

# **By-Product From the Lowly Soybean Creates Jobs and Saves the Planet**

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by

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# People & Money

## Collaborators

- J.K. Bewtra and N. Biswas, Civil & Environmental Engineering

## Recent Students

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- Mohammad Mousa Al-Ansari
- Ram Mantha
- Joey Patapas

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- Natural Sciences and Engineering Research Council
- Ontario Ministry of Agriculture and Food

# Introduction

## Wastewater – Process Water

Phenolic and aryl amine compounds in process- and wastewater streams from various industries such as:

- petroleum refining.
- coal conversion
- wood preservation.
- metal casting.
- pulp, paper, dyes, resin, plastics and textiles manufacturing.

These compounds are considered to be **toxic** and have been classified as hazardous pollutants.



# Water Treatment Strategy

Phenols in Solution

enzyme +  
↓  
oxidant

Oligomer/Polymer  
(separate solid)

- Capture solid precipitate, use as pre-adhesive, *etc.*
- Immobilize solid on soil organic matter (Bollag)

# Enzyme-based Wastewater Treatment

- Capture organic material in minimally-modified form
- Remediation but not degradation
- Enabling technology: availability of enzymes as commodities (peroxidases, but not HRP, and laccases)
- By recombinant fermentation techniques (ARP, laccase)
- Cheaper wild-type sources (SBP)
  
- **Cost-effective?**

# Advantages of Enzyme-Based Treatment

Advantages over conventional **biological treatment**:

- Easy to handle and store; simpler process control
- High and low concentrations of contaminant
- No shock loading effects
- Broad range of pH and temperature
- Contact time of seconds to minutes, small footprint
- Reduced burden on biox plant and gravity separators

Advantages over **chemical/physical treatments**:

- High specificity and efficiency in removing target pollutants
- Operation under milder, less corrosive, conditions
- Reduced consumption of oxidants, sludge formation

