Saltwater intrusion affects peroxidase-mediated polymerization for remediation of coastal soils

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We all need water

The United States consumes approximately 1.35×10^{14} gallons water/yr in total to maintain its current population and economy.

- Approximately 3.01×10^{13} gallons of this are groundwater.
- Just over 50% of the total was used for human drinking water or food production.*

Groundwater Depletion in the United States (1900–2008)

Over 1000 km³ of groundwater have been withdrawn from 1900 to today

Base from U.S. Geological Survey digital data, 1972, 1:2,000,000
Albers Equal-Area Conic Projection
Standard parallels 29° 30' N and 45° 30' N, central meridian 96° 00' W

Groundwater contamination by anthropogenic chemicals

- is widespread: **10-15%** of all groundwaters assayed are detectably contaminated with chemicals on the EPA “priority pollutant” list. The National Research Council (NRC) estimates there are at least 126,000 sites in the continental US with groundwater too contaminated to drink.
- is expensive: The NRC also estimates total cleanup costs at those sites to sum to a **minimum** of **\$130 billion**.

Current strategies for groundwater remediation

Extractive: Pump contaminated water out of the aquifer and treat residual contaminants.

- Bioremediation; Adsorption onto activated carbon; Advanced oxidation processes, etc.

In-situ: Inject reactive species into contaminated groundwater to consume contaminants in the aquifer.

- Zero-valent iron; In-situ chemical oxidation; Microbial fertilization; **Polymerize in place.**

Why is this an interesting idea?

Higher molecular weight hydrophobic materials decrease in solubility. Polymerized hydrophobic products are not soluble, not mobile, and therefore not functionally toxic.

We chose to look at enzymatic polymerization

Horseradish peroxidase (HRP) has Fe(III)-heme active site, are activated by H_2O_2 to generate oxidizing centers.

Proposed mechanism and structures

Experimental approach to model porewater

- Phosphate buffer, 50 mM, pH 7.5
- Model Contaminants
- Horseradish peroxidase
- Suwannee river natural organic matter (NOM) as a major soil component were added to chosen reactor.

UPLC – ESI – MS/MS

- Polymer analysis
- Model contaminants

UV-Vis Spectroscopy

- Enzyme
- H_2O_2

4-Chlorophenol formed oligomers analyzed by mass spectrometry

Model contaminants removal efficiency

Condition:

- 2 mM of Substrate
- 1 units/mL HRP in phosphate buffer (50 mM, pH 7.5).
- Initiated by adding 2 mM H_2O_2 at $T=0.01\text{m}$.
- (B) Adding 30 mg/L NOM

Particle size is also growing rapidly for chlorophenols

The dynamics of particle formation with size were measured in-situ using a Zetasizer™

Condition:

- 2 mM of Substrate
- 1 units/mL HRP in phosphate buffer (50 mM, pH 7.5).
- Initiated by adding 2 mM H_2O_2 at $T=0.01\text{m}$.
- (B) Adding 30 mg/L NOM

Modeling steady state of peroxidase and hydrogen peroxide

Condition: Initially added 2 mM 4CP in phosphate buffer (50 mM, pH 7.5).
Then adding steady stream of

- HRP: $50 \text{ mU} \cdot \text{mL}^{-1} \cdot \text{h}^{-1}$
- H_2O_2 : $1 \text{ } \mu\text{M} \cdot \text{min}^{-1}$

Study the effects of this process by asking three questions:

1. How saltwater intrusion will affect the removal efficiency?
2. Are immobilized particles releasing contaminants back to the freshwater?
3. Can these formed particles act as an adsorbent?

Saltwater improves the 4-chlorophenol removal efficiency

- ❑ Varying ionic strength has the most impact to the removal efficiency under the seawater condition
- ❑ NOM generally increase the removal efficiency in buffer and seawater condition

Condition:

- 1 mM of Substrate
- 0.57 units/mL HRP in pre-set conditions
- 30 mg/L NOM added to specific conditions
- Initiated by adding 1 mM H_2O_2 at $T=0.01\text{m}$.
- Final solutions were withdrawn at 1 hour

Immobilized particles will not release contaminants back to the freshwater

- Bulk number of 4-chlorophenol particles were synthesized in two condition: 1) Seawater, 2) 30 mg/L of NOM added seawater
- Collected particles were transferred back to initial pH and ionic strength conditions and releases of residual 4CP were monitored; <1% desorbed.

Condition:

- Ionic strength solutions were prepared by titrating seawater with DI water.
- pH solutions were made by titrating seawater with 1 M HCl and NaOH.
- Samples were withdrawn at 3 hours when reactor equilibrated.

Polymeric products adsorbed co-contaminants

Adsorbate 1,2-dichlorobenzene (12DCB) was used as a co-contaminant.

How effective is the polymeric product as a adsorbent comparing with activated carbon

$$\text{Freundlich: } q = K_f c^{1/n}$$

- n and K_f are system specific constant.
- K_f is an indicator of adsorption capacity. Higher the maximum capacity, higher the K_f , smaller the n .
- q = amount of solute adsorbed per unit weight of solid at equilibrium (unit g/g).
- c = equilibrium concentration of solute remaining in solution when amount adsorbed equals q (unit mg/L).

Adsorbent	n	K_f
4CP Polymers	0.875	0.00692
Activated Carbon	0.600	0.0478
Zeolite	0.394	0.0415

The 4CP polymers were about **15%** as effective as powdered activated carbon.

Novel *Lyngbya wollei* peroxidase has a potential to remove contaminants

Harmful algal bloom in Lake Wateree, South Carolina

Condition:

- 1 mM of Substrate
- Activity pre-determined enzyme solution
- In phosphate buffer (50 mM, pH 7.5)
- Initiated by adding 1 mM H₂O₂ at T=0.01m.
- Final solutions were withdrawn at 1 hour

Conclusions

- The chlorophenols can be removed in environmental conditions with steady state peroxidase and H_2O_2 , achieving significant removal efficiency for soil contaminants over short period of time.
- Resulting particulates were qualified by mass spectrometry and shown to consist of oligomers with significantly reduced solubility ($<5 \mu\text{g/L}$) than the starting phenols.
- Resulting particulates also acted as adsorbents for other non-reactive co-contaminant, comparable to but less than activated carbon.
- Saltwater intrusion will enhance the remediation efficiency and the resulted particles binding to the contaminant are irreversible.

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