OXIDATION OF ALGAL METABOLITES AND TOOLS FOR OPERATORS

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AGENDA

Background
Oxidation
  Summary, Effectiveness, Considerations
Tools for Operators
Conclusions
INTRACELLULAR VS EXTRACELLULAR

- What is inside versus outside the algal cells
- Concentrations inside and outside vary
  - Number of algal cells
  - Type of algae
  - Growth cycle
  - Dilution/volume
- Oxidation can cause cell lysing
  - What was inside is now outside
WHY IS THIS A CONCERN IN WTP?

• Many utilities practice some form of preoxidation
  • Taste and odor control
  • Biological control in raw water pipeline
  • Iron and manganese
  • Enhance coagulation/sedimentation
  • Reduce chlorinated disinfection byproducts (TTHM)

• Preoxidation could make removal more difficult
REMOVAL OF CELLS VS TOXINS

• First goal – remove cells
  • Sedimentation/Softening
  • Floatation
  • Filtration

• Second goal – remove toxins
  • Adsorption
  • Oxidation
THIS CREATES CHALLENGES TO WTPS WITH THE POTENTIAL FOR ALGAL TOXINS

• Can I discontinue preoxidation?
  • Can I still meet my disinfection requirements?
  • What about other biological growth?
  • Do I have adequate time or a place downstream?

• Alternative oxidant locations
  • May have less reaction time
  • May be at “high” pH
  • Barrier is close to my finished water
  • Will lose my preoxidation benefits
OXIDATION
### WHICH OXIDANTS ARE EFFECTIVE?

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Adapted from Westerick et al. 2010
CHLORINE - SUMMARY

- **Effective**
  - Microcystin, Cylindrospermopsin, Saxitoxin

- **Not Effective**
  - Anatoxin

- **Impact of pH??**
  - Microcystin – lower pH better
    - Rate at pH 9 is ~10% of pH 7
  - Cylindrospermopsin – low or high pH?
  - Saxitoxin – high pH better

- **Lower overall toxicity**
Oxidation of *Microcystis aeruginosa* and MC-LR in solution during free chlorine (HOCl/OCl⁻) treatment

**Fig. 9** *Microcystis aeruginosa* inactivation and resulting MC-LR concentration (left), and removal of MC-LR standard from separate aqueous solution (right) during free chlorine (HOCl/OCl⁻) treatment

**Source:** Ding et al. 2010
CHLORINE - CONSIDERATIONS

- Impact of high pH
  - Especially lime softening plants
  - Preoxidation – more effective but before cell removal
  - After sedimentation
    - Less effective?
    - Less reaction time

- Impact on algal cells

- Disinfection byproduct formation
OZONE - SUMMARY

• Effective
  • Microcystin, Cylindrospermopsin, Anatoxin

• Not Effective
  • Saxitoxin

• Very effective for taste and odor control
• Preozone or intermediate ozonation
• High initial cost
• Low operating cost
WHAT IS OZONE?

• Unstable form of oxygen
• Produced on-site (electricity and oxygen)
• Reversible reaction \(2O_3 \leftrightarrow 3O_2\)
• Temperature sensitive (lower is better)
• Dust and moisture sensitive
  • fouling impacts electrical efficiency
  • acid production from nitrogen and water
OZONE GENERATION PRINCIPLES

High Voltage Power Supply

Metallic Coating

Glass/Ceramic Dielectric

Stainless Steel

Cooling Water

Ground Electrode

Feed gas with Oxygen

23 to 99 %wt O₂

O₂ → e⁻ → O₂⁻ → O₄⁺ → e⁻ → O₃

1 to 15 %wt O₃

Gap (0.5 to 3.0 mm)
WHAT IS IT USED FOR?

- Disinfection
- DBP control
- Microflocculation
- Taste and odor control
- Iron and manganese oxidation
- Organics oxidation
- Hydrogen sulfide oxidation

Ozone contactor gallery
WHAT OTHER IMPACTS ARE THERE?

• Inorganic byproduct - bromate
  • High pH, raw bromide concentrations
  • Counteract by optimized dose, ammonia, lower pH

• Organic byproducts
  • Oxygenated byproducts
  • Assimilable organic carbon (AOC)

• Dissolved oxygen
OZONE EFFECTIVENESS

Oxidation of Microcystis aeruginosa

Effective

Oxidation of MC-LR in solution

Effective

Fig. 12 Microcystis aeruginosa inactivation and resulting MC-LR concentration (left), and removal of MC-LR standard from separate aqueous solution (right) during ozone treatment

Source: Ding et al. 2010
OZONE - CONSIDERATIONS

- Cost effectiveness
  - Also address T&O or DBPs
- Meet disinfection requirements
- May need biological filtration
- Bromate formation
CHLORAMINE - SUMMARY

• Not Effective
  • Microcystin, Cylindrospermopsin, Anatoxin
  • Saxitoxin?