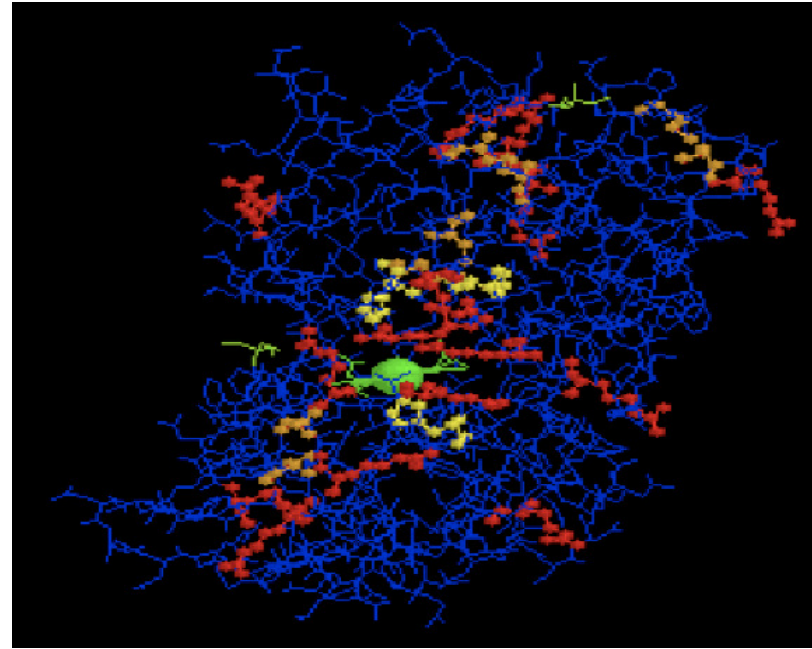
# Enzymes

## Laccase



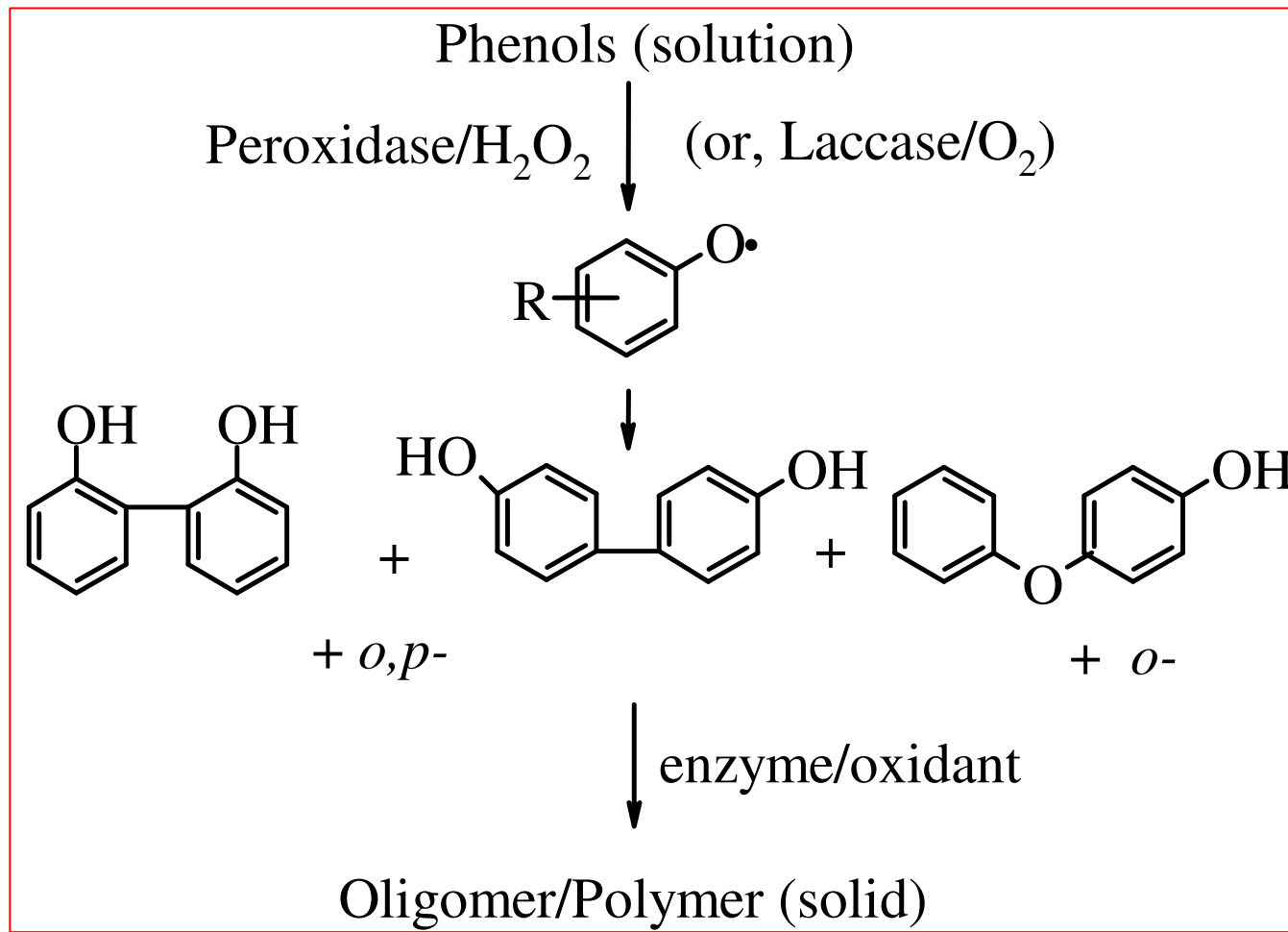
- Fungal source
- Requires molecular oxygen

