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Two Better Than One: UV/Chlorine Advanced Oxidation Process

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Outline

- Challenges of Cyanobacteria Induced Contaminants
- Overview of Advanced Oxidation Process (AOP)
- UV/Chlorine AOP
- Conclusions & Next Steps

Challenges of Cyanobacteria Induced Contaminants

Challenges of Cyanobacteria Induced Contaminants
Who is the trouble maker?

Cyanobacteria

- AKA blue-green algae
- Photosynthesizing bacteria
- Not true algae
- Most release contaminants due to cell damage/natural decay

Cyanobacteria

40 µm

Challenges of Cyanobacteria Induced Contaminants
What are the contaminants?

Taste & Odor (T&O) Compounds	Cyanotoxins	Cyanotoxins on Draft CCL4
• MIB • Geosmin	• Anatoxins • Cylindrospermopsin • Microcystins • Saxitoxins	• Anatoxin-a • Cylindrospermopsin • Microcystin-LR

Challenges of Cryanobacteria Induced Contaminants

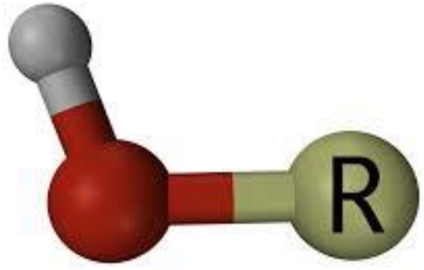
Treatment Technologies Effectiveness

Treatment Effectiveness	Conventional Treatment	Activated Carbon (GAC & PAC)	RO/NF	Ozone	UV-Mediated AOP
MIB & Geosmin	Poor	Good	Good	Good	Good
Anatoxin-a	Poor	Good	Good	Good	Good
Cylindrospermopsin	Poor	Good	Inadequate Information	Good	Good
Microcystin	Poor	Good	Good	Good	Good
Saxitoxin	Poor	Good	Inadequate Information	Poor	Inadequate Information

Overview of Advanced Oxidation Process (AOP)

Overview of AOP
What is AOP?

AOP generates hydroxyl radicals ($\cdot OH$)



- Extremely reactive
- Short lived ~ 10 µS
- Unselective

Overview of AOP
How effective are hydroxyl radicals?

Oxidizing Species	Relative Oxidation Power
Chlorine	1.00
Hypochlorous Acid	1.10
Permanganate	1.24
Hydrogen Peroxide	1.31
Ozone	1.52
Hydroxyl Radical	2.05

(Munter, 2001)

Overview of AOP

Hydroxyl radical formation can be accomplished by

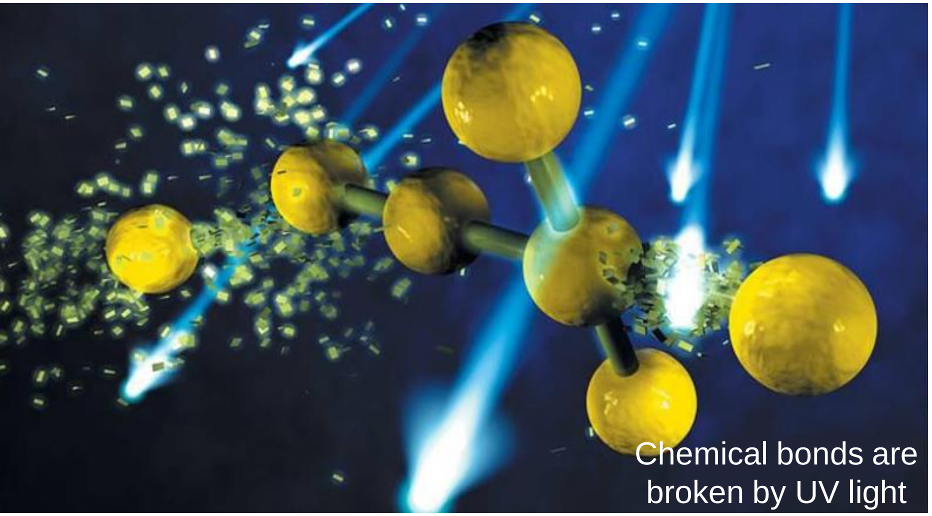
- Ozone/peroxide
- UV/peroxide
- UV/chlorine
- Ozone/UV/peroxide
- TiO2-catalyzed UV
- Fenton’s reactions

