Water Treatment Methods for Control and Management of Algae

Everett J. Nichols, Ph.D., MSPH
Scientific Director of Biopolymer Research
Presentation Overview

1. Algae & Cyanobacteria Classification
2. Nutrient Requirements and Assimilation
3. Algae Control Measures
4. Flocculation with the Biopolymer Chitosan
5. Phosphates
6. Phosphate Control Measures
7. Summary
Algae & Cyanobacteria Waterblooms

Green, red or brown colored water resulting from high density growth of algae or cyanobacteria

- Marine Water
  Red & brown tide coastal water & estuaries worldwide. Chesapeake Bay, North Carolina, Gulf of Mexico, Washington & Oregon Coast (red & green tides)

- Freshwater
  lakes, reservoirs, ponds (green scum) common indicator of eutrophication swimming pools, fountains, etc.
Algae & Cyanobacteria

Algae

Kingdom – Protista

- Eukaryotic (cell structure similar to multicellular plants and animals – contain cell nucleus, cytoplasmic organelles such as mitochondria, chloroplasts)
- Complex tissue development or multicellular reproductive structures lacking
- Oxygenic photosynthesis – chlorophyll a
- Incapable of fixing nitrogen
- Some toxin producing (marine dinoflagellates) – neurotoxins and hepatotoxins
Algae & Cyanobacteria

Cyanobacteria
Kingdom – Monera

- prokaryotic (no cell nucleus or cytoplasmic organelles such as mitochondria, chloroplasts)
- Simple single cell structure (rods, cocci, spirals and nonbranching filaments)
- Oxygenic photosynthesis – chlorophyll a
- Accessory pigments – phycobiliproteins
- Capable of fixing atmospheric nitrogen
- Some toxin producing (similar to marine algae dinoflagellate toxins)
  - Gelatinous toxin released upon killing by chlorination or copper sulfate
## Major Algae Groups

<table>
<thead>
<tr>
<th>Common Name</th>
<th># Species</th>
<th>Common Habitat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green Algae</td>
<td>~7,000</td>
<td>Fresh water, salt water, damp soil</td>
</tr>
<tr>
<td>Yellow Green Algae</td>
<td>~600</td>
<td>Freshwater, salt water</td>
</tr>
<tr>
<td>Red Algae</td>
<td>~4,000</td>
<td>Saltwater, some freshwater</td>
</tr>
<tr>
<td>Brown Algae</td>
<td>~1,500</td>
<td>Saltwater, seaweeds, kelp</td>
</tr>
<tr>
<td>Golden Brown Algae (Diatoms)</td>
<td>~6,000</td>
<td>Freshwater, saltwater, soil</td>
</tr>
<tr>
<td>Dinoflagellates</td>
<td>~2,000</td>
<td>Saltwater, freshwater (red tides, fish kill)</td>
</tr>
<tr>
<td>Euglenoids</td>
<td>~6,000</td>
<td>Freshwater</td>
</tr>
</tbody>
</table>
Major Cyanobacterial Groups

<table>
<thead>
<tr>
<th>Order</th>
<th># Genera</th>
<th>Heterocysts</th>
<th>General Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chroococcales</td>
<td>5</td>
<td>_</td>
<td>Unicellular, rods/cocci, nonfilamentous aggregates</td>
</tr>
<tr>
<td>Pleurocapsales</td>
<td>3</td>
<td>_</td>
<td>Unicellular, rods/cocci, nonfilamentous aggregates</td>
</tr>
<tr>
<td>Oscillatoriales</td>
<td>4</td>
<td>_</td>
<td>Filamentous, unbranched trichomes containing vegetative cells</td>
</tr>
<tr>
<td>Nostocales</td>
<td>6</td>
<td>+</td>
<td>Filamentous, unbranched trichomes may contain specialized cells</td>
</tr>
<tr>
<td>Stigonematales</td>
<td>3</td>
<td>+</td>
<td>Filamentous trichomes with either branches or more than one row of cells</td>
</tr>
</tbody>
</table>

Algae & Cyanobacteria

Photosynthetic

\[ \text{light} \quad \text{CO}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O}) + \text{O}_2 \]

Cyanobacteria

Fix Nitrogen

\[ \text{Nitrogenase} \quad \text{N}_2 + 8\ e^- + 16\ \text{ATP} + 8\ \text{H}^+ \rightarrow 2\ \text{NH}_3 + \text{H}_2 + 16\ \text{ADP} + 16\ \text{P}_i \]
Nutrient Requirements of Algae & Cyanobacteria