## SBP



- Crude extract from seed hulls
- Requires hydrogen peroxide

# Oxidase-catalyzed Phenol Removal (Klibanov, Bollag)

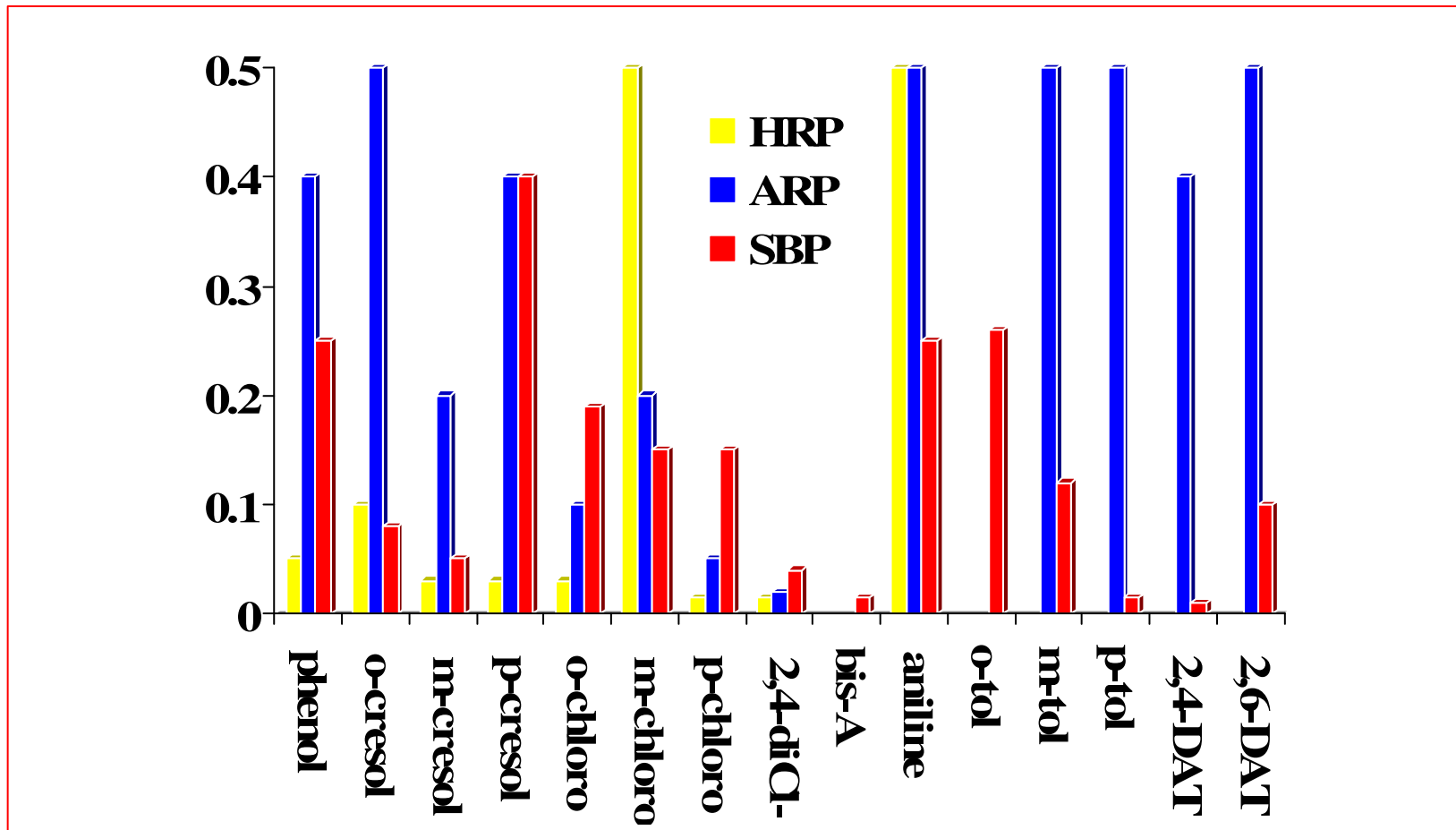




# Experimental Parameters

- substrates at 1.0 mM (94 ppm for parent, 128 ppm for chloroderivatives)
- examine:
  - pH effect
  - enzyme dose (activity “units”/mL = U/mL)
  - peroxide stoichiometry
  - influence of PEG in reaction, alum in settling
  - (reactor design)
- analysis by UV and colorimetric tests; HPLC

