Water Treatment Methods for Control and Management of Algae

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Clean Water & Antimicrobial Solutions

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

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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.

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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*

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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*

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Major Algae Groups

Common Name	# Species	Common Habitat
Green Algae	~7,000	Fresh water, salt water, damp soil
Yellow Green Algae	~600	Freshwater, salt water
Red Algae	~4,000	Saltwater, some freshwater
Brown Algae	~1,500	Saltwater, seaweeds, kelp
Golden Brown Algae (Diatoms)	~6,000	Freshwater, saltwater, soil
Dinoflagellates	~2,000	Saltwater, freshwater (red tides,fish kill)
Euglenoids	~6,000	Freshwater

Major Cyanobacterial Groups

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

From: Prescott, L.M., Harley, J.P., Klein, D.A. Microbiology, *Third Edition*, Wm. C. Brown Publishers, Dubuque, IA. 1996.

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Algae & Cyanobacteria

Photosynthetic

$$CO_2 + H_2O \xrightarrow{\textit{light}} (CH_2O) + O_2$$

Cyanobacteria

Fix Nitrogen

$$N_2 + 8\,e^- + 16\,ATP + 8\,H^+ \xrightarrow{\textit{Nitrogenase}} 2\,NH_3 + H_2 + 16\,ADP + 16\,P_i$$

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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

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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

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Phosphorus – Primary Growth Limiting Nutrient

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

- Schindler, D.W. *et al. (2008)* Eutrophication of lakes cannot be controlled by reducing nitrogen input: Results of a 37-year whole-ecosystem experiment. PNAS 105 (32): 11254-11258.

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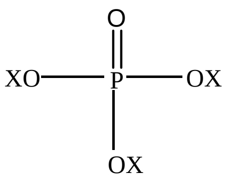
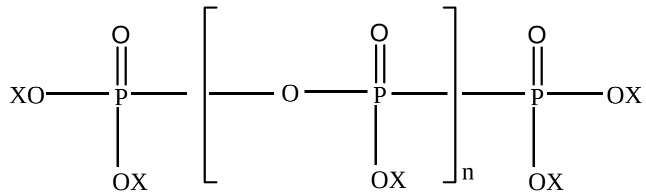
Phosphorus

