Impact of Heavy Metals on Microalgae Growth and Conversion into Biofuel and Biogas Production: Bioremediation and Flue Gas Integration Potential

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Motivation

Why are waste stream heavy metals important?

- Unaccounted for in current sustainability models
- Inherent in waste streams
- Possibly detrimental to microalgae productivity
  - Effects of many metals unknown
- Knowing effects necessary for TEA LCA analysis
Outline

PHASE 1

CONVERSION

COAL POWER PLANT

14 HEAVY METALS & CO₂

INDIVIDUAL HEAVY METALS & CO₂

PHASE 2

CONVERSION

ALGAE

LEA

BMP

METHANE

BIOFUEL

PHASE 3

INHIBITIVE HEAVY METALS

PRODUCTIVITY

RESULTS

LIPID YIELD

FATE OF METALS

As Cd Co Cr

FATE OF METALS

0%
20%
40%
60%
80%
100%
120%
140%
160%
180%
200%

PRODUCTIVITY

0%
20%
40%
60%
80%
100%
120%
140%
160%
180%
200%

LIPID YIELD

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0%
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As Cd Co Cr
COAL POWER PLANT

Outline

PHASE 1

14 HEAVY METALS & CO₂

CONVERSION

PHASE 2

INDIVIDUAL HEAVY METALS & CO₂

PHASE 3

HEAVY METALS & CO₂

INHIBITIVE HEAVY METALS

RESULTS

COAL POWER PLANT

As  Cd  Cr  Co  Cu  Pb  Ni  Hg  Se  Zn

LIPID YIELD

PRODUCTIVITY

FATE OF METALS

LEA  BMP  METHANE  BIOFUEL

PHASE 1

PHASE 2

PHASE 3

ALGAE

CO2

CO2 & conversion

CO2 & biomass production

CO2 & lipid yield

LIPID YIELD

PRODUCTIVITY

FATE OF METALS

Colorado State University
14 Heavy metals used

<table>
<thead>
<tr>
<th>Element</th>
<th>Fly Ash (mg metal·kg⁻¹)</th>
<th>PBR (mg metal * L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>391.0</td>
<td>0.078</td>
</tr>
<tr>
<td>Cd</td>
<td>76.0</td>
<td>0.015</td>
</tr>
<tr>
<td>Co</td>
<td>79.0</td>
<td>0.016</td>
</tr>
<tr>
<td>Cr</td>
<td>651.0</td>
<td>0.130</td>
</tr>
<tr>
<td>Cu</td>
<td>655.0</td>
<td>0.131</td>
</tr>
<tr>
<td>Hg</td>
<td>49.5</td>
<td>0.010</td>
</tr>
<tr>
<td>Mn</td>
<td>745</td>
<td>0.149</td>
</tr>
<tr>
<td>Ni</td>
<td>1270.0</td>
<td>0.250</td>
</tr>
<tr>
<td>Pb</td>
<td>273.0</td>
<td>0.054</td>
</tr>
<tr>
<td>Sb</td>
<td>203.0</td>
<td>0.041</td>
</tr>
<tr>
<td>Se</td>
<td>49.5</td>
<td>0.010</td>
</tr>
<tr>
<td>Sn</td>
<td>18.8</td>
<td>0.004</td>
</tr>
<tr>
<td>V</td>
<td>565.0</td>
<td>0.113</td>
</tr>
<tr>
<td>Zn</td>
<td>2200.0</td>
<td>0.440</td>
</tr>
</tbody>
</table>

_Nannochloropsis salina_
Microalgae Productivity and Conversion Results

Biomass Productivity

- Impact of metals on production:
  - Growth: 45.5% decrease
  - Lipid Yield: 18.6% decrease

Productivity: 56% decrease in total lipid production

Recovery Efficiencies

- Impact of metals on extraction:
  - Control: 80% ± 7%
  - Metals: 89% ± 7%

Conversion: 9% increase in recovery efficiency

Combined impact (productivity & recovery): 51% decrease in lipid production
ICPMS: Fate of Metals