# Minimum Enzyme Concentrations (U/mL)

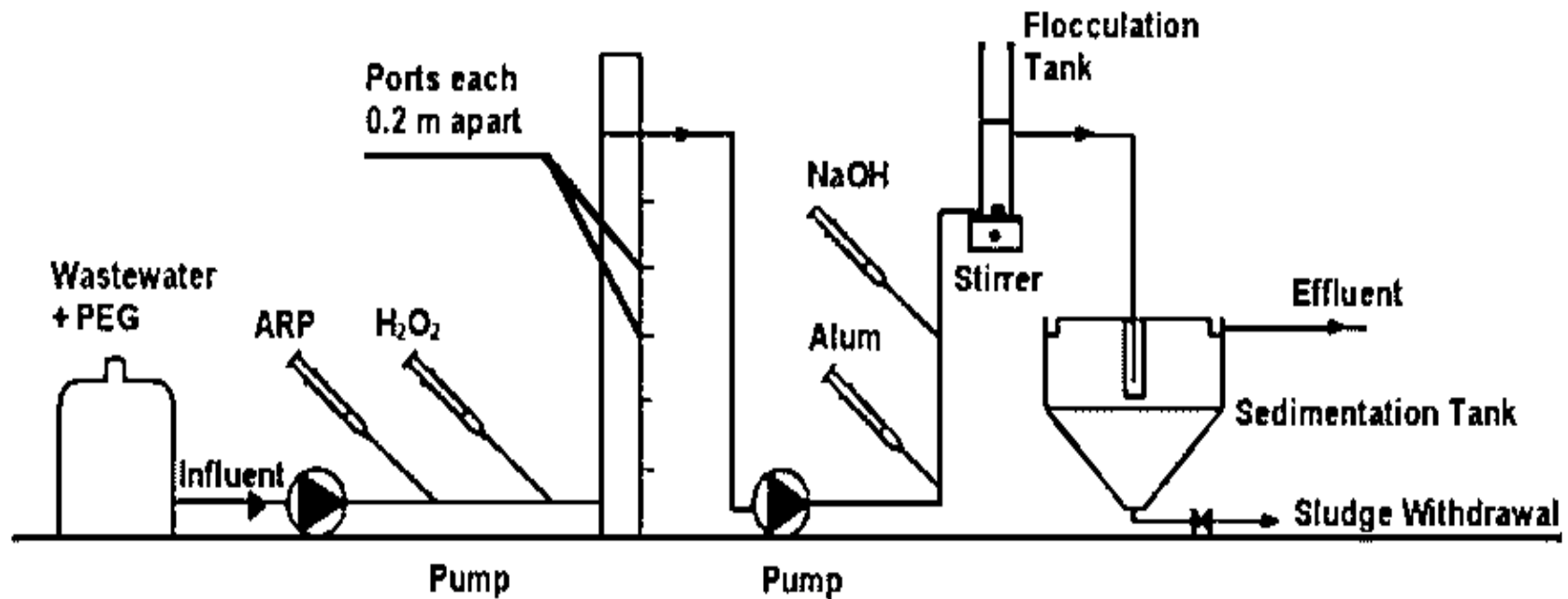


# Broadening the Scope

- Convert other aromatics into phenols or anilines
- Chemical ‘front end’ for the enzymic process
- For nitro- and azo-aromatics:  
    zero-valent iron to produce anilines
- For unfunctionalized aromatics  
    hydroxylation (via limited Fenton reaction) to phenols

# Continuous-flow System for Phenol

Water Environment Research 73 165 (2001)



# Operating Cost - Incremental, but Offset

- Water Environment Research **73** 165 (2001)
- 600 bbl/h@ 100 ppm phenols; 100 m<sup>3</sup>/h with 10kg/h phenols
- SBP needed at 0.5 MU/m<sup>3</sup>; 50 MU/h; \$100/h\*
- Peroxide required at \$0.25/m<sup>3</sup> for treatment, possibly \$0.25/m<sup>3</sup> for additive (eg. PEG or surfactant); ca. \$50/h
- Expendables cost, \$150/h (\$0.25/bbl)
- \* **Could SBP be produced at a profit for \$2/MU??**

# Save the Planet? Jobs Too?

- Refinery case: 5 MU/kg phenol, a bit much; \$2/MU, a bit low
- Processing at higher [phenol], eg. 2000 ppm, more efficient, 1.5 mU/kg
- room to pay more for enzyme?
  
- SBP is in the seedcoat, the first thing stripped off before beans are crushed for oil and protein
- SBP easily extracted with water; remaining hull still as good a fibre source for animal feed
- Value of hulls more than doubled
- **A business opportunity! (actually, two!)**

# Lots of Cheap SBP

- 120,000 tonnes of hulls in Ontario (Michigan, two-thirds; Iowa, 4-fold)
- Could they be “borrowed”, or “rented”, to extract SBP?
- Trillions of U of catalytic activity (many refineries!)
- Costs: “rent”, concentrating extract, re-drying hulls
- Environmental stewardship of the petroleum economy aided by bioproducts
- Including non-conventional sources: oil sands, oil shale, upgrading by-products (stranded carbon), coal gasification

# Save the Planet



- Improve existing refinery aqueous streams with a green process
- Begin to address air emissions by capture and treatment
- Products of enzyme-based treatment captured and used
- Optimal and responsible use of existing carbon sources