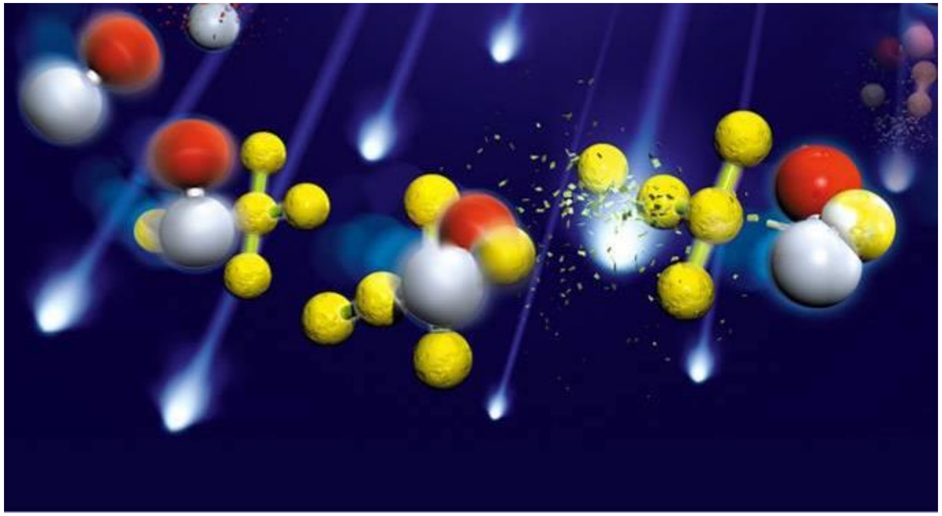
Overview of AOP
UV-mediated AOP

Destruction = **Photolysis** + **Oxidation**

Depends on contaminant characteristics

Oxidation occurs when peroxide or chlorine is added





UV/peroxide AOP has been more widely used in reuse applications.

UV/chlorine AOP is the emerging technology.

UV/Chlorine AOP

UV/Chlorine AOP

What is the process?

$HOCl + hn \longrightarrow \bullet OH + \bullet Cl$

$OCl^{-} + hn \longrightarrow \bullet Cl + \bullet O^{-}$

$\bullet O^{-} + H_2O \longrightarrow \bullet OH + OH^{-}$

$H_2O_2 + hn \longrightarrow 2\bullet OH$

HOCl/OCl- and H_2O_2 absorb UV light and produce hydroxyl radicals.

$\bullet OH + HOCl \longrightarrow H_2O + ClO\bullet$

$\bullet OH + OCl^{-} \longrightarrow ClO\bullet + OH^{-}$

$\bullet OH + H_2O_2 \longrightarrow H_2O\bullet + H_2O$

$\bullet OH + HO_2^{-} \longrightarrow \bullet O_2^{-} + H_2O$

HOCl/OCl- and H_2O_2 are also scavengers.

H_2CO_3, CO_3^{2-}, HCO_3^{-}, NOM, etc

Other •OH scavengers are also present in natural water.

UV/Chlorine AOP
Adsorption Spectra of Chlorine Species

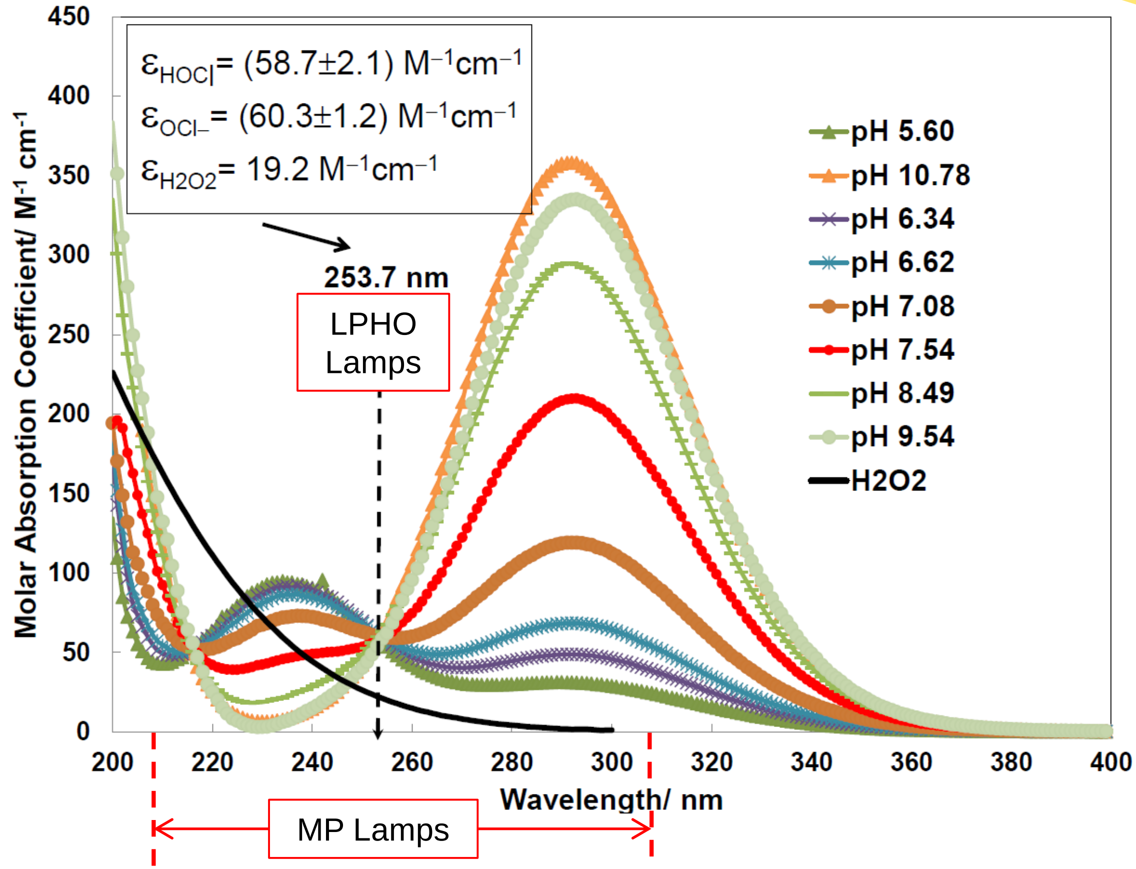
$HOCl + hn \longrightarrow \bullet OH + \bullet Cl$

