Water quality assessments using hydroxyl radical probes in gamma irradiations

in Water Quality Monitoring Through Cross Disciplinary Approaches

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Wastewater treatment problems and challenges

1. PPCPs and others – require advanced treatment
2. Infrastructure
3. Combined Sewer Overflows
4. 2° treated wastewater quality - variable

CSOs: Combined Sewer Overflows

http://cfpub.epa.gov/npdes/cso/demo.cfm
Present Day Wastewater Treatment

Approximately 70% of WWTF in United States treat through the secondary treatment. Many dissolved substances remain:

- Dissolved anions: nitrate, nitrite, sulfate, bicarbonate, etc.
- Dissolved metal ions: iron, magnesium, sodium, nickel, potassium, etc.
- Dissolved organic nitrogen compounds (ie,: NDMA), ammonium compounds
- **Dissolved organic compounds** (emerging contaminants; chemicals of concern)

http://www.waterencyclopedia.com/images/wsci_04_img0570.jpg
For water treatment challenges and reclamation/reuse, implement ADVANCED WasteWater TREATMENTS

Can we PREDICT or determine advanced treatment EFFECTIVENESS of secondary treated WW?

Some Major Factors to consider in advanced treatment:

1) Water quality of the secondary treated wastewater.

2) Type of advanced treatment

3) Problematic contaminants
How can we assess the quality of $2^\circ$ treated wastewater?

2 different locations

WEST COAST

MIDWEST GREAT LAKES
• OH production using Radiolysis

Radiolysis: Use of ionizing radiation (ie.: gamma rays) to induce chemical changes.

\[ \text{H}_2\text{O} \rightarrow \text{•OH, H}^\text{•}, \text{e}^-\text{(aq), H}^\text{+}, \text{H}_2\text{O}_2, \text{H}_2 \]

• Oxidizing or reducing conditions can be established.

• Conditions for oxidation:

\[ \text{e}^-\text{aq} + \text{N}_2\text{O(g)} + \text{H}_2\text{O} \rightarrow \text{N}_2 + \text{•OH} + \text{OH}^- \]

\[ \text{•H} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{•OH} \]
Removal Constant and Efficiency of •OH

• The **Removal Constant** represents the change in concentration of the chemical contaminant (CC) due to reaction with the radiation-generated radical species, •OH, with radiation dose, kGy.

• The **Removal Constant** is the initial slope of the curve of Δ[CC] vs Dose (kGy).

• Focus is on the early stages of the radical transformations, MAJOR rxn: •OH + CC →.

• Can compute the % efficiency since the OH radical yield is known, 0.59 µM/Gy.
Variations in hydroxyl radical reaction efficiencies in pure water

SOME compounds are 100% efficient in their reactions with the hydroxyl radical, while others are not.

- **1,3,7-trimethylxanthine (caffeine)**: stimulant; Human marker

- **DEET**: Personal care product

- **BPA**: Endocrine disruptor; Industrial Chemical for production of polymers (BPA-polycarbonate)

- **Sulfa Drugs, Sulfamethoxazole**: Pharmaceuticals

- ~75% Efficient

- ~50% Efficient
• Removal Constants afford a way to determine the efficiencies of hydroxyl radical reactions in Advanced Oxidation Technologies

\[
\text{[CONTAMINANT]} + \cdot \text{OH} \rightarrow
\]

• Individual dissolved organic components show wide variations in \( \cdot \text{OH} \) efficiencies

• Mixtures of dissolved organics show dependency on concentration and rate constant; more work needs to be done to better understand the complexity of contaminant mixtures

\[
\text{CONTAMINANT} + \cdot \text{OH} + \text{other dissolved substances} \rightarrow
\]

• Can Removal Constants be used to determine the general quality of treated wastewaters?
Model Compounds as Water Quality Probes for secondary treated wastewater

• CAFFEINE (100%) AND SULFAMETHOXAZOLE (50%)
• ASSUMPTION: the lower the experimentally determined % efficiency, the lower the water quality (more dissolved substances as hydroxyl radical competitors)
• Treated wastewater supplied from: Orange County, CA (pop = 2.4 million; 350 square miles) & Portage, IN (pop = 50,000; 35 square miles)
• Probe Solution concentrations: 10µM
Caffeine - An •OH Probe

IN PURE WATER:

\[ \bullet \text{OH} + 1,3,7\text{-trimethylxanthine (caffeine)} \rightarrow 100\% \text{ efficient} \]

IN 2° treated WASTEWATER

\[ \bullet \text{OH} + 1,3,7\text{-trimethylxanthine (caffeine)} + \text{Dissolved ions} + \text{Dissolved organics} + \text{Dissolved metals} \rightarrow \]

