An Integrated Solar Fuels System

Caltech RTTC Project: Development of a Self-Contained, PV-Powered Domestic Toilet and Wastewater Treatment System
Time-lapse Video of Reaction Progress
Total coliform

Fecal coliform

E. Coli
IrO$_2$/Ta$_2$O$_5$/SnO$_2$/Bi$_2$O$_3$/TiO$_2$ Composite Anodes
IrO$_2$/Ta$_2$O$_5$/SnO$_2$/Bi$_2$O$_3$/TiO$_2$ Composite Anodes

Distance ~ 2 mm

Anode

$4e \rightarrow$ Ti--OH

$\rightarrow$ 2H$_2$O

$\rightarrow$ O$_2$ + 4H$^+$

Cathode

$\rightarrow$ 2H$^+$

$\rightarrow$ H$_2$

$\rightarrow$ 2e

$\rightarrow$ Cl$^-$

$\rightarrow$ 2Cl$^-$

$\rightarrow$ CO$_2$

$\rightarrow$ e

$\rightarrow$ Cl$_2$$^-$

$\rightarrow$ e

$\rightarrow$ Cl$^-$

$\rightarrow$ 2OH$^-$

$\rightarrow$ Cl$^-$

$\rightarrow$ 2H$_2$O

$\rightarrow$ ClO$^-$

$\rightarrow$ H$^+$

$\rightarrow$ HoCl

$\rightarrow$ pK$_a$ = 7.46

$\rightarrow$ H$^+$ + ClO$^-$

$\rightarrow$ ClO$^-$ + H$_2$O

$\rightarrow$ Cl$^-$ + 2OH$^-$

$E$ (HClO,H$^+$/H$_2$O,Cl$^-$) = -0.46 V; $E$ (HOCl/Cl$^-$,*OH) = -0.04 V; $E$ (ClOH$^+$/Cl$^-$,HO$^-$) = 1.90 V

$E$ (Cl$^-$/Cl$^-$) = 2.55 V; $E$ (Cl$_2$$^-$/2Cl$^-$) = 2.3 V; Cl$^-$ + Cl$^-$ $\leftrightarrow$ Cl$_2$$^-$ $K$ = 1.4x10$^6$ M$^{-1}$
\[ v_{in} = 0.3 \text{ m}^3/\text{s} \]
\[ v_{pump} = 0.12 \text{ m}^3/\text{s} \]
pH 5.41, 2.11 mS/cm
pH 7.02, 1.76 mS/cm (15 mM NaCl)
COD: 1,420 mg/g dry Fecal Simulant
COD: 1,580 mg/g dry Human Feces
Elapsed Time (min)
0 30 60 90 120 150 180
Free Chlorine (mM Cl)
0 2 4 6 8 10 12
Col 1 vs Col 6
50 mM, 3 V
Charge Passed (Ah/L)
0 2 4 6 8 10 12
Free Chlorine (mM Cl)
50 mM, 3 V
30 mM, 3 V
50 mM, 2.2 V
Bench-Top Tests of Fresh Urine & Actual Wastewater
### Composition of Domestic Wastewater

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.6 ~ 7.3</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>180.3</td>
</tr>
<tr>
<td>SCOD (mg/L)</td>
<td>99.4</td>
</tr>
<tr>
<td>TN (mM N)</td>
<td>2.594</td>
</tr>
<tr>
<td>NH$_4^+$ (mM)</td>
<td>1.910</td>
</tr>
<tr>
<td>NO$_3^-$ (mM)</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Cl$^-$ (mM)</td>
<td>3.880</td>
</tr>
<tr>
<td>ClO$_3^-$ (mM)</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Organic Acids (mM)</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Mg (mM)</td>
<td>0.6387</td>
</tr>
<tr>
<td>Ca (mM)</td>
<td>1.287</td>
</tr>
<tr>
<td>Protein (mg/L)</td>
<td>70.55</td>
</tr>
<tr>
<td>Carbohydrate (mg/L)</td>
<td>29.47</td>
</tr>
</tbody>
</table>
Domestic Wastewater Treatment

- **E. Coli Cells Remaining (%)**
  - Replicate #1
  - Replicate #2
  - Control

- **Time (hr.)**

- **TOC (mg L⁻¹)**
  - Disinfection rate
  - TOC (left)