$OCl^- + hn \longrightarrow \bullet Cl + \bullet O^-$

$\bullet O^- + H_2O \longrightarrow \bullet OH + OH^-$

$H_2O_2 + hn \longrightarrow 2\bullet OH$

(Royce, TrojanUV, 2015)



HOCl and OCl^- absorb over 3 times more UV photons than H_2O_2 at the same molar concentration.

UV/Chlorine AOP

UV/Chlorine vs. UV/Peroxide

$\bullet OH + HOCl$	$\longrightarrow$	$H_2O + ClO\bullet$	$k=8.46\times10^4\ M^{-1}s^{-1}$
$\bullet OH + OCl^-$	$\longrightarrow$	$ClO\bullet + OH^-$	$k=9.0\times10^9\ M^{-1}s^{-1}$
$\bullet OH + H_2O_2$	$\longrightarrow$	$H_2O\bullet + H_2O$	$k=2.7\times10^7\ M^{-1}s^{-1}$
$\bullet OH + HO_2^-$	$\longrightarrow$	$\bullet O_2^- + H_2O$	$k=7.5\times10^9\ M^{-1}s^{-1}$

Scavenging reaction constant rates: $HOCl << H_2O_2 < OCl^-$

HOCl and OCl^- absorbs over 3 times more UV photons than H_2O_2 at the same molar concentration.