Elements for Growth

- Carbon, hydrogen, nitrogen, oxygen, phosphorus, sulfur, calcium, potassium, magnesium, manganese, molybdenum, copper, iron, zinc, silicon, sodium, boron
Nitrogen, Phosphorus and Sulfur

1. Need to incorporate large quantities
   • Acquired from same source of carbon nutrients
   • Inorganic sources

2. Nitrogen
   • Synthesis of amino acids, purines, pyrimidines, enzyme cofactors
   • Nitrate reduction to ammonia and assimilation via glutamate dehydrogenase, glutamate synthase etc.
   • Cyanobacteria reduce atmospheric N$_2$ and assimilate via nitrogenase system

3. Sulfur
   • Synthesis of sulfhydryl-containing amino acids, enzyme cofactors

4. Phosphorus
   • Energy transfer (ATP), DNA, RNA (protein synthesis), membrane lipids
Phosphorus – Primary Growth Limiting Nutrient

- Published studies strongly support phosphate as the growth limiting nutrient for algae & cyanobacteria growth

Phosphorus

- **Inorganic forms**
  - Igneous rocks (calcium phosphates)
  - Phosphate salts and esters of phosphoric acids

- **Organic forms**
  - Contain 1-3 organic groups in ester linkage to oxygen
  - ATP, DNA, RNA, phospholipids, inositol phosphates, all formed by biological processes from orthophosphates
Examples of Inorganic Phosphates

Orthophosphate

Linear polyphosphate

Pyrophosphate

Cyclic trimetaphosphates

Cyclic tetrametaphosphate
Examples of Organic Phosphates

Adenosine triphosphate (ATP)

Glucose 1,6-diphosphate

Phosphatidyl chlorine

Creatine phosphate
Control Measures for Algae & Cyanobacteria

1. Chemical Disinfection
   - Halogens (chlorine, bromine)
   - Ionic silver chelates
   - Copper sulfate
   - Quaternary ammonium compounds

2. Ultraviolet Light

3. Ozone

4. Ultrasound

5. Aeration (dissolved oxygen)

6. Nutrient Control
   - Bioremediation
   - Nutrient Stripping
Nutrient Stripping

Reduce Phosphates (growth limiting nutrient)

- Flocculation & filtration of organic phosphates
- Precipitation & filtration of inorganic phosphates
Orthophosphate \( P_i \) is assimilated by algae & cyanobacteria

Organic phosphate is a source for orthophosphate

Enzymatic hydrolysis
Removal of Organic Phosphates by Flocculation & Filtration

Chitosan-induced flocculation

Filtration

HALOsource
Removal of Inorganic Phosphate (Orthophosphate) by Precipitation & Filtration

\[
\text{La}^{+3} + \text{Pi} \rightarrow \text{La} \cdot \text{Pi} \\
\text{Filtration Removal}
\]
Natural Flocculant Biopolymer
Chitosan

- Derived from chitin (structural polysaccharide of exoskeletons of crustaceans, insects, fungi)
- Structurally related to cellulose
- Cationic polysaccharide
- Biodegradable
- Binds to anionic suspended solids in water
Structural Comparison of Chitosan

(a) CHITIN

(b) CHITOSAN

(c) CELLULOSE

Molecular structures of Chitin (a), chitosan (b) and cellulose (c)
Chitin/Chitosan Structure

Figure 1  Molecular structures of (a) chitin and (b) chitosan.

<table>
<thead>
<tr>
<th></th>
<th>CHITIN</th>
<th>CHITOSAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>n'</td>
<td>10 %</td>
<td>60-85%</td>
</tr>
<tr>
<td>n</td>
<td>90%</td>
<td>40-50%</td>
</tr>
</tbody>
</table>
N-Halochitosan - a patent protected derivative of chitosan flocs non-polar organics such as oils

*N-Halochitosan is formed in the presence of halogens such as chlorine (hypochlorite and hypochlorous acid)*

![Diagram of molecular structures of Chitosan and N-Halochitosan]

*Figure 5 – Molecular Structure of N-Halochitosan*
Colloid suspensions: surface charges cause mutual repulsion
Chitosan (cationic polymer): charge neutralization reduces repulsion and suspension becomes unstable to form flocs.
Sand bed filters can trap stable, firm floccules, and remove flocced sediment or colloidal insoluble organic phosphates from the flow of water.
Backwash flushes trapped floccules into sanitary sewer system
Chitosan-Mediated Flocculation of Sediment

