Using Rapid Small Scale Column Testing to Evaluate Granular Activated Carbon Adsorption of Cyanotoxins from Drinking Water

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Outline

• Background – cyanotoxins, local conditions, previous research
• Objectives
• RSSCTs (Rapid Small Scale Column Tests)
• Developing RSSCTs and overcoming MC-LR biodegradation
• RSSCT GAC adsorption and the effects of preloading
• UV254/TOC and competitive adsorption
• Biological analysis and practical implications
• Conclusions
• Recommendations for future research
Cyanotoxins

- Cyanotoxins released by cyanobacteria through lysing or cell death (USEPA, 2012)
  - Extracellular toxins
- Health concerns to humans and environment (Falconer 2008)
  - Hypoxia, carcinogenic, organ damage
- Most common (Merel et al. 2013)
  - *Microcystins-LR, RR, LY* (100+ congeners exist)
  - Cylindrospermopsin
  - Anatoxins
  - Saxitoxins
- Guideline of 1.0 µg L\(^{-1}\) for MC-LR (WHO, 2011)
- OH EPA action level of 0.3 µg L\(^{-1}\) (USEPA, 2015a)
Treatment

• Cyanotoxin contamination of drinking water is a growing area of concern
  • Increased nutrient load, population etc.
• Incorrect treatment practices could result in release rather than removal
  (WRF and AWWA, 2015)
• Intracellular (I)
• Extracellular (E)

• Typical treatment methods include:
  (WRF and AWWA, 2015)
  • Pretreatment Oxidation (I)
    • Potassium permanganate (E)
  • Coagulation/Sedimentation/Filtration (I)
  • Membranes (I + E)
  • DAF (I)
  • **GAC (E)**
  • PAC (E)
  • Ozone (E)
  • Chlorination (E)
Local Utility

• Worked with a local utility partner on practical questions
• Process
  • Potassium permanganate > Alum > Polymer > Filters > **GAC** > Cl₂
• Three GAC contactors in operation (April 2013)
  • GAC intended for reduction of DBP precursors
  • Carbon is regenerated with 15% virgin makeup
  • Each contactor regenerated twice per year
• What utility wants to know?
  • What is the best way to manage GAC contactors for toxin removal?
  • If the GAC is loaded with NOM...then how effective for toxins?
    • Competition, fouling etc.
• Toxins detected (Allen 2015)
  • MC-LR (Max-1.55 ppb)
  • MC-RR (Max-0.52 ppb)
  • MC-LY (Max-0.19 ppb)
  • 7-desmethylated-MC-LR
• 2014 sampling resulted in max. 
  MC-LR = 3.10 µg L⁻¹ (Ohio EPA, 2010-2017)
• Saxitoxin has also been detected (Ohio 
  EPA, 2010-2017)
Previous Research

• **GAC**
  - Represents an efficient solution for the removal of extracellular toxins (Sorlini and Collivignarelli 2011)
  - GAC + conventional methods very effective (Karner et al. 2001)
  - Mesoporous carbon is more effective at removing cyanotoxins (Westrick 2008)
  - 70-80% TOC in effluent, media replaced (Antoniou et al. 2014)
  - MC adsorption during bloom event may not be viable (Karner et al. 2001)

• **GAC + MC-LR**
  - Flat, long breakthroughs and small steep curves (Huang et al. 2007, Carlile 1994)
  - Bacterial colonization a hindrance and an important mechanism (Wang et al. 2007, Drogui et al. 2012, UKWIR 1996, Wang et al. 2006)

• **RSSCTs**
  - Some work on SBAs (Short Bed Adsorbers)
  - RCT showed 80% after 30,000 BVs (Hall et al. 2000)

• **Research Gaps**
  - Lack of data regarding the performance of GAC in removing cyanotoxins
  - Reliable way to simulate full scale GAC adsorption (RSSCTs)
  - Competitive adsorption of source water NOM and cyanotoxins
Objectives

- Use RSSCTs to assess the effectiveness of GAC in treating cyanotoxins, particularly MC-LR.
- Determine competitive adsorption/inhibition of NOM (TOC) and cyanotoxins.
- Use RSSCTs to evaluate the adsorption capacity of GAC in treating cyanotoxins when columns are preloaded with NOM at multiple levels.
RSSCTs

- RSSCTs are small scale models of full scale processes (Poddar, Nair and Mahindrakar 2013)
  - Reduced time and resources
- Mass transfer methods used to simulate performance (Poddar, Nair and Mahindrakar 2013)
- Carbon ground to reduced sieve size
  - Possibility to overestimate performance of preloaded GAC (Ho and Newcombe 2007)

- Proportional Diffusivity Model (Crittenden et al. 1991)
  - Intraparticle diffusivity changes with particle size
  - Scaling relationship is a function of carbon particle size used in large and small scale
RSSCT Design