Value will
1) offer a measure of water quality
2) indicate the effectiveness of •OH in remediation
Sulfamethoxazole - An •OH Probe

**IN PURE WATER:**

\[ \text{•OH} + \text{Sulfamethoxazole} \rightarrow \text{50% efficient} \]

**IN 2° treated WASTEWATER**

\[ \text{•OH} + \text{Dissolved ions} + \text{Dissolved organics} + \text{Dissolved metals} \]

Value will
1) offer a measure of water quality
2) indicate the effectiveness of •OH in remediation
Rate Constants and Efficiencies for organic contaminants with •OH in DI water and in secondary treated wastewater

<table>
<thead>
<tr>
<th>Solution / Contaminant</th>
<th>Caffeine</th>
<th>Sulfamethoxazole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate Constant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DI Water, M⁻¹s⁻¹</td>
<td>6.9 (± 0.4) x 10⁹</td>
<td>8.3 (± 0.8) x 10⁹</td>
</tr>
<tr>
<td>•OH EFFICIENCY in Deionized Water</td>
<td>92 ± 8 %</td>
<td>56 ± 7 %</td>
</tr>
<tr>
<td>Adjusted Rate Constant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DI Water, M⁻¹s⁻¹</td>
<td>6.3 (± 0.4) x 10⁹</td>
<td>4.6 (± 0.8) x 10⁹</td>
</tr>
<tr>
<td>EFFICIENCY in Q1, 50µM, (2º treated wastewater)</td>
<td>37 ± 4 %</td>
<td>29 ± 7 %</td>
</tr>
</tbody>
</table>


Average of ~50-60% drop in removal efficiency in 2º treated wastewater
Selected secondary treated wastewater data from Orange Co, CA

<table>
<thead>
<tr>
<th>Organic N</th>
<th>pH</th>
<th>TOC</th>
<th>Turbidity</th>
<th>Total Alkalinity (as CaCO$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7 mg/L</td>
<td>7.4</td>
<td>9.21 mg/L</td>
<td>1.4 NTU</td>
<td>171 mg/L</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sulfate</th>
<th>Chloride</th>
<th>Calcium</th>
<th>magnesium</th>
<th>Sodium</th>
</tr>
</thead>
<tbody>
<tr>
<td>223 mg/L</td>
<td>215 mg/L</td>
<td>80.7 mg/L</td>
<td>28.1 mg/L</td>
<td>190 mg/L</td>
</tr>
</tbody>
</table>
Caffeine in secondary treated wastewater

Rate constant: $6.9 \pm 0.4 \times 10^9$ M$^{-1}$s$^{-1}$

<table>
<thead>
<tr>
<th>month</th>
<th>INDIANA</th>
<th>CA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Removal constant</td>
<td>Efficiency</td>
</tr>
<tr>
<td>NOV ’11</td>
<td>0.072</td>
<td>12%</td>
</tr>
<tr>
<td>DEC ’11</td>
<td>0.016</td>
<td>3%</td>
</tr>
<tr>
<td>JAN ’12</td>
<td>0.086</td>
<td>14%</td>
</tr>
<tr>
<td>APRIL</td>
<td>0.028</td>
<td>5%</td>
</tr>
<tr>
<td>MAY</td>
<td>0.068</td>
<td>11%</td>
</tr>
<tr>
<td>JULY</td>
<td>0.086</td>
<td>15%</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>0.078</td>
<td>13%</td>
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Removal efficiency: $92 \pm 8\%$
Sulfamethoxazole in secondary treated wastewater

Rate constant: $8.3 \pm 0.8 \times 10^9$

Removal efficiency: $56 \pm 7\%$

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<td>DEC ’11</td>
<td></td>
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## Probe compound comparison:

'OH reaction efficiencies in Indiana 2° treated wastewater

<table>
<thead>
<tr>
<th>month</th>
<th>INDIANA CAFFEINE Removal constant</th>
<th>-OH efficiency</th>
<th>INDIANA SX Removal constant</th>
<th>-OH efficiency</th>
</tr>
</thead>
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<tr>
<td>NOV ’11</td>
<td>0.072</td>
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Caffeine = 100% efficiency in pure water.
Rate constant: $6.9 \pm 0.4 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$

Sulfamethoxazole = 56% efficiency in pure water.
Rate constant: $8.3 \pm 0.8 \times 10^9$
Conclusions

- Hydroxyl Radical Probes can be used for the general assessment of treated wastewater quality.
- The OH efficiencies, calculated from the removal constants, also indicate the effectiveness of advanced oxidation processes for secondary treated wastewater.
- Different radical probes can be used.
- From our experiments, the secondary treated wastewater in Portage Indiana contains less dissolved substances (cleaner!) than the Orange County, CA secondary wastewater.
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Thank you!