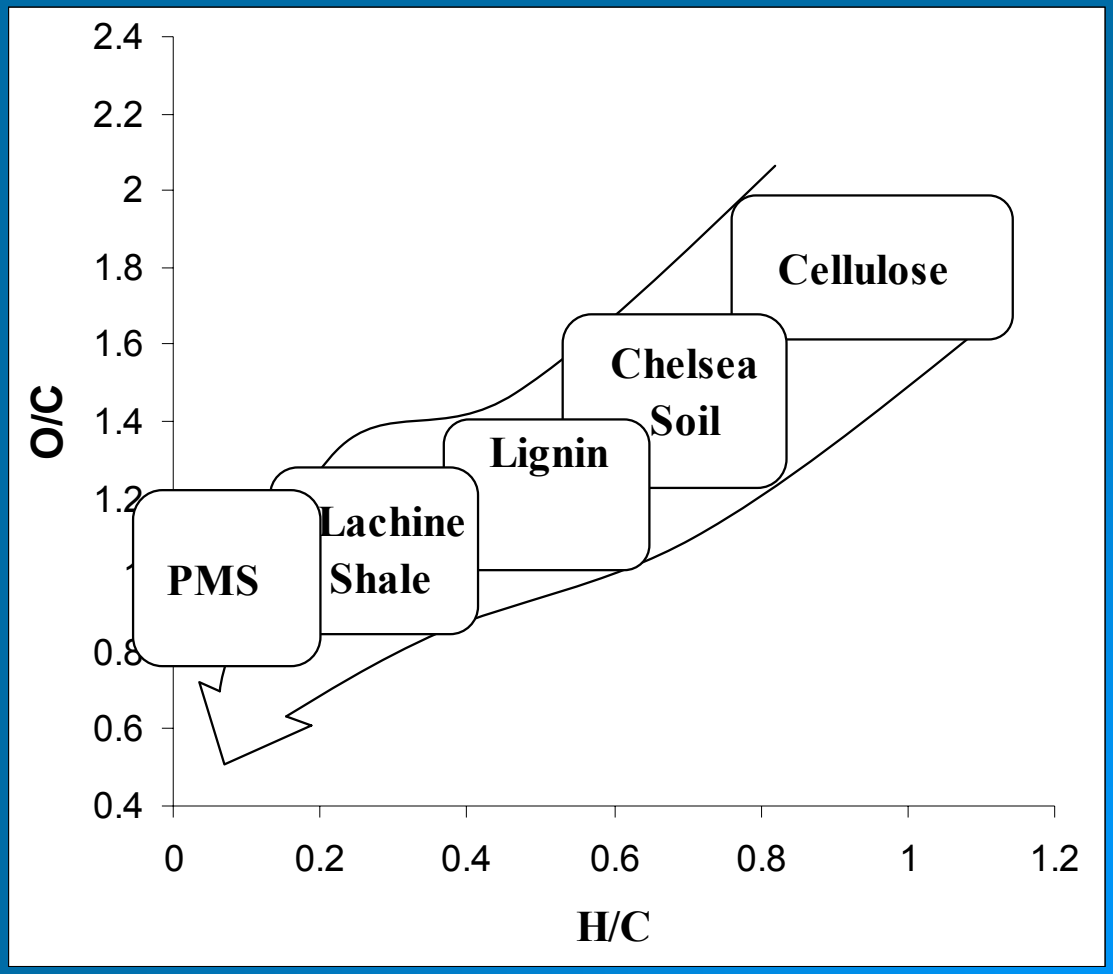
Conclusions Regarding CFaST of POPs in Phenol-Based Oxidative Coupling Systems

- **Chemical transformation and irreversible sequestration**
  - **Activation of POPs through radical transfer processes**
    - Hydrogen abstraction
    - Free radical addition
  - **Incorporation in products through covalent bonding**
    - Permanently immobilized
    - Loose chemical identity
    - Detoxified
- **Enhanced physical sequestration**
  - **Concomitant sorption and sorbent formation processes**
    - Sorbate distribution profiles
    - Desorption energies

Conclusions Regarding Sorbent Effects on CFaST with Phenol as a Surrogate "POP"

- **Mitigation of enzyme inactivation**
  - **Enzyme sorption**
  - **Relatively hydrophilic and oxygen-containing solids**
- **Cross-coupling**
  - **Aromatic features**
  - **Substituents**
  - **Lignin > Chelsea soil > Lachine shale > PMS > Cellulose**
    - **Lignin > Lachine Shale > PMS**
    - **Lignin > Chelsea Soil > Cellulose**

Conclusions Regarding Sorbent Effects on CFaST with Phenol as a Surrogate "POP"



Conclusions Regarding Technology Development Needs

- Creating optimal NOM conditions
  - Engineered geosorbents amendments
    - Sub-critical water treatment of geosorbents
- Facilitating chemical sequestration and transformations of specific POPs
  - PCBs, PCDDs, PCDFs
  - Different catalysts
  - Enzyme consortia
    - Hydroxylation + Coupling