- $V = 15$ L water
- Estimated RSSCT run time = 33 days
- $EBCT_{sc} = 0.84$ min
- Hydraulic loading rate ($v$) = 1.73 m h$^{-1}$
- Flow Rate = 0.32 mL/min
- Sieve size = 100x200
- $M_{GAC} = 0.128$ g
- RSSCT column diameter = 3.74 mm
- Bed Volume = 0.27 mL
- Bed Length = 2.42 cm
- $d_{p\,LC} = 1.29$ mm
- $d_{p\,SC} = 0.11$ mm
- SF = 11.8
GAC Prep and GACI (CFE)

- GAC was collected from Clermont County Water Resources Department
  - Regenerated with 15% virgin makeup

- GAC was ground to meet 0.11 mm avg. particle size (100x200 sieve size)

- GAC rinsed to separate “fines” to prevent pressure buildup in column

- GACI (CFE) was procured from CCWRD
  - 240 L
Chemicals and Analyses

- **MC-LR**
  - LC/MS/MS
  - USEPA Method 544

- **NOM (Natural Organic Matter)**
  - TOC
    - Combustion Catalytic TOC analyzer (TOC-Vcph Shimadzu Corporation, MD)
    - USEPA method 415.3
  - UV254
    - Analyzed on day of extraction
    - Standard Method 5910

- **MC-LR stock solutions**
  - Beagle Bioproducts (Columbus, OH)
  - Verified by Beagle to be ≥ 95% pure HPLC
  - Provided as dried film in 2 mL vial
  - Dissolved in 1 mL Milli Q water and diluted for analysis of stock via LC/MS/MS
    - USEPA method 544
Experiments to Minimize Biological Activity

- Refrigeration at 5 °C
- Sodium Azide Inhibition
  - Bottle tests
  - RSSCT tests
- Sterile Techniques
Sodium Azide RSSCT Confirmation Test

- Influent A (0 mg/L)
- Influent B (50 mg/L)
- Influent C (100 mg/L)
- Effluent A
- Effluent B
- Effluent C

Bed Volumes

MC-LR (µg L⁻¹)

0 10000 20000 30000 40000 50000 60000 70000

0 1 2 3 4 5 6 7 8 9 10
Sterile Techniques

• Sterile techniques
  • Autoclaving
  • Filtering (0.2 µm) GACI water collected from CCWRD
  • Teflon tubing, pump, pulse dampener and RSSCT apparatus
    • Cl₂ (10 mg L⁻¹)
    • Ascorbic acid purge of Cl₂ (25 mg L⁻¹)
    • Milli-Q for 4 days

• R2A HPCs
  • Plate counts taken 2-3 times a week
    • Influent and effluent
• **Preloaded RSSCTs**
  • Preloading the GAC after grinding to prevent overestimation
  • Design of RSSCTs
    • A – 0% preloaded (control)
    • B – 55% preloaded
    • C – 100% preloaded
  • Columns preloaded with GACi NOM
    • Assumptions based on previous TOC data and current UV254 data
      • NaN₃ contributes to UV254 absorbance!
  • Simulates real-world scenario

• **Preloading**
  • RSSCT B
    • 55% preloaded with TOC at 2,100 BVs
  • RSSCT C
    • 100% preloaded with TOC at 22,900 BVs
## Biological Parameters

<table>
<thead>
<tr>
<th></th>
<th>Temp. (°C)</th>
<th>Lag Phase (days)</th>
<th>k (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial</strong></td>
<td>25</td>
<td>6.86</td>
<td>0.07</td>
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<tr>
<td><strong>Low Temp.</strong></td>
<td>5</td>
<td>5.78</td>
<td>0.04</td>
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<tr>
<td><strong>Confirmation</strong></td>
<td>25</td>
<td>8.63</td>
<td>0.05</td>
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<tr>
<td><strong>Inhibition</strong></td>
<td>25</td>
<td>12.75</td>
<td>0.05</td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td>-</td>
<td>8.51</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Practical Implications – Full Scale Simulation

GAC Effluent MC-LR (µg L⁻¹)

Days

0% Preloaded LC
50% Preloaded LC
100% Preloaded LC
Practical Implications – Biodegradation

- Evaluated simulated biodegradation in full scale using EBCT = 10 min
- Biodegradation within the GAC column reduces MC-LR by 0.03 µg L⁻¹
- Biodegradation within the GAC column is likely not significant at measured rates
- However, in presence of biological activity from WTP intake to distribution system, perhaps some significant biodegradation
Conclusions

- RSSCTs appear effective and inexpensive for simulating GAC processes with MC-LR
- RSSCTs with natural source water complicated by biodegradation - countermeasures required
- Adsorption only RSSCTs resulted in gradual breakthrough
  - Flat MC-LR breakthrough curve
  - Exceeded OH EPA action level quickly (0.3 µg L⁻¹)
- Competitive inhibition (NOM/MC-LR) - NOM preloaded GAC impacts adsorption of MC-LR
- 100% NOM preloaded column resulted in fast and steep MC-LR breakthrough
- However, 50% NOM preload not much different than control
- Biodegradation rates observed in experimental influents relatively insignificant for GAC EBCT
Future Research

• Pilot scale study
• BET/pore surface area analysis on the GAC collected from the water utility
  • Size and distribution of the pores
• Additional investigation of competitive adsorption
• Multiple toxins
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