Photochemical Dechlorination of Highly Chlorinated PCBs

What are PCBs?

- Known as Polychlorinated Biphenyls
- Thermally stable organic compounds
- Used in transformer oils, high temp. lube oils, capacitors, fire retardants, inks and paints
- Commercially sold under brand names- Aroclor
- Most common
- Loosely classified as highly and lower chlorinated PCBs
Generic PCB Structure

- $C_{12}H_{(10-n)}Cl_n \ (n=1 \ to \ 10)$
- Chlorine atoms attached to different positions
- 206 different congeners
- Nomenclature: Aroclor 1254 contains 54% Cl
Concerns with PCBs

- **Lipophilicity (or organophilicity)**
  - Get adsorbed in soils and organic matter
  - Enter food chain through sediment dwelling microbes
  - Bioconcentration factor = 73,000

- **Toxicity**
  - Acute effects
    - facial edema, ocular discharge, swollen eyelids, conjunctival hyperemia, visual and hearing disturbances, low blood pressure, weakness and numbness of the extremities, neurobehavioural and psychomotor impairment, gastrointestinal upset, diarrhea, hepatitis, chloracne, and asymptomatic hyperthyroxinemia
Concerns with PCBs

- Non-carcinogenic chronic effects
  - damage to the liver, blood, immune system, nervous system and reproductive system
- Probable human carcinogens - USEPA

Environmental Persistence
- Known to exist “as is” for decades
- Some anaerobic dechlorination may occur under favourable conditions
  - Requires soil microbe adaptation
Estimated Problem

- An estimated 1/3 of the US production ($1.4 \times 10^9$ lbs) has been released into the environment – Weigel and Wu (2000)
- UNEP has identified PCBs as one of 12 Persistent Organic Pollutants (POPs) that need immediate attention
Remediation of PCB contaminated soils and sediments
Remediation Technologies

- Physical and Chemical Methods
  - Solidification and Stabilization
  - Vitrification
  - Soil washing
  - Proprietary processes (BEST, KPEG, KGME, CHLOROFF etc.)

- Thermal Desorption
Remediation Technologies

- Biological Methods
  - Aerobic microbes (*Burkholderia* sp. LB400) can degrade only lower chlorinated PCBs
  - Anaerobic Dechlorination feasible only on highly chlorinated PCBs

- Issues
  - Requires anaerobic microbial adaptation
  - Slow growth of microbes
  - Temperature and nutrient requirements
  - Need to know when to switch from anaerobic to aerobic
Current Practice in Canada

- Incineration in special burners
- Incineration
  - Only two incinerators in Canada
  - Transportation and liabilities associated with it
  - Very expensive
  - Only known technology that is complete and known to work
- An area of intense research
Objective of the study

Technology development for complete degradation of PCBs – A cradle to grave approach

Would include

- Extraction of PCBs from soils and sediments
- Degradation of PCBs
Materials and Methods

PCB Type
- Use commercial Aroclor 1254
- Use extracted PCBs

Photodegradation
- Use ultraviolet (UV) light at 350 nm with phenothiazine (PT) as photosensitizer
- Use commercial Aroclor 1254 pretreated with Fenton’s reagent and then photodegraded using UV light at 350 nm with PT
- Use UV light at 254 nm (without any catalyst or photosensitizer)
Results
Commercial Aroclor 1254
Results – PCBs subjected to 350 nm UV with PT as photosensitizer

- Intensity = 0.2 mW/cm²
- Feasibility of Photodegradation
- Impact of Different Solvents
  - Hexane
  - Acetonitrile
  - Alkaline Isopropanol
PCB Degradation in Hexane
PCB Degradation in Acetonitrile

The graph shows the degradation of PCBs in neutral and alkaline (0.1N NaOH) acetonitrile over time. The concentration (ppm) is measured on the y-axis, and time (hours) is on the x-axis. The neutral acetonitrile shows a slower degradation rate compared to the alkaline (0.1N NaOH) acetonitrile.
PCB Degradation in Alkaline IPA