- **Concentration / mM**
  - 
  - 
  - 

- **Time / minutes**
### Caltech Synthetic Feces Chemical Composition

<table>
<thead>
<tr>
<th>Organic Components</th>
<th>Amount (wt. %)</th>
<th>COD (mg L(^{-1}))</th>
<th>Molecular Wt. (g mole(^{-1}))</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yeast (active)</td>
<td>30</td>
<td>2,960</td>
<td>-</td>
<td>E. Coli substitute</td>
</tr>
<tr>
<td>Cellulose</td>
<td>15</td>
<td>1,240</td>
<td>(10^6 - 10^7)</td>
<td>Insoluble fiber</td>
</tr>
<tr>
<td>PEG400</td>
<td>15</td>
<td>2,088</td>
<td>400 (avg.)</td>
<td>Soluble fiber</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td>20</td>
<td>2,588</td>
<td>280</td>
<td>Fatty acid</td>
</tr>
<tr>
<td>Soy Protein</td>
<td>8</td>
<td>692</td>
<td>(\sim 10^6)</td>
<td>Undigested protein</td>
</tr>
<tr>
<td>Inorganics</td>
<td>12</td>
<td>808</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SUM ((\Sigma))</strong></td>
<td><strong>100</strong></td>
<td><strong>10,736</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Salt Added</th>
<th>MW (g mole(^{-1}))</th>
<th>Added (mg g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>58.4</td>
<td>40</td>
</tr>
<tr>
<td>KCl</td>
<td>74.6</td>
<td>40</td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>111</td>
<td>20</td>
</tr>
<tr>
<td>MgCl(_2)</td>
<td>95.2</td>
<td>20</td>
</tr>
<tr>
<td>ZnCl(_2)</td>
<td>136.3</td>
<td>0.8</td>
</tr>
<tr>
<td>FeCl(_2)</td>
<td>126.8</td>
<td>0.6</td>
</tr>
<tr>
<td>MnCl(_2)</td>
<td>125.8</td>
<td>0.3</td>
</tr>
<tr>
<td>CuCl(_2)</td>
<td>134.5</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Electrochemical Treatment of Synthetic and Human Feces

Graph showing Chemical Oxygen Demand (mg/L) over time for different conditions:
- Total COD (Human*) + 15mM Chloride
- Total COD (Simulant), 20mM Chloride
- Soluble COD (Human*) + 15mM Chloride
- Soluble COD (Simulant), 20mM Chloride

COD₀ = 8,100 mg/L

Graph showing COD Remaining (%) over time for different voltages:
- TCOD@3.0V
- TCOD@3.5V
- TCOD@4.0V
- TCOD@4.5V
Treatment Flow with Resource Recovery for 40 persons per day Usage

- Water-Free Urinal
- Squat Toilet
- Water Reuse (Flushing)
  - 120 L/d (Disinfected, Colorless)
- Gas Evolution
  - Flow rate = 1.46 L/min
  - H₂ Fraction = 73%
  - H₂ production = 68.8 mol/d

<table>
<thead>
<tr>
<th>COD</th>
<th>TN</th>
<th>TP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200 mg/L</td>
<td>55 mM N (NH₄⁺ 10%)</td>
<td>15 mM P</td>
</tr>
</tbody>
</table>

- Septic Tank Effluent
- Electrochemical Reactor
  - Retention Time = 6 hr
  - V_{apply} = 5.7 V
  - I = 135 A
  - Power = 0.77 kW (From Solar Cell)

- Nutrient Production
  - N production = 1.6 mol/d
  - P production = 1.8 mol/d

- Sterilized Liquid Fertilizer (Nitrogen)
<table>
<thead>
<tr>
<th>COD</th>
<th>TN</th>
<th>Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>~ 0 mg/L</td>
<td>40 mM N (NH₄⁺ 80%)</td>
<td>18 mM</td>
</tr>
</tbody>
</table>

* All extensive values (current, molar production, power) by arithmetic scale up of 55 mL reactor to 40 L reactor
* Fecal supernatant is assumed to be analogous to the domestic wastewater
* COD: Chemical Oxygen Demand, TN: Total Nitrogen, TP: Total Phosphorus, MAP: Mg₂NH₄PO₄
Future work - Helminth Egg Elimination

Helminth eggs:
1. Cause helminthiases (e.g., Schistosoma);
2. Remain viable for 1-2 months in crop, wastewater and sludge; for several years in feces;
3. Difficult to inactivate using chlorine, UV-light or ozone.