ICPMS analyses of the biofuel, and all by-products

Majority of heavy metals found in LEA and Methanol / Water by-products. Minimal Biofuel Contamination

* The metal Zn was removed due to contamination
** The metal Hg conc. was below ICPMS detection limit
Methane Concentration increased by 12%
Methane Production is 65% of optimum

### % Methane

<table>
<thead>
<tr>
<th>Treatment</th>
<th>% Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algae (Metals)</td>
<td>36.28</td>
</tr>
<tr>
<td>LEA (Metals)</td>
<td>49.45</td>
</tr>
<tr>
<td>Algae (Control)</td>
<td>37.47</td>
</tr>
<tr>
<td>LEA (Control)</td>
<td>36.87 *</td>
</tr>
<tr>
<td>+ Control</td>
<td>46.94</td>
</tr>
<tr>
<td>- Control</td>
<td>36.87 *</td>
</tr>
</tbody>
</table>

* Estimation of conc. Volume produced was below GC detection limit.
Weaknesses of Phase 1

- Which heavy metal(s) inhibit growth is unknown

- Chemostat addition of heavy metals would be more representative of actual growth system than batch addition of heavy metals.
Outline

1. **COAL POWER PLANT**

2. **PHASE 1**
   - 14 Heavy Metals & CO₂
   - Conversion
   - BMP
   - Methane
   - Biofuel

3. **PHASE 2**
   - Individual Heavy Metals & CO₂
   - Algae
   - LEA
   - Inhibitive Heavy Metals
   - Productivity

4. **PHASE 3**
   - Heavy Metals & CO₂
   - Algae
   - Lipid Yield
   - Fate of Metals

**RESULTS**

- 0%
- 10%
- 20%
- 30%
- 40%
- 50%
- 60%
- 70%
- 80%
- 90%
- 100%

As Cd Co Cr

FATE OF METALS
Experimental Design

Nannochloropsis salina

![Experimental Design Diagram]
Effects on Growth - 1X Concentration

Nickel inhibits growth
Effects on Growth - 40X Concentration

Growth (% of Control)

- Hg
- Cd
- Pb
- Se
- Co
- As
- Zn
- Cr
- Ni
- Cu

- Low Light
- Med Light
- High Light

Slight decrease in growth

High light overcomes inhibitory effects

Copper kills the algae while Ni inhibits growth
**Outline**

**PHASE 1**
- **Conversion**
- **BMP**
- **Methane**
- **Biofuel**

**PHASE 2**
- **Algae**
- **LEA**
- **Individual Heavy Metals**
- **Hazardous Heavy Metals**
- **Ni**
- **Cu**

**PHASE 3**
- **Heavy Metals & CO₂**
- **Metals & CO₂**

**RESULTS**
- **Productivity**
- **Lipid Yield**
- **Fate of Metals**

**COAL POWER PLANT**

14 **Heavy Metals & CO₂**

14 **As Cd Co Cr**

**CO2**

**INDIVIDUAL HEAVY METALS & CO₂**

**FATE OF METALS**

**RESULTS**

**PRODUCTIVITY**

**LIPID YIELD**

**FATE OF METALS**
12 Heavy Metals and Chemostat

4X Heavy Metal Concentration

12 Heavy Metal: 23.31% decrease
12 Heavy Metals and Chemostat

12 Heavy Metal: 23.31% decrease
Chemostat 14 Heavy Metal: 27.33% decrease
Future Work

- Further investigation of chemostat approach at various heavy metal concentrations.
- Model relationship between chemostat and batch cases.
- Model media reuse by combining batch and chemostat approaches.
Conclusions

- Metals Negatively Impact Biofuel Production

- Reduction of Ni and Cu increases microalgae growth

- Microalgae shows greater resistance to chemostat approach

- Chemostat approach should be utilized for TEA and LCAs.
Thank You

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