- 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

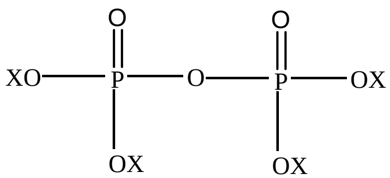
Examples of Inorganic Phosphates



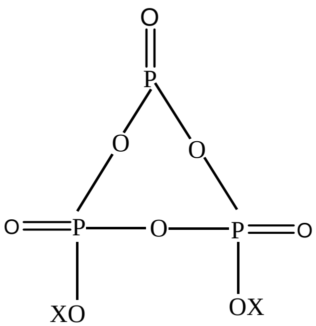
Orthophosphate



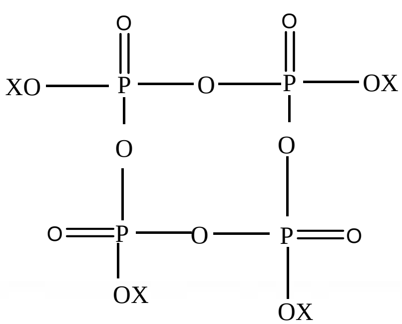
Linear polyphosphate



Pyrophosphate

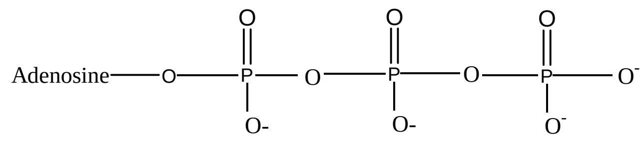


Cyclic trimetaphosphates

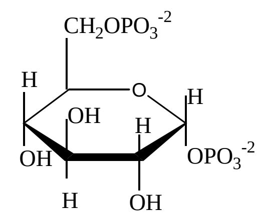


Cyclic tetrametaphosphate

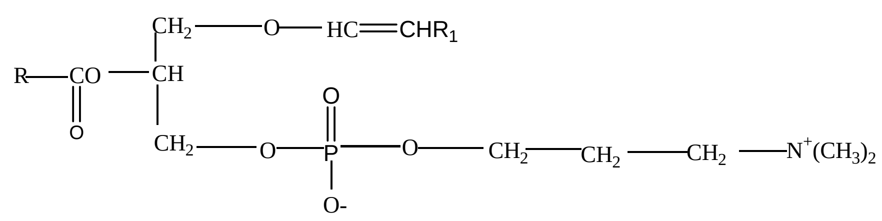
Examples of Organic Phosphates



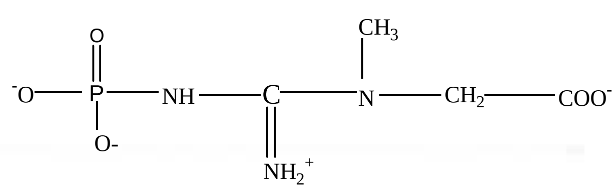
Adenosine triphosphate (ATP)