Electrochemical disinfection:
1. Initially with non-pathogenic nematodes (with Prof. Sternberg)
2. Quantify the numbers, survivability, and kinetics of Helminth egg disinfection.

Schistosomiasis
Michael R. Hoffmann, Principal Investigator
Clément Cid, PhD Student
Daejung Kwon, PhD Student
Kangwoo Cho, PhD Student
Asghar Aryanfar, PhD Student
Hao Zhang, PhD Student
Qu Yan, Post-doctoral Scholar

http://tinyurl.com/caltechtoilets
Big Bang Theory: Howard’s Space Toilet Prototype Test
Electrochemical Disinfection

Cathode: \(2H^+ + 2e^- \rightarrow H_2\)

Anode: \(2H_2O \rightarrow 4e^- \rightarrow O_2 + 4H^+\)
\(2Cl^- \rightarrow Cl_2 + 2e^-\)

Bulk Aqueous Phase:

\[Cl_2(aq) + H_2O \leftrightarrow HOCl + H^+ + Cl^-\]
\[HOCl \leftrightarrow H^+ + OCl^-\]
Disinfection of domestic wastewater in 20 L Reactor

Initial Voltage = 3.89 V, Initial Current = 16.7 A, Reactor volume = 20 L, Reaction time = 240 min. (Membrane Filtration Methods)

Disinfection rate of bacteria with time

Disinfection achieved after 180 min with a 4-log decrease in coliform bacteria
Membrane Filtration Methods

- Filter water through a 0.45 μm membrane filter
- Place membrane on selective media
  - mEndo agar LES for total coliform
  - mFC agar for fecal coliform
  - mTEC agar for E.coli
- Incubate
  - 23±1 hours at 35.0±0.5°C for total coliform
  - 24±2 hours at 44.5±0.2°C for fecal coliform
  - 2 hours at 35.0±0.5°C + 22-24 hours at 44.5±0.2°C for E.coli
- Count colonies
  - Pink to dark-red color with a shiny, greenish-gold, metallic surface sheen for total coliform
  - Light or dark blue for fecal coliform
  - Red to magenta colonies for E.coli
1. Eggs pass from the host in feces and urine.

2. Miracidia hatch in water.

3. Miracidia penetrate a snail.

4. Two generations of sporocysts develop in the snail.

5. Cercariae are released in water and penetrate the host's skin.

6. During penetration, cercariae become schistosomula and are transported to the liver to mature.

7. Paired adult worms migrate to intestinal veins or the GU venous plexus, where they lay eggs.
Helminths eggs

Table 1 Helminth ova content in wastewater and sludge from different countries. Modified from Jiménez, 2007; Hays, 1977; Schwartzbod et al., 1989; Bennani et al., 1992; Strauss, 1997* and Ensink et al., in press.

<table>
<thead>
<tr>
<th>Country/region</th>
<th>Municipal wastewater, HO/L</th>
<th>Sludge, HO/g TS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Developing countries</td>
<td>70-3000</td>
<td>70-735</td>
</tr>
<tr>
<td>Mexico</td>
<td>6 – 98 in cities, Up to 330 in rural and peri-urban areas</td>
<td>73-177</td>
</tr>
<tr>
<td>Brazil</td>
<td>166 – 202</td>
<td>75</td>
</tr>
<tr>
<td>Egypt</td>
<td>67 (mean); 735 (max)</td>
<td></td>
</tr>
<tr>
<td>Ghana</td>
<td></td>
<td>76</td>
</tr>
<tr>
<td>Morocco</td>
<td>214-840</td>
<td></td>
</tr>
<tr>
<td>Jordan</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>Ukraine</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>United States</td>
<td>1-8</td>
<td>2-13</td>
</tr>
<tr>
<td>France</td>
<td>9-10</td>
<td>5-7</td>
</tr>
<tr>
<td>Germany</td>
<td>≤ 40</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Great Britain</td>
<td></td>
<td>&lt; 6</td>
</tr>
<tr>
<td>Pakistan (Faisalabad)</td>
<td>142 (Ascaris)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>558 hookworms (Ancylostoma, Necator and Ascaris)</td>
<td></td>
</tr>
<tr>
<td>Russia</td>
<td>≤ 2000</td>
<td></td>
</tr>
<tr>
<td>Irkutsk, USSR</td>
<td>19</td>
<td></td>
</tr>
</tbody>
</table>

* cited as: from an oral communication with Schwartzbod. Standard level is ≤ 1 helminth egg per liter for agriculture irrigation.