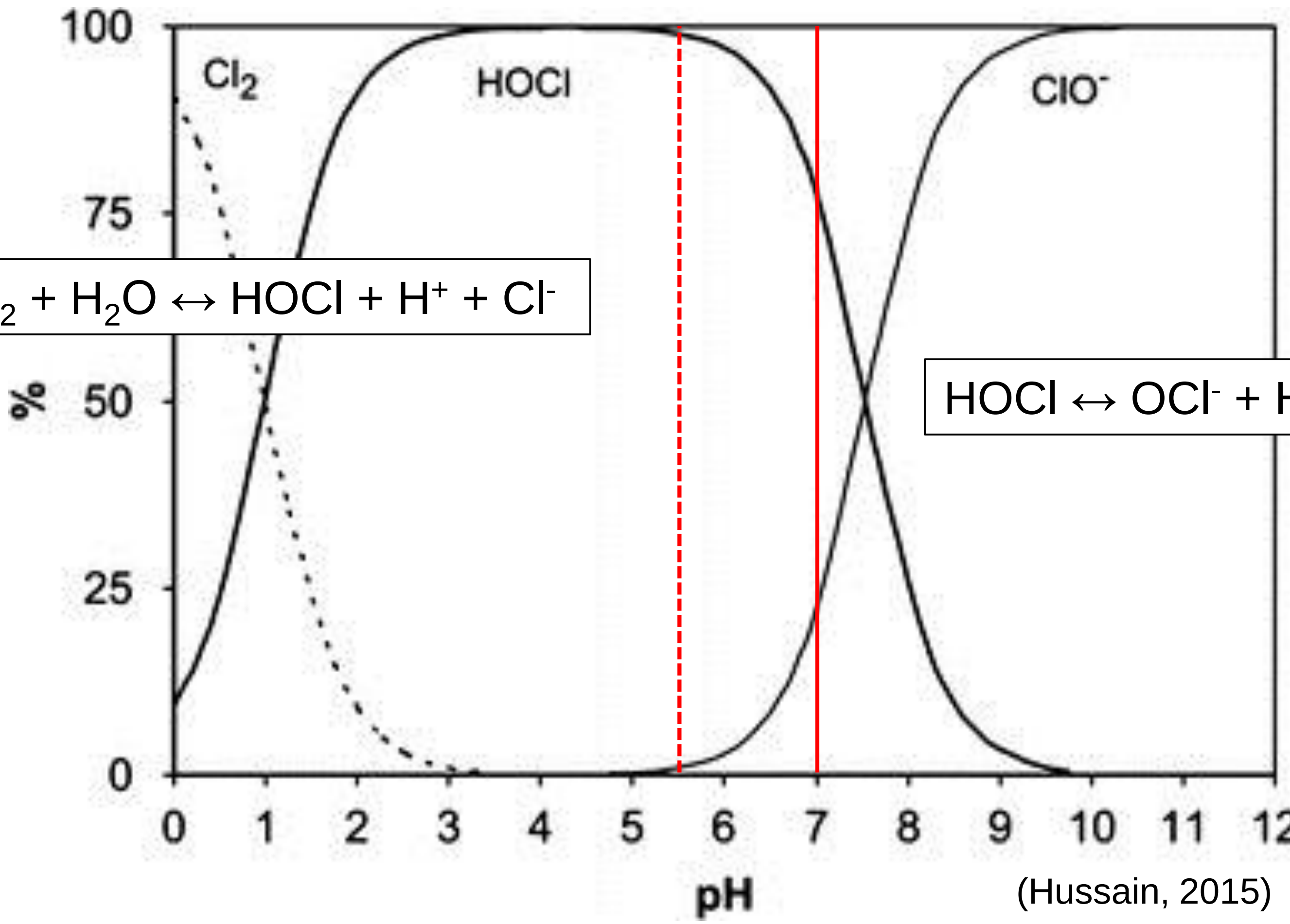
The quantum yields of •OH by the photolysis of HOCl, OCl^-, and H_2O_2 are comparable.

HOCl is a potentially promising candidate for UV-mediated AOP.

UV/Chlorine AOP
Chlorine Chemistry – pH could be an important factor

$\bullet OH + HOCl \longrightarrow H_2O + ClO\bullet$ $\quad k=8.46\times10^4\ M^{-1}s^{-1}$

$\bullet OH + OCl^- \longrightarrow ClO\bullet + OH^-$ $\quad k=9.0\times10^9\ M^{-1}s^{-1}$