![Graph showing PCB degradation over time in alkaline IPA. The x-axis represents time in hours, ranging from 0 to 20. The y-axis represents concentration in ppm, ranging from 0 to 120. The graph shows a significant initial decrease in concentration, followed by a slower decline over time.](image-url)
Change in chloride ion conc. with photodechlorination

<table>
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<th>Time (h)</th>
<th>0</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>19</th>
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<tr>
<td>Chloride ion conc. (mg/L)</td>
<td>0.0</td>
<td>1.11</td>
<td>1.48</td>
<td>1.35</td>
<td>2.12</td>
<td>2.02</td>
<td>2.52</td>
<td>4.03</td>
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</table>
Results – PhotoFenton Reactions

(Commercial Aroclor 1254)

Impact of treating PCBs with Fenton’s reagent followed by UV treatment (350 nm with phenothiazine)
Fenton’s Reactions

- $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}_2^-$
- $\text{OH}^- + \text{C}_x\text{H}_y \rightarrow \text{H}_2\text{O} + \text{CO}_2 + \text{heat}$
- $\text{H}_2\text{O}_2 + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}_2^-$
- $\text{OH}^- + \text{Fe}^{2+} \rightarrow \text{OH}^- + \text{Fe}^{3+}$
- $\text{HO}_2^- + \text{Fe}^{3+} \rightarrow \text{O}_2 + \text{H}^+ + \text{Fe}^{2+}$
- $\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HO}_2^-$
Photolysis of PCBs pretreated with Fenton’s Reagent for varying periods using PT Sensitized UV light
Gas Chromatographs of PCBs pretreated with Fenton’s Reagent followed by photodechlorination
Results

Photodegradation (UV 254 nm) of PCBs in IPA
(Commercial Aroclor 1254)

- Intensity = 1.5 mW/cm²
- Impact of varying alkalinity
- Impact of hydrogen peroxide addition
- Biphenyl production and degradation
PCBs degradation in UV 254 nm – impact of varying alkalinity and hydrogen peroxide
Dechlorination of 100ppm commercial Aroclor 1254 with UV (254nm) in alkaline (0.1N NaOH) IPA
Dechlorination of 300ppm commercial Aroclor 1254 with UV (254nm) in alkaline (0.1N NaOH) IPA
Dechlorination of 500ppm commercial Aroclor 1254 with UV (254nm) in alkaline (0.1N NaOH) IPA
Dechlorination of commercial Aroclor 1254 with UV (254nm) in alkaline (0.2N NaOH) IPA
Dechlorination of commercial Aroclor 1254 with UV (254nm) in alkaline (0.1N NaOH) IPA and 0.5mL of 30%H$_2$O$_2$
PCBs degradation in 254 nm UV – Biphenyl production and degradation

![Graph showing PCBs degradation in 254 nm UV](image)

- **Concentration (ppm)**
- **Time (Hours)**
  - 0 2 4 6 8 10
  - 0 20 40 60 80 100 120 140

- **Samples**:
  - Biphenyl-1
  - Aroclor 1254-1
  - Aroclor 1254-2
  - Biphenyl-2
PCBs degradation in 254 nm UV – Biphenyl production and degradation
Biphenyl degradation with time (UV at 254 nm)
Results
(Photodegradation of PCBs extracted from soil)
Photodegradation in 350 nm UV (with PT) in Alkaline IPA (different extractants/wash used)
Photodegradation of extract from wet soil using UV irradiation (350 nm), in alkaline (0.1N NaOH) IPA.
Gas Chromatographs of wet soil extracts
Conclusions

- Photochemical degradation of highly chlorinated PCBs is a viable way to treat these hazardous compounds.

- Solvent plays a significant role in photochemical degradation.

- Photochemical degradation of highly chlorinated PCBs occurs fastest in alkaline IPA and when 254 nm UV light is used.
Conclusions

- Biphenyls are also degraded using UV at 254 nm
- Use of Fenton’s reagent decreases PCB concentration with time
- Use of photo-Fenton reactions for PCB degradation is feasible but requires more study
- Photochemical degradation (using 254 nm UV light) of soil extracts in alkaline IPA is a viable technology for remediation
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