• Not a powerful primary disinfectant

• Used by many as a secondary disinfectant
  • Long reaction times
  • A barrier to protection?
**CHLORAMINE EFFECTIVENESS**

Fig. 16 *Microcystis aeruginosa* inactivation and resulting MC-LR concentration (left), and removal of MC-LR standard from separate aqueous solution (right) during monochloramine treatment.

Source: Ding et al. 2010
CHLORAMINE - CONSIDERATIONS

- Would not be considered as a primary barrier
- Would still be part of overall treatment as secondary disinfectant
CHLORINE DIOXIDE - SUMMARY

• Not Effective
  • Microcystin, Cylindrospermopsin, Anatoxin
  • Saxitoxin?

• Lower toxicity reported

• Primarily used as a preoxidant
  • Potential lysing of algal cells

• Impact at “high” pH?
WHY USE CHLORINE DIOXIDE?

- Powerful oxidant for Mn
- Some phenolic T&O, minimal MIB & geosmin
- Effective algicide and mollusk control
- Doesn’t react with NOM to form halogenated DBPs
- Reduces oxidant demand for subsequent disinfectant(s)
- Effective against viruses, bacteria and *Giardia*
- Control nitrification is the distribution system
PREOXIDATION WITH CHLORINE DIOXIDE IS EFFECTIVE AT REDUCING TTHM FORMATION

SDS Testing with 1.5 mg/L of Free Chlorine
CHLORITE BASED GENERATION

2 Chemical
Sodium Chlorite Solution
Chlorine Gas

Solid Chlorite
Sodium Chlorite Solid
Chlorine Gas

3 Chemical
Sodium Chlorite Solution
Sodium Hypochlorite
Hydrochloric Acid

2 Chemical - Acid
Sodium Chlorite Solution
Hydrochloric Acid

Electrochemical
Sodium Chlorite Solution
Energy

CHLORATE BASED GENERATION

Three Chemical
Sulfuric Acid
Premixed
(Hydrogen Peroxide &
Sodium Chlorate)
ISSUES WITH CHLORINE DIOXIDE

• 60-70% of applied ClO₂ goes to chlorite ion
  • ~1.5 mg/L maximum dose

• Compliance requirements

• Chlorite and free chlorine as secondary disinfectant may lead to “cat urine odor”

• Marginally effective against Cryptosporidium

• Operating costs

• Supply chain issues
CHLORINE DIOXIDE EFFECTIVENESS

Fig. 10 Microcystis aeruginosa inactivation and resulting MC-LR concentration (left), and removal of MC-LR standard from separate aqueous solution (right) during chlorine dioxide treatment

Source: Ding et al. 2010
CHLORINE DIOXIDE - CONSIDERATIONS

• Consider stopping during an event
  • Prevent lysing of cells
  • Must consider other impacts – Mn, preoxidation, CT

• Must consider chlorite formation
ADVANCED OXIDATION - SUMMARY

- **Effective**
  - Microcystin, Cylindrospermopsin, Anatoxin

- **Not effective**
  - Saxitoxin??

- **Effective for disinfection and taste and odor**

- **After filtration**

- **High initial cost**

- **High operating cost**
WHAT IS ADVANCED OXIDATION?

• Process that generates reactive species - radicals
  • hydroxyl radicals (●OH)

• Stronger oxidizer than ozone

• Fast kinetics

• Short half-life

• Yield/concentration

• Scavenging potential of water
EXAMPLE PROCESSES/REAGENTS

- Ozone
- Ozone/$\text{H}_2\text{O}_2$
- Ozone/UV
- UV/$\text{H}_2\text{O}_2$
- UV/PAA
- UV/TiO$_2$
- UV/Fe/$\text{H}_2\text{O}_2$
- Fe/$\text{H}_2\text{O}_2$
- UV/$\text{S}_2\text{O}_8$
- Ag/$\text{S}_2\text{O}_8$
- Fe/$\text{S}_2\text{O}_8$
- UV/HSO$_5$
- Co/HSO$_5$
- E beam
UV/H₂O₂ PROCESS

- UV light absorbed by hydrogen peroxide
  \[ \text{H}_2\text{O}_2 \xrightarrow{h\nu\text{(energy)}} 2 \cdot\text{OH} \]
  \[ \text{P} + \cdot\text{OH} \xrightarrow{k_{\text{OH,P}}} [\text{radical species}] \text{O}_2 \xrightarrow{} \text{Products} \]

- Degradation rate depends on:
  - OH radical rate constant \( k_{\text{OH,P}} \)
  - H₂O₂ concentration
  - \( \cdot\text{OH} \) radical demand in water
  - Intensity and spectral distribution of the light source
  - Absorption of water background
DIFFERENT TYPES OF LAMPS DISINFECT DIFFERENTLY