$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^-$

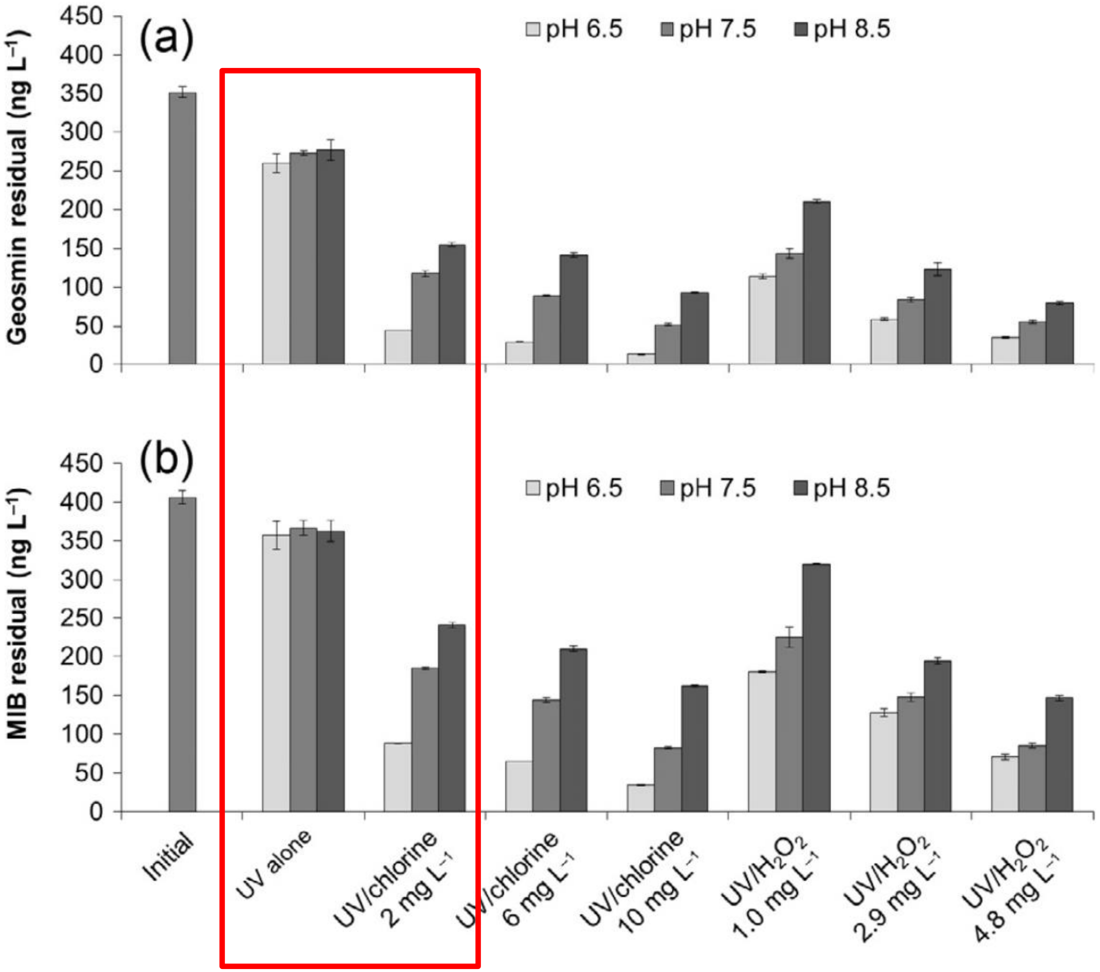
$HOCl \leftrightarrow OCl^- + H^+$

(Hussain, 2015)

UV/Chlorine AOP
To Destruct T&O Compounds

Key Parameters

- UV Dose: 2,000 mJ/cm^2
- Turbidity: 0.02 NTU
- Alkalinity: 92 mg/L
- TOC: 1.5 mg/L
- Nitrate: 1.2 mg/L



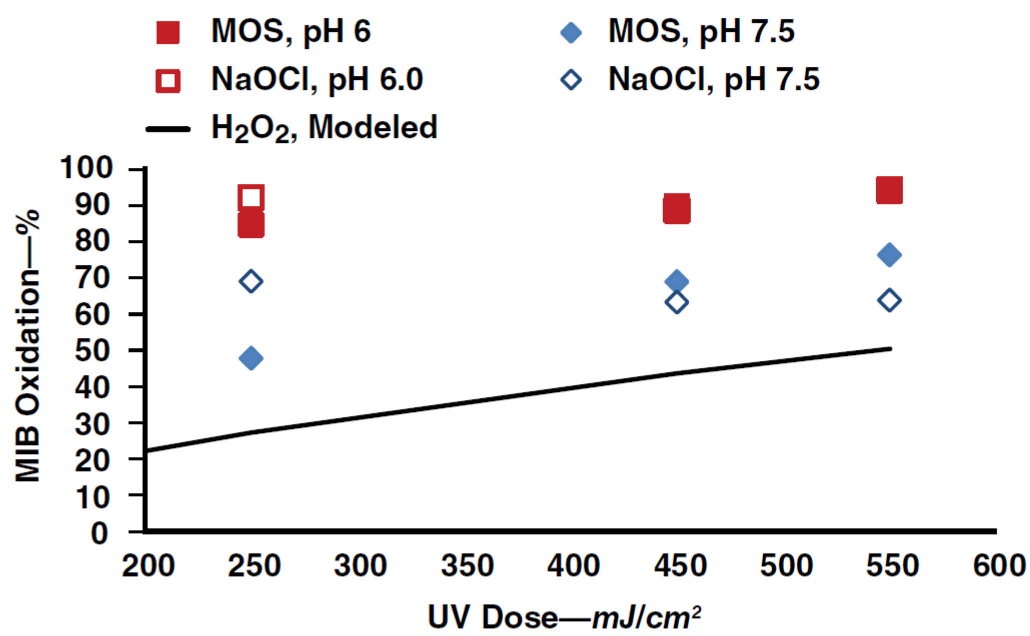
(Wang, 2015)