- Suspended sediment-untreated
- Seconds following addition of chitosan
- Suspended sediment-untreated
- Minutes following addition of chitosan
Treatment of Fish Waste with Chitosan and Lanthanum Chloride

E1 (supernatant of diluted fish waste) Total phosphorus-572 ppm

E2 (E1 was treated w/ chitosan, allowed to settle and supernatant tested) Total phosphorus-142 ppm

E3 (E2 was further treated w/lanthanum chloride and supernatant tested) Total phosphorus-2 ppm
Flocculation & Filtration of Organic Phospholipid w/Chitosan

untreated  Chitosan treated  Untreated-sand filtered  Chitosan treated & sand filtered

CF-total Phosphorus-33 ppm

CF-total Phosphorus-6.0 ppm
Flocculation & Filtration of Green Algae w/Chitosan

- Algae non-treated
- Algae chitosan-treated
- Algae non-treated & sand filtered
- Algae chitosan-treated & sand filtered
Chemical Treatment Options for Orthophosphate Removal

**Alum - Al₂(SO₄)₃** – most common

\[
\text{Al}_2(\text{SO}_4)_3 + 6 \ \text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + \text{H}_2\text{SO}_4 \\
\text{HCO}_3^- + \ \text{H}^+ \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{Al}_2(\text{SO}_4)_3 + 3 \ \text{Ca(HCO}_3)_2 \rightarrow 2\text{Al(OH)}_3 + 3\text{CaSO}_4 + 6 \ \text{CO}_2
\]

**Ferric Sulfate - Fe₂(SO₄)₃** – similar chemistry to alum

\[
\text{Fe}_2(\text{SO}_4)_3 + 3\text{Ca(HCO}_3)_2 \rightarrow 2\text{Fe(OH)}_3 + 3 \ \text{CaSO}_4 + 6 \ \text{CO}_2
\]
Removal of orthophosphate with alum and ferric sulfate is a sorption process.

Al(OH)₃ sorbs orthophosphates \[ \rightarrow \] Al(OH)₃ • H₂PO₄

**Advantages**
- Low cost

**Disadvantages**
- Reduction of alkalinity (acid neutralization of HCO₃⁻)
- Gelatinous precipitates
- Large quantities required to reduce PO₄³⁻ to low levels
- Toxicity concerns have been raised (Al³⁺)
- Potential for staining (iron)
- Increased CO₂ – photosynthesis & algae growth
Lanthanides (trivalent rare earth metals)

1. Anion Substitution/Ion Exchange
   \textit{Lanthanum carbonate}

2. Direct Precipitation
   \textit{Lanthanum chloride}
Anion Substitution - exchange of carbonate for phosphate
Lanthanum carbonate $\text{La}_2(\text{CO}_3)_3$ (insoluble)

$$\text{La}_2(\text{CO}_3)_3 + 2\ PO_4^{-3} \underset{\text{Slow}}{\longrightarrow} 2\ \text{LaPO}_4^{-3} + 3\ \text{CO}_3^{-2}$$

$$\text{CO}_3^{-2} + \text{H}_2\text{O} \longrightarrow \text{HCO}_3^{-3} + \text{OH}^{-}$$

$$\text{Ca}^{+3} + \text{CO}_3^{-2} \longrightarrow \text{CaCO}_3$$

Direct Precipitation of Orthophosphate
Lanthanum chloride $\text{LaCl}_3$ (soluble)

$$\text{La}^{+3} + 3\ \text{Cl}^{-} + \text{PO}_4^{-3} \underset{\text{VeryFast}}{\longrightarrow} \text{La PO}_4 + 3\ \text{Cl}^{-}$$
Advantages of LaCl$_3$ Compared to La$_2$(CO$_3$)$_3$

- Faster reaction kinetics
- Soluble reactant vs insoluble reactant
- No contributions of carbonate & potential CO$_2$
- Low potential for formation of scale
- Low potential for decreased hardness
Summary

- Algae and Cyanobacteria both contribute to water blooms.
- Cyanobacteria capable of fixing atmospheric nitrogen.
- Phosphorus is the key growth limiting nutrient.
- Important to remove both organic and inorganic forms of phosphate.
- Phosphorus removal accomplished by chitosan-mediated flocculation of organic phosphate and direct precipitation of orthophosphate by lanthanum chloride followed by filtration.
Acknowledgements

James Scott
Frank Kneib
Questions

For Additional Information

HaloSource Booth (SeaKlear)
- Frank Kneib
- Nick Scappini
- Everett Nichols