Low Pressure

Medium Pressure
MUST BALANCE ENERGY AND HYDROGEN PEROXIDE

- Less peroxide requires more energy
- More peroxide requires less energy
- Diminishing returns?
- Residual hydrogen peroxide
UV EFFECTIVENESS

**Oxidation of Microcystis aeruginosa**

*Not Effective*

**Oxidation of MC-LR in solution**

*Not Effective*

**Fig. 16** *Microcystis aeruginosa* inactivation and resulting MC-LR concentration (left), and removal of MC-LR standard from separate aqueous solution (right) during ultraviolet (UV) treatment

**Source:** Ding et al. 2010
ADVANCED OXIDATION - CONSIDERATIONS

- Cost effectiveness
  - Also address T&O or DBPs
- Meet disinfection requirements
- Quenching of residual hydrogen peroxide
  - High chlorine doses
PERMANGANATE - SUMMARY

- **Effective**
  - Microcystin, Anatoxin

- **Not effective**
  - Cylindrospermopsin, Saxitoxin

- **Does not impact intact cells?**
  - Non-impact has been observed at DAF plants

- **Somewhat simple feed system that is common**
  - Could be used a preoxidant
PERMANGANATE EFFECTIVENESS

Oxidation of *Microcystis aeruginosa*

**Effective**

![Graph showing the effectiveness of permanganate treatment on cell viability and MC-LR concentration.](image)

**Cell Viability**
- Cell Viability
- MC-LR

**Effective**

![Graph showing the removal of MC-LR standard from aqueous solution.](image)

**Oxidation of MC-LR in solution**

**Fig. 11** *Microcystis aeruginosa* inactivation and resulting MC-LR concentration (left), and removal of MC-LR standard from separate aqueous solution (right) permanganate ($\text{MnO}_4^-$) treatment

Source: Ding et al. 2010
PERMANGANATE - CONSIDERATIONS

- Must consider demand
  - Reliable residual measurement
  - Potential for pink water

- Fate of manganese in treatment plant
  - Need a waste point for residuals

- Handling of dry systems can be problematic

- Liquid systems better, but more costly
**EFFECTIVENESS CAN CHANGE WITH MICROCYSTIN VARIANTS**

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Half lives ($t_{1/2}$) (minutes) based on a constant 0.5 mg/L oxidant concentration

Source: Ding et al. 2010
TOOLS FOR OPERATORS
LIMITED PRACTICAL GUIDANCE IDENTIFYING AND TREATING ALGAL TOXINS

• No simple method for detection
  • Many different toxins and variants
  • Many require LC/MS (liquid chromatography/mass spec)
  • Some by ELISA (Enzyme-linked immunosorbent assay)

• Can we use taste and odor?
  • T&O ≠ toxin
  • Toxin ≠ T&O

• Can we correlate toxin removal to T&O control?
  • PAC for MIB/geosmin also removed toxins
REQUIREMENTS FOR EFFECTIVE MANAGEMENT OF T&O (AND TOXINS?)

- Appropriate goals & implementation plans
- Suitable methods of analysis
- Assessment of potential control measures
- Implementation of effective and affordable control measures
- Collection, evaluation, and storage of appropriate monitoring data
- Dedication of sufficient resources to get the job done
DETECTION AND MONITORING

• Monitoring considerations
  • Frequency
  • Location
  • Method(s) and cost
  • Other parameters and information, e.g.,
    • Temperature, algal ID & counts, chlorophyll, lake stratification, turbidity
    • HPC, residual chlorine, Cl2:N ratio, Fe & Mn, LSI

• The importance of consumer complaints
• The importance of good record keeping
SOME PRACTICAL TOXIN INFORMATION

- **YSI sondes**
  - DO, conductivity, temp, pH, depth, chlorophyll a, phycocyanin
  - North Carolina reservoirs

- **General chlorine recommendations (WRF 3148)**
  - pH < 8
  - Residual > 0.5 mg/L after 30 min
  - Chlorine dose > 3 mg/L
  - CT on the order of 20 mg*min/L

- **General ozone recommendations (WRF 3148)**
  - pH > 7
  - Residual > 0.3 mg/L after 5 min
  - CT on the order of 1.0 mg*min/L
CONCLUSIONS
TAKE HOME MESSAGES

• Oxidation can be effective
  • No silver bullet for all toxins
  • Consider multiple barrier

• Consider oxidant and location
  • Preoxidation may help or hurt
  • Remove cells first
  • Then remove dissolved toxins

• Operation plan
  • Source
  • Taste and odor
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REFERENCES


• WRF 3148 “International Guidance Manual for the Management of Toxic Cyanobacteria”
Building a world of difference.

Together

BLACK & VEATCH

www.bv.com