UV/Chlorine AOP
To Destruct T&O Compounds

Key Parameters

- Alkalinity: 40-60 mg/L
- TOC: ~ 1 mg/L
- Nitrate: <1 mg/L

FIGURE 3 Advanced oxidation process comparison—1-mg/L oxidant dose



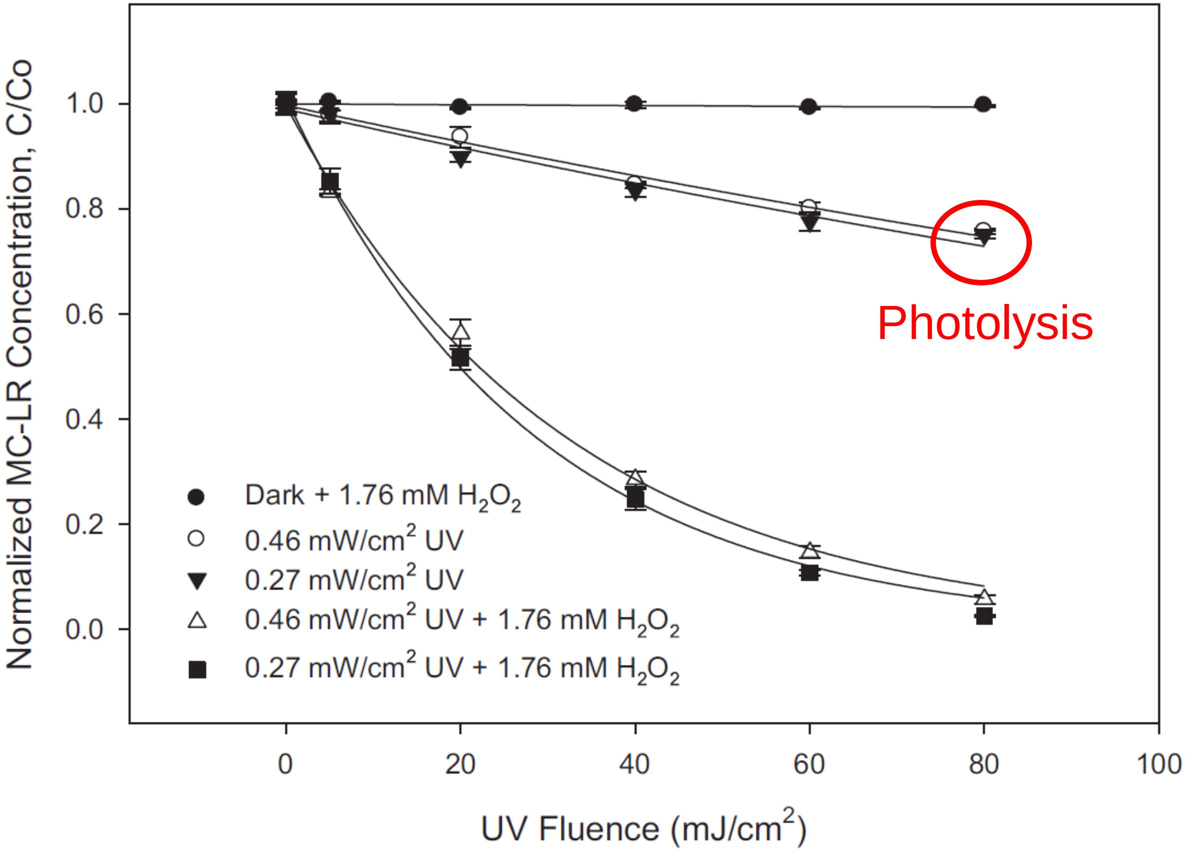
H_2O_2—hydrogen peroxide, MIB—2-Methylisoborneol, MOS—mixed oxidant solution, NaOCl—sodium hypochlorite

(Rosenfeldt, 2013)