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

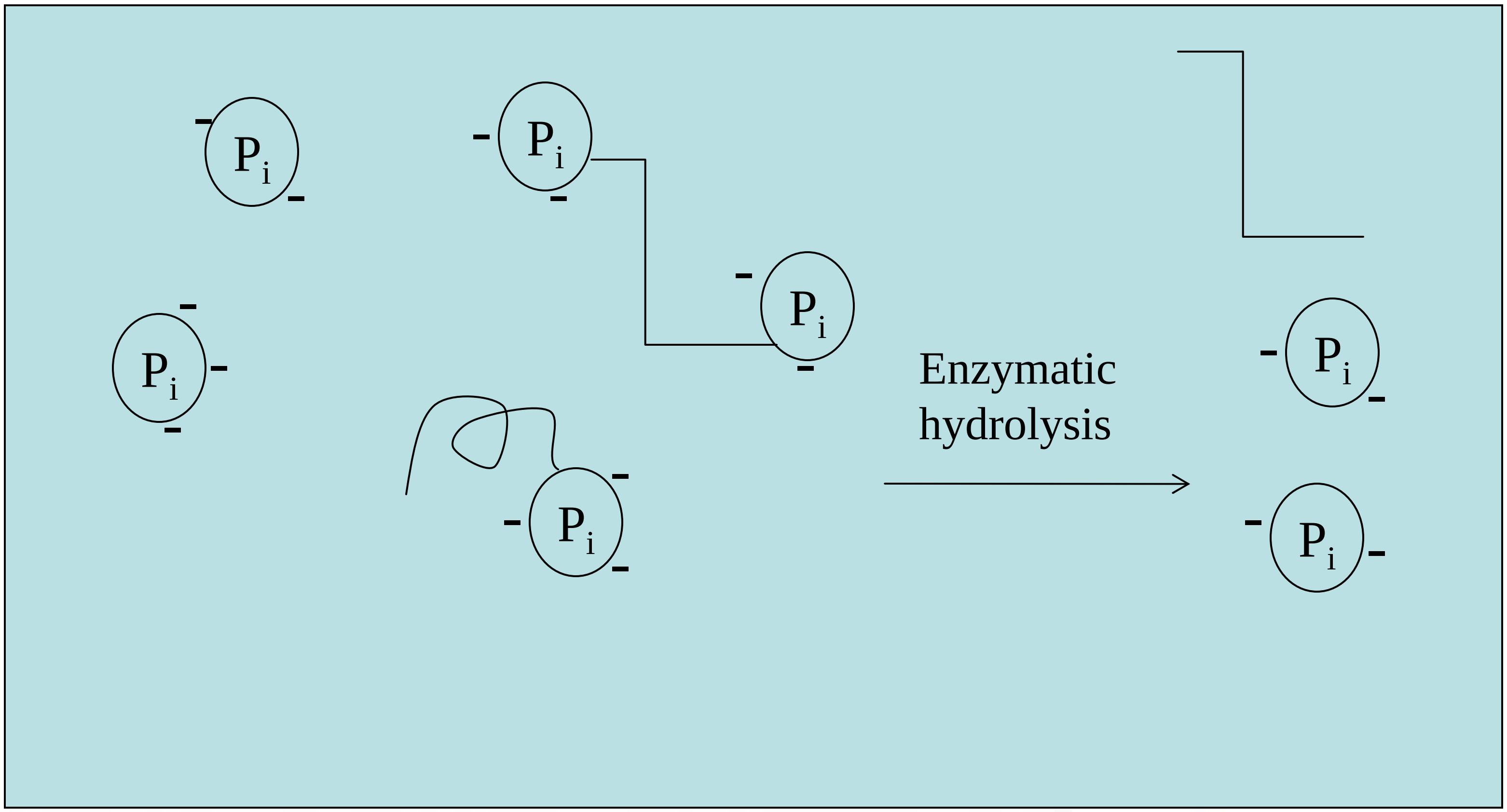
Nutrient Stripping

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 P_i – P_i is a source for orthophosphate



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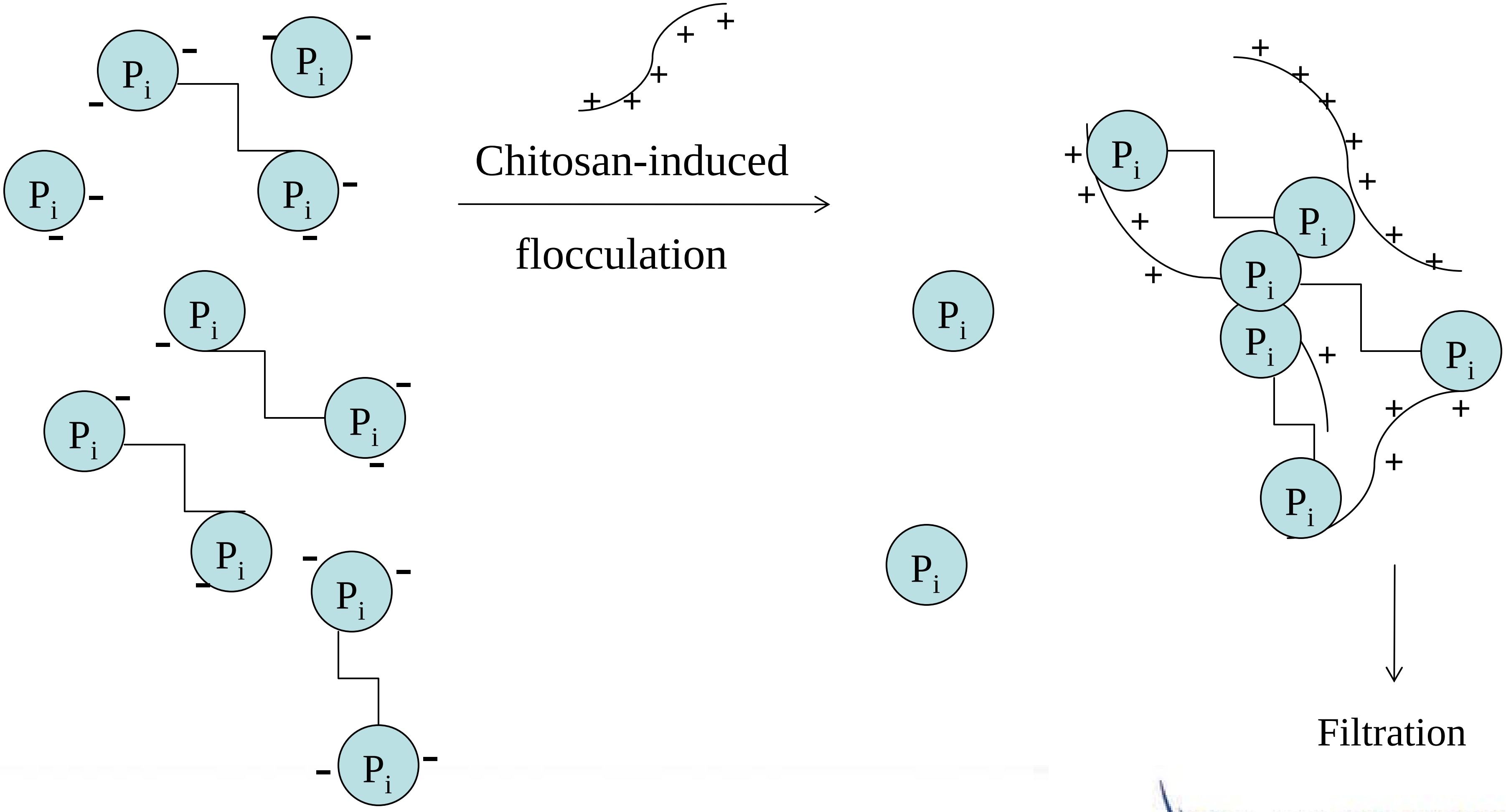
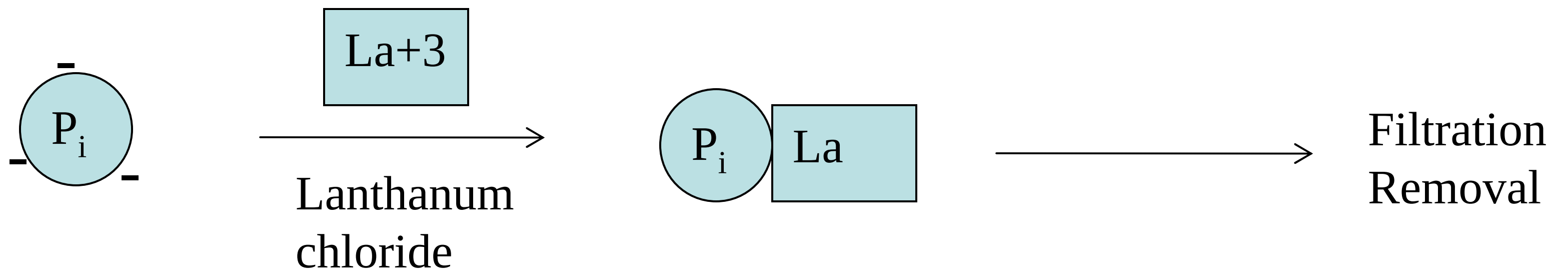
Removal of Organic Phosphates by Flocculation & Filtration



Removal of Inorganic Phosphate (Orthophosphate) by Precipitation & Filtration



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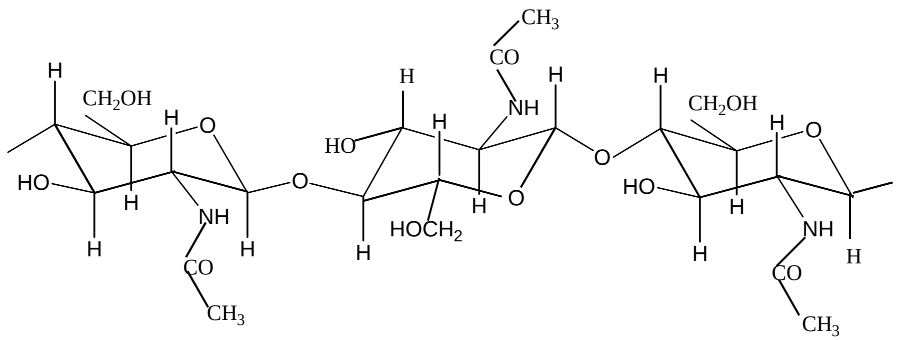
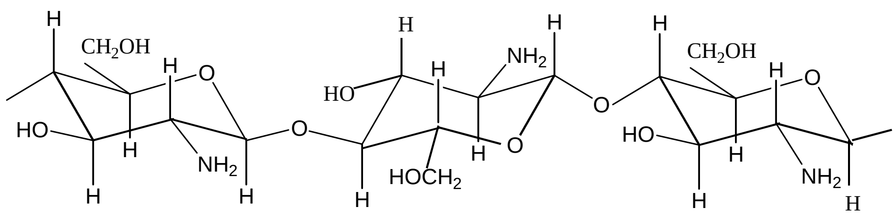
Natural Flocculant Biopolymer Chitosan

- 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

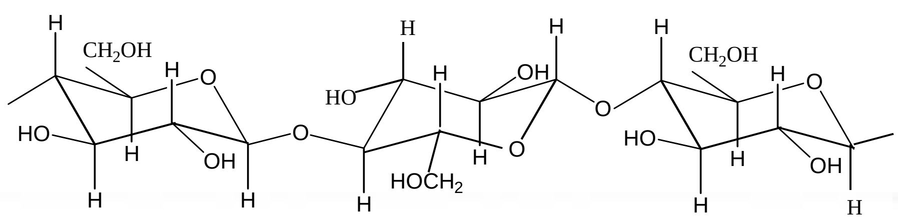
Structural Comparison of Chitosan



(a) CHITIN



(b) CHITOSAN



(C) CELLULOSE

Melecular structures of Chitin (a), chitosan (b) and cellulose (c)

Chitin/Chitosan Structure

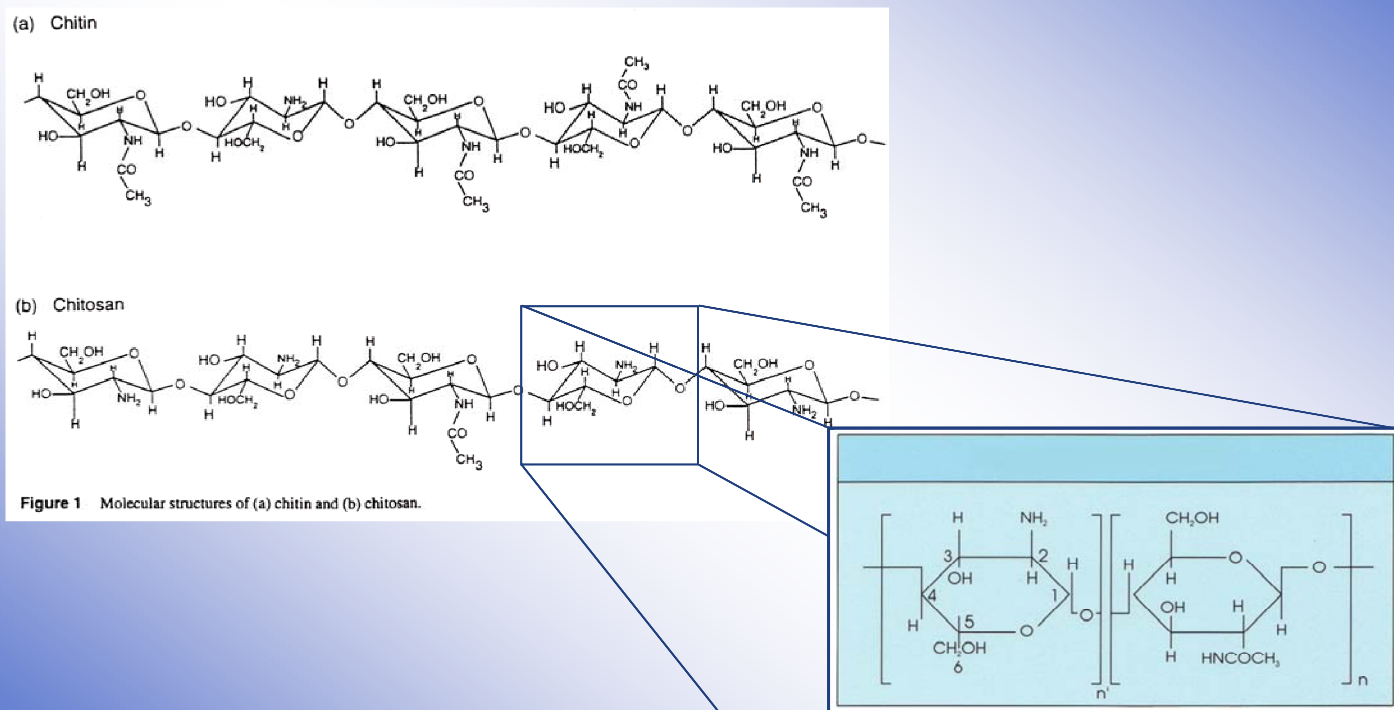


Figure 1 Molecular structures of (a) chitin and (b) chitosan.

	n'	n
CHITIN	10 %	90%
CHITOSAN	60-95%	40-5%

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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)

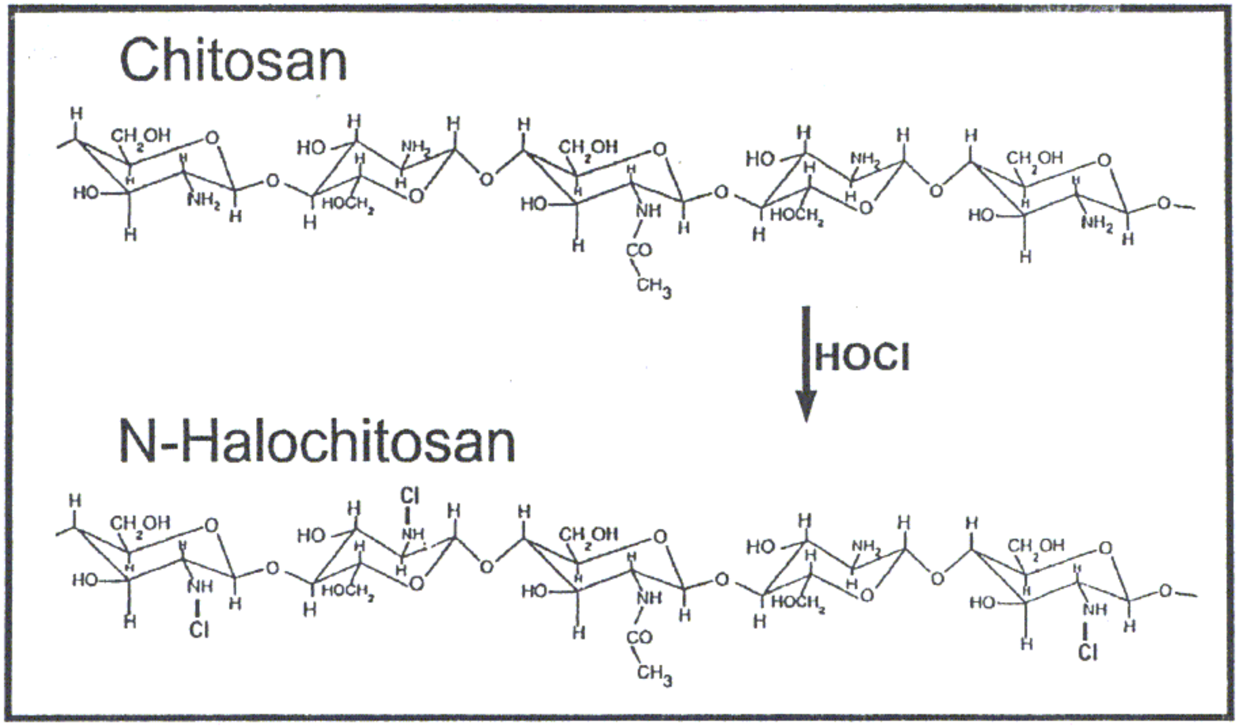
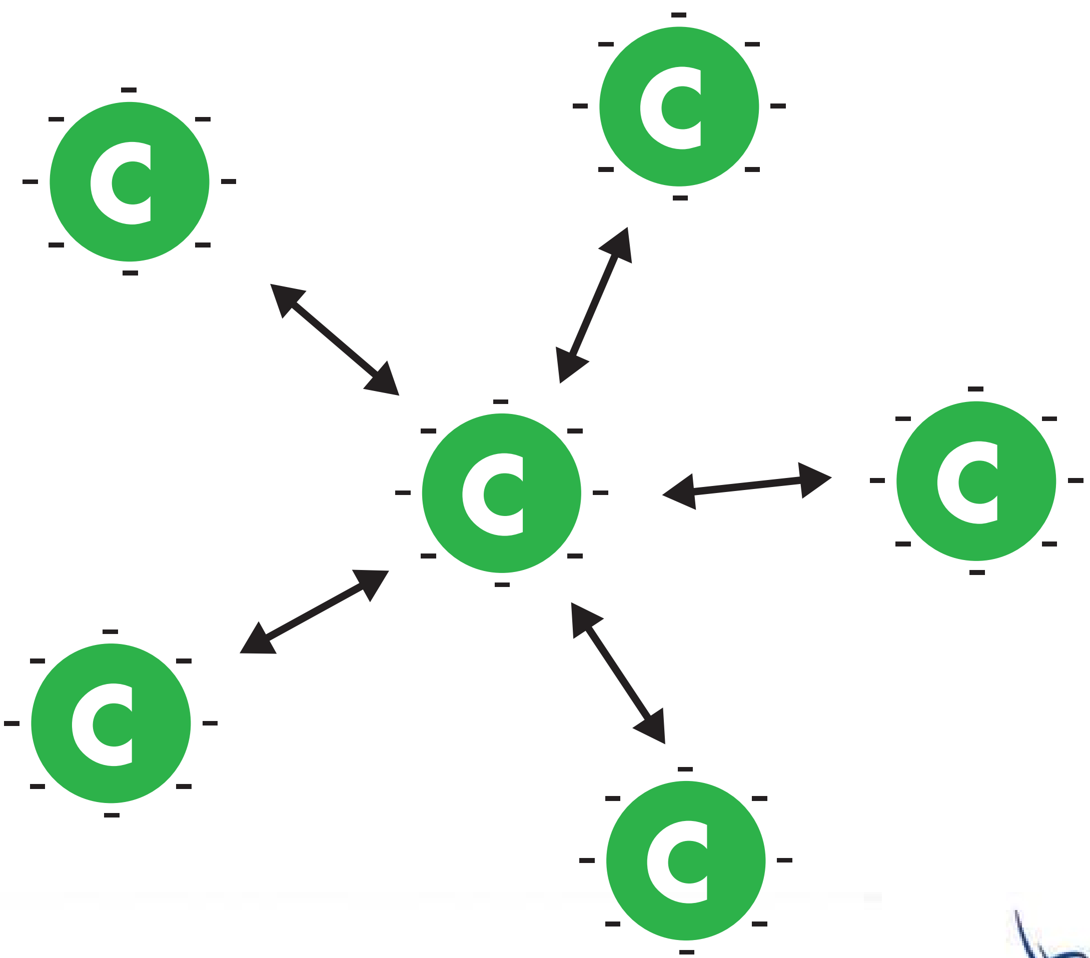


Figure 5 – Molecular Structure of N–Halochitosan

Colloid suspensions: surface charges cause mutual repulsion



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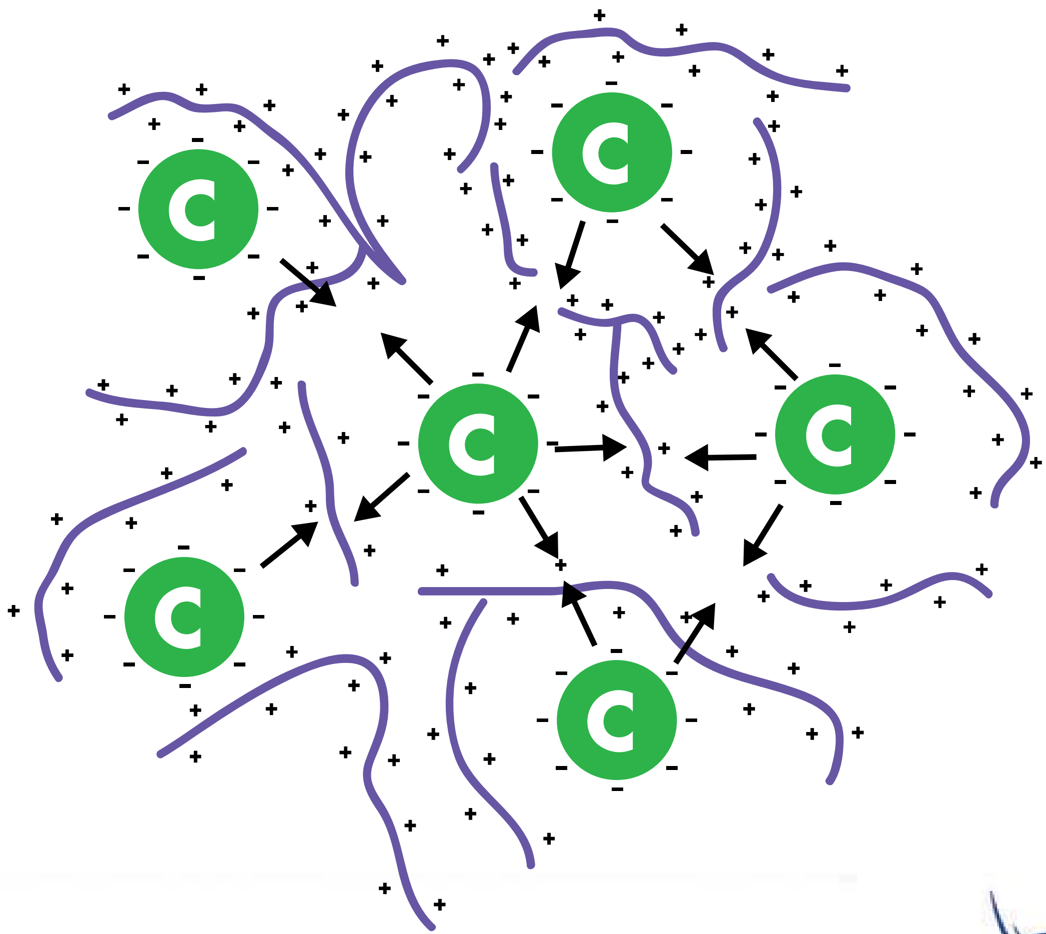
Chitosan (cationic polymer) : charge neutralization reduces repulsion and suspension becomes unstable to form flocs



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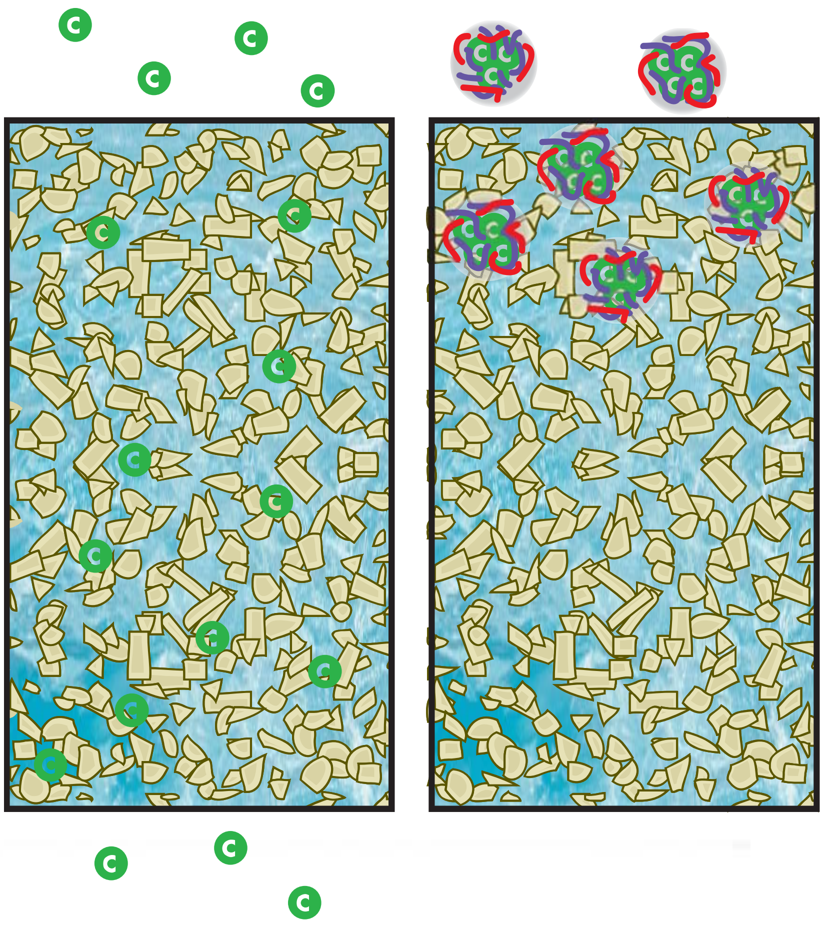
