Advanced Oxidation Processes for the Destruction and Detoxification of Cyanotoxins

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Outline

• Background - Advanced Oxidation Processes (AOP)

• HABs - Harmful Algae Blooms & Cyanotoxins

• Ultrasonic Destruction of Microcystin-LR

• Titanium dioxide Photocatalysis of Cylindrospermopsin

• Conclusions
Advanced Oxidation Technologies

Organic Toxin/Pollutant $\rightarrow$ AOTs $\rightarrow$ CO$_2$ + H$_2$O + HX

Supercritical Water
Fenton
H$_2$O$_2$, O$_3$ and/or UV

Photocatalysis
Cavitation and Sonolysis

H$_2$O$_2$, O$_3$ and/or UV

Gamma Rays
Electron Beams
CyanoHAB Environmental Impact

Harmful Algal Bloom

Marina in Port St Lucie, Florida following hurricane Katrina 2005


Microcystin-LR

C_{49}H_{74}N_{10}O_{12} - HO• + C-H; k~10^{-7-8} M^{-1} sec^{-1}


0.001 mg/litre (for total microcystin-LR, free plus cell-bound)
Degradation and Detoxification of MC-LR by Ultrasonic Irradiation
Ultrasonic Irradiation

Reaction Zones

1) Vapor Region - Extreme Conditions Pyrolysis of water vapor and volatiles
2) Interface - Supercritical, (HO• + H•), Hydrophobic, LT Pyrolysis, hydrolysis
3) Bulk liquid - Limited to reactions of radicals diffusing from the interfacial region

Ultrasonic Induced Degradation of Microcystin-LR

Degradation of Crude and pure MC-LR

![Graph showing the degradation of Crude and pure MC-LR over time.

- **X-axis**: Time (min)
- **Y-axis**: MC-LR (mg/L)

- Two lines represent the degradation of crude isolate and pure MC-LR.
- Data points are plotted for each condition.

The graph illustrates the rate at which MC-LR concentrations decrease over time for both crude isolate and pure MC-LR samples.
Ultrasonic irradiation of MC-LR

**Bulk Solution**
Ambient condition

**Gas Region**

**Interfacial Region**
Hydrophobic region, hydrolysis, low temperature pyrolysis

**Cavitating bubble**
Production of OH and H by thermolysis of H₂O, high and low temperature pyrolysis

**Volatiles**

**polar region**

**non-polar region**
Evaluation of toxicity by brine shrimp assay

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<th>Number Exposed</th>
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<th>Concentration (ppm)</th>
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**LC50 = 3.01 ug/mL (1.98, 4.56 )**
95% confidence

**LC50 >> 50 ug/mL**

Alice Hudder, Weihua Song, Kevin E.O’Shea and Patrick Walsh Toxicology and Applied Pharmacology, 2007
Detoxification of Microcystin-LR upon ultrasonic irradiation

[Graph showing changes in [MC-LR] (µM) over time (min) with error bars for HPLC and PP1]

Cylindrospermopsin [143545-90-8]

([C15H21N5O7S]; mol. wt. = 415.43) Chemical name = 2,4(1H,3H)-Pyrimidinedione, 6-[(R)-hydroxy[2aR,3S,4R, 5aR,7S)-2,2a,3,4,5,5a,6,7- octahydro-3-methyl-4-(sulfoxy)-1H-1,8,8b-triazaacenaphthylen-7-yl]methyl]-, rel-(−)-

Cylindrospermopsin is relatively stable at extreme temperatures (no degradation at 100 °C for 15 minutes) and pH (~25% degraded at pH of 4, 7, and 10 for 8 weeks).


Not effectively treated by traditional waste water treatments

Ultrasonic Induced Degradation of CYN and MCs

Degradation of CYN and MCs by ultrasound; 640 KHz, air saturated, initial concentrations 4-5 ppm

Solar Powered Decontamination

UV and solar TiO2 photocatalysis of brevetoxins (PbTxs), Toxicon 2010, 1008-1016.
UV TiO$_2$ photocatalysis of CYN

Previous Reports on UV TiO$_2$ Photocatalysis
Summary of Reactivity of CYN with HO•

\[
\text{H}_2\text{O} \rightarrow (0.28)\cdot\text{OH} + (0.06)\text{H}^\bullet + (0.27)e^-_{\text{aq}} + (0.05)\text{H}_2 + (0.07)\text{H}_2\text{O}_2 + (0.27)\text{H}^+ 
\]

<table>
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<th>(k_{\text{OH}} ) (M(^{-1}) s(^{-1}))</th>
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<tbody>
<tr>
<td>Uracil</td>
<td>(5.7 x 10(^9)) (\text{average of 7 literature values})</td>
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<tr>
<td>CYN</td>
<td>(5.08(\pm)0.16) x 10(^9) (\text{overall})</td>
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<td>Growth transient</td>
<td>(4.75 (\pm) 0.02) x 10(^9) ((4.75/5.08) \Rightarrow 84%)</td>
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Degradation products and proposed reaction pathways for •OH + CYN

Conclusions

- Ultrasonic treatment of microcystin-LR (MCLR) results in the predominant and selectively oxidation of the ADDA diene and aromatic ring leading to detoxification even in the presence of dissolved organic material. Taste and odor compounds associated with HABs are also readily degraded.

- PP1 and Brine shrimp assays indicate the oxidation products produced from advanced oxidation of MCs are not toxic.

- AOPs should be effective for all ADDA chain containing MC variants (>80) and nodularins.

- Cylindrospermopsin, a charged species, is more effectively degraded by titanium dioxide photocatalysis than ultrasonic irradiation. Ultrasonic induced destruction may be particularly attractive for treatment of hydrophobic toxins, while photocatalysis may be more effective for polar and charged species.

- The initial water quality and treatment objectives are critical in determining the feasibility of real applications of different AOPs. Treatment trains, for example careful separation of algal cells, subsequent treatment with an AOP and bioremediation, also need to be considered among treatment options.
THANK YOU
FOR YOUR ATTENTION

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