UV/Chlorine AOP
To Destruct Cyanotoxins

Key Parameters

- Milli-Q water
- Peroxide dose: ~60 mg/L
- pH: 5.7

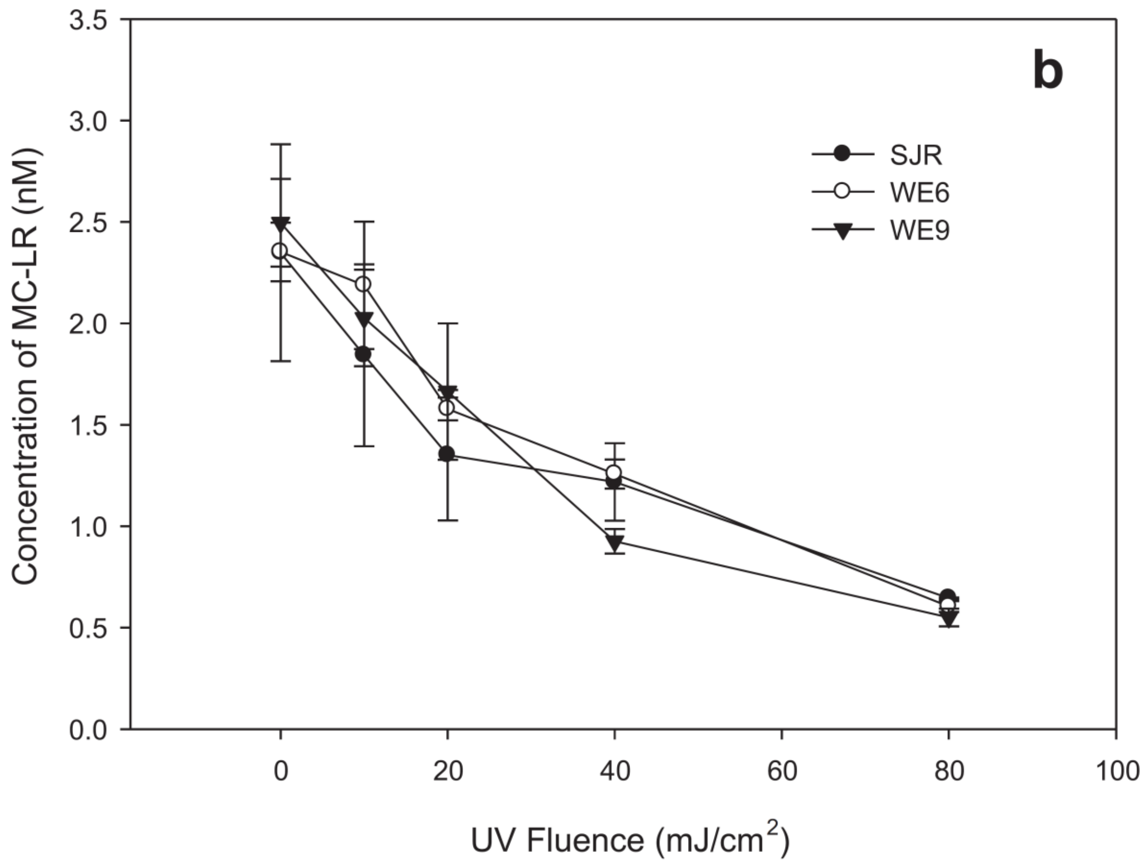


(Hiskia, 2011)

UV/Chlorine AOP
To Destruct Cyanotoxins

Key Parameters

- Natural Water
- Peroxide Dose: 30 mg/L
- pH: 7.4 (SJR); 8.5-8.6 (WE6 & WE9)
- Alkalinity: 90-120 mg/L
- Turbidity: 0.2-0.5 mg/L
- TOC: 9.5 mg/L (SJR); ~4 mg/L (WE6 & WE9)

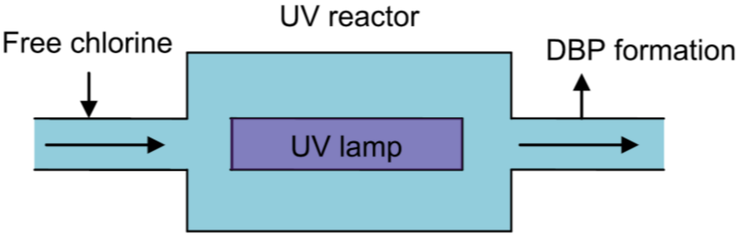


(Hiskia, 2011)

UV/Chlorine AOP
Pros & Cons

AOP Options	Pros	Cons
UV/Peroxide	• Effective oxidation	• Peroxide residual needs quenching • Peroxide requires special handling for onsite storage
UV/Chlorine	• Effective oxidation • More cost effective than UV/Peroxide	• DBP formation?

