Cyanotoxin Removal in Drinking Water Treatment Process and Recreational Waters

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Overview Water Treatment

- Source and Recreational Waters
- Treatment to remove intracellular algal toxins
  - Conventional treatment
    - Filtration
    - Membrane technologies
- Treatment to remove extracellular algal toxins
  - Oxidation
  - Physical removal
  - Biologically active filters
- New technologies

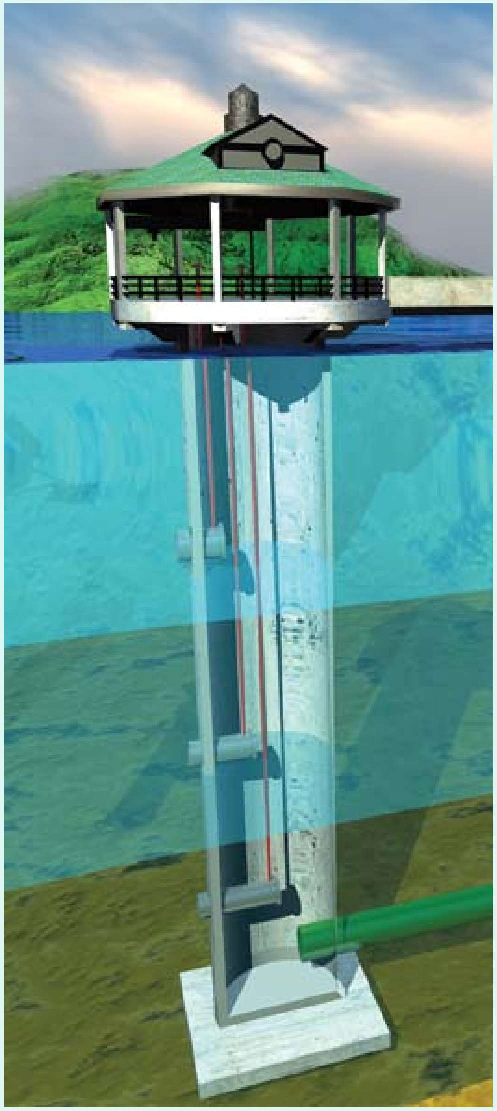
Source and Recreational Waters

Photo courtesy of John Lehman, University of Michigan

- INTRACELLULAR TOXIN (particulate toxin)
  - Flushing
  - Harvesting
  - Diversion
  - Flocculants
  - Algaecides
    - Copper based
    - Sodium carbonate peroxyhydrate

EXTRACELLULAR TOXIN
(dissolved toxin)
Awareness and get ready to treat

Intake



- INTRACELLULAR TOXIN

  Adjustable Intake

  Night vs Day

- EXTRACELLULAR TOXIN

  Oxidants

  Inline Powdered Activated Carbon (PAC)