UV/Chlorine AOP
Concerns – DBP Formation



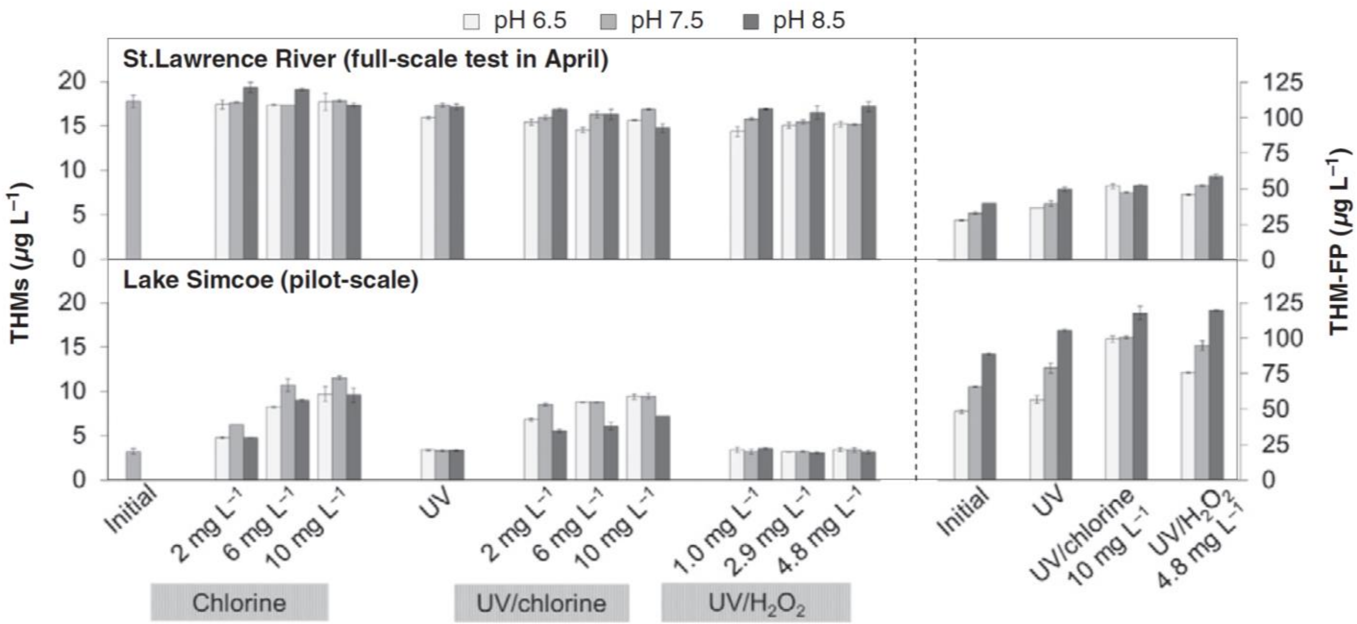
THMs & HAAs: < 14 μg/L
HANs: < 6 μg/L
AOX: < 70 μg Cl/L
Bromate: < 2 μg/L

Chlorate: 2–17% of photolyzed chlorine

UV/chlorine AOP

Chlorine: 2–10 mg/L
UV dose: 1800 mJ/cm^2
Contact time: < 1 min

(Wang, 2015)



Very little research work was done to investigate DBP formation by UV/chlorine AOP.

Conclusions & Next Steps

Take Home Messages (THMs)

UV/chlorine AOP showed great potential to remove T&O and cyanotoxins.

- Photolysis alone contributes to the destruction of T&O compounds and some cyanotoxins.
- UV/chlorine AOP effectiveness could be pH dependent and site specific.

Cyanotoxins destruction by UV/chlorine AOP has not been well studied.

Very little research work was done to investigate DBP formation by UV/chlorine AOP.

MWH project is looking for participants

Bench-scale Test → Pilot Test and/or Full-scale Test → Empirical Model

Questions?

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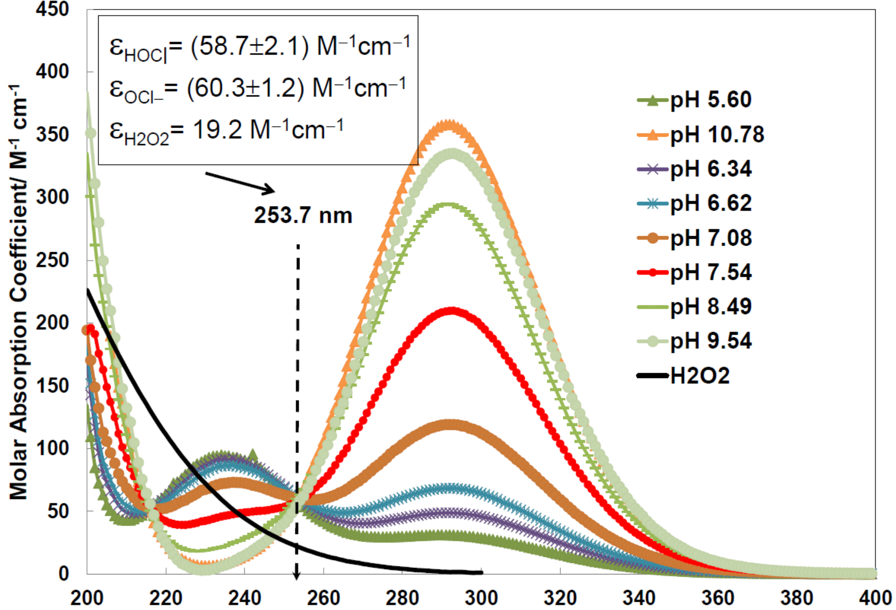

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(Royce, TrojanUV, 2015)