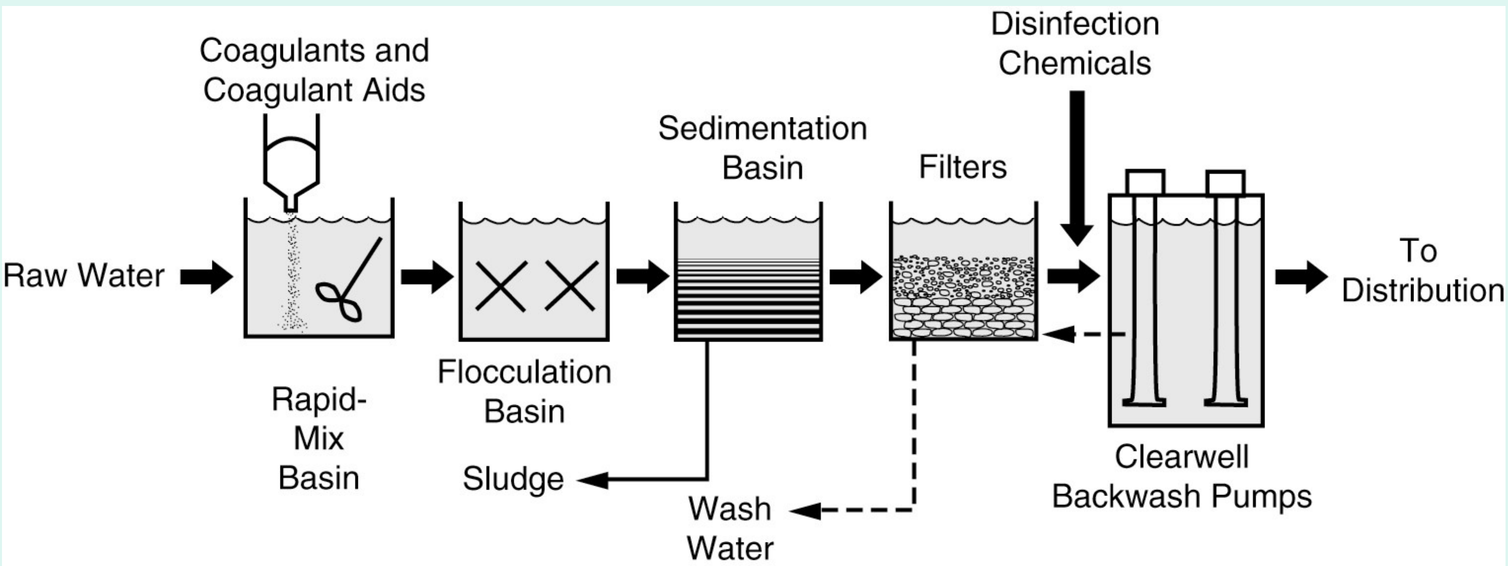
Balancing Act

A conventional treatment plant will want to keep the cells intact.

Coagulation/Sedimentation

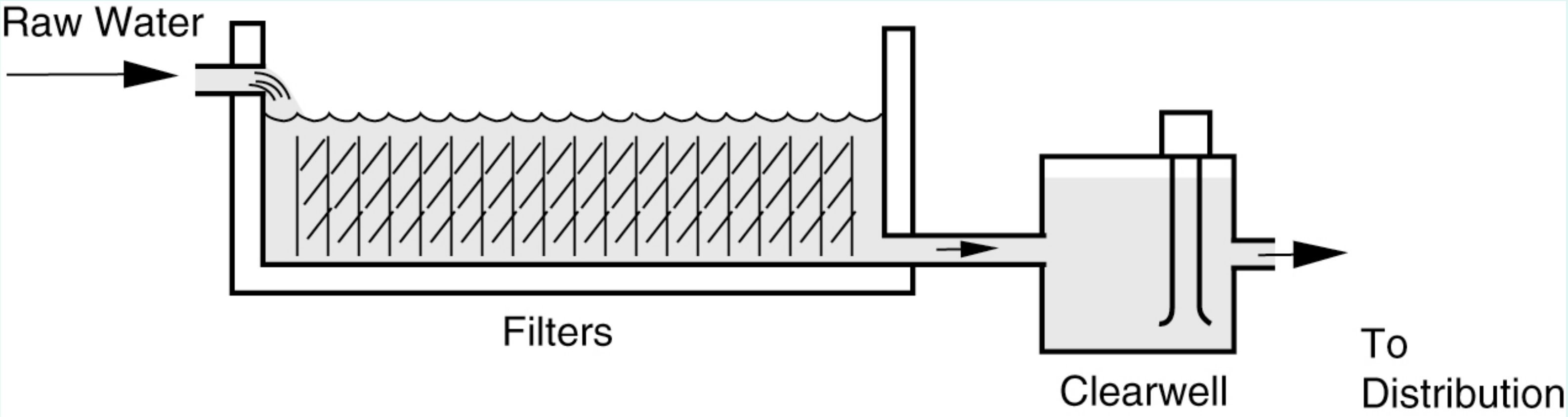
- INTRACELLULAR TOXIN
- Oxidants.
- Flocculant aides
- Settled water with less than 100 units/mL

- Monitoring Techniques to determine treatment
  - Turbidimeter
  - Streaming current detector
  - Particle Counter
  - Chlorophyll a
  - Cell counts



Filtration

- Conventional
- Biologically Active
- GAC – regenerate or biologically active
- Low Pressure Membrane
  - Micro and ultra filtration



Oxidation Treatment Processes Extracellular toxins

- Chlorine
- Ozone
- Chlorine dioxide
- Chloramines
- UV
- UV and catalyst

Chlorine CT values for reducing microcystin concentration to 1 ugL^{-1} (Acero et al 2005)

pH	$[MCLR]_0$	CT-values, $mgL^{-1}min$			
	ugl^{-1}	10^oC	15^oC	20^oC	25^oC
6	50	46.6	40.2	34.8	30.3
	10	27.4	23.6	20.5	17.8
7	50	67.7	58.4	50.6	44.0
	10	39.8	34.4	29.8	25.9
8	50	187.2	161.3	139.8	121.8
	10	110.3	94.9	82.3	71.7
9	50	617.2	526.0	458.6	399.1
	10	363.3	306.6	269.8	234.9

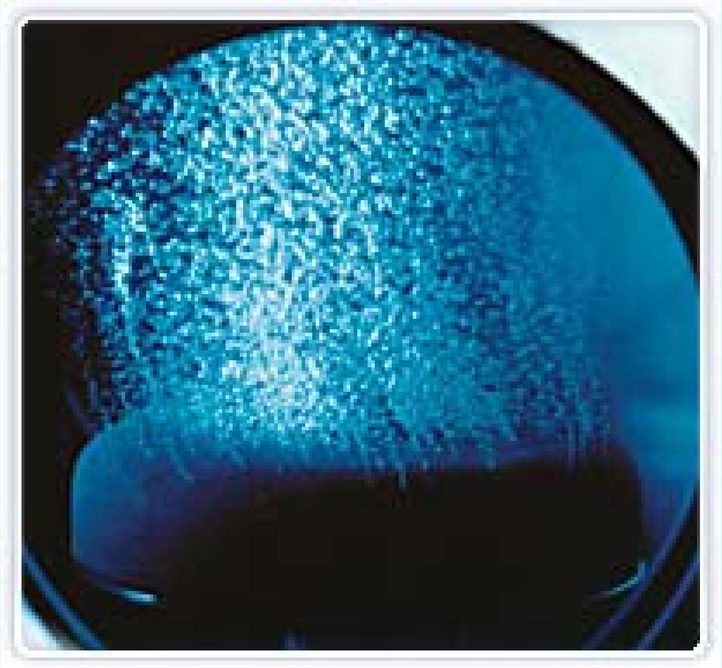
Compared to CT Values for Disinfectants to inactivate 99.9 (3-logs) of *Giardia Lamblia* cysts.

Chlorination

- Effective against nodularin similar to microcystin.
- Not effective at inactivating anatoxin-a.
  - Carlile 1994
- Cylindrospermopsin –a free chlorine residual of 0.5 mg/L at pH above 6.
  - Senogles et al 2000
- Saxitoxins– a free chlorine residual of 0.5 mg/L and more effective at high pHs.

Ozonation

- Microcystins and anatoxin-a
  - Residual must be maintained for several minutes
  - Moderate temperatures (16-22^{o}C)
- Saxitoxins --- Not very effective
- Cylindrospermopsin -- yes



Other oxidants and disinfectants

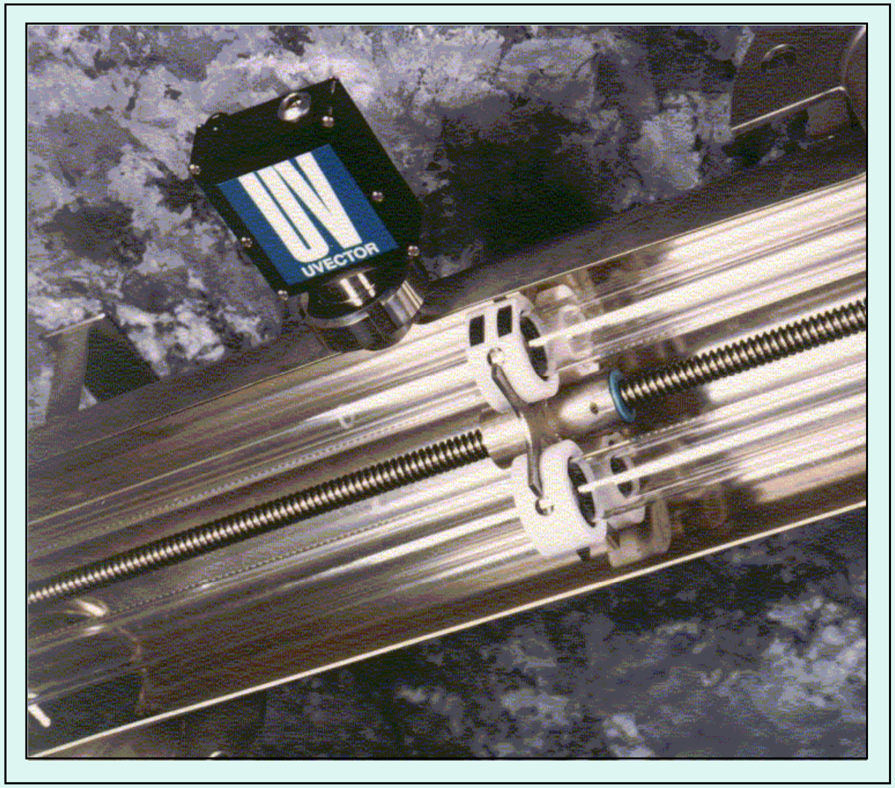
- Chloramines – Not effective
- Chlorine dioxide – Not effective (Kull et al. 2004)
- Hydrogen peroxide – Not effective
- $KMnO_4$ – Appears to be effective against microcystin

Byproduct formation

- Chlorination
  - Microcystins – not a problem
  - Saxitoxin – no acute toxicity
  - Cylindrospermopsin – liver damage and genotoxicity (Shaw et al 2001 and Senogles-Derham et al 2003)
- Ozonation
  - Microcystin – not a problem

UV Treatment

- UV inactivation dose is about 40 mJ/cm^2 – inactivation of *Crytosporidium parvum*.
- Photolytic destruction dose for microcystin, cylindrospermospin, anatoxin-a and saxitoxin is 1530 to 20,000 mJ/cm^2.



Advanced oxidation process

- Hydrogen peroxide and ozone (ratio of 0.5)
  - 1 mg/L MCYLR was completely removed in 30 minutes
- Hydrogen peroxide and UV light

- Titanium dioxide and UV light
  - MCYLR – varying degrees of success
  - Cylindrospermopsin – 2,000 mJ/cm^2 1 log decrease,
  - significantly better at high (9) pHs (Senogles et al 2001)
  - DOC and cyanobacterial pigments reduces the efficiency

High Pressure Membrane Filtration

- Nanofiltration and Reverse Osmosis Filtration

A summary of intact algal cell removal performance

Treatment	Intact Cell Removal
Coagulation/sedimentation or dissolve air flotation /rapid sand filtration	> 99.5% auxiliary
Lime precipitation/sedimentation/ rapid sand filtration	> 99.5 % ancillary
Microfiltration/Ultrafiltration	> 75% (becoming auxiliary)

Summary of cyanotoxin physical removal by treatment

	Microcystin	Anatoxin-a	Cylindrospermopsin	Saxitoxin
Microfiltration /Ultrafiltration	No	No	No	No
PAC	Yes	Yes	Yes	Yes
GAC	Yes	Yes	Yes	Yes
Ultrafiltration	*	*	*	*
Nanofiltration/ RO	Yes	Has not been investigated.	Yes	Has not been investigated.

Summary of cyanotoxin inactivation by oxidants

	Microcystin	Anatoxin-a	Cylindrospermopsin	Saxitoxin
Chlorine	Yes	No	Yes	Yes
Ozone	Yes	Yes	Yes	No
Chloramine	No	No	No	Has not been investigated.
Chlorine dioxide	No	No	No	Has not been investigated.
Hydroxyl radical	Yes	Yes	Yes	Has not been investigated.
Potassium permanganate	Yes	Yes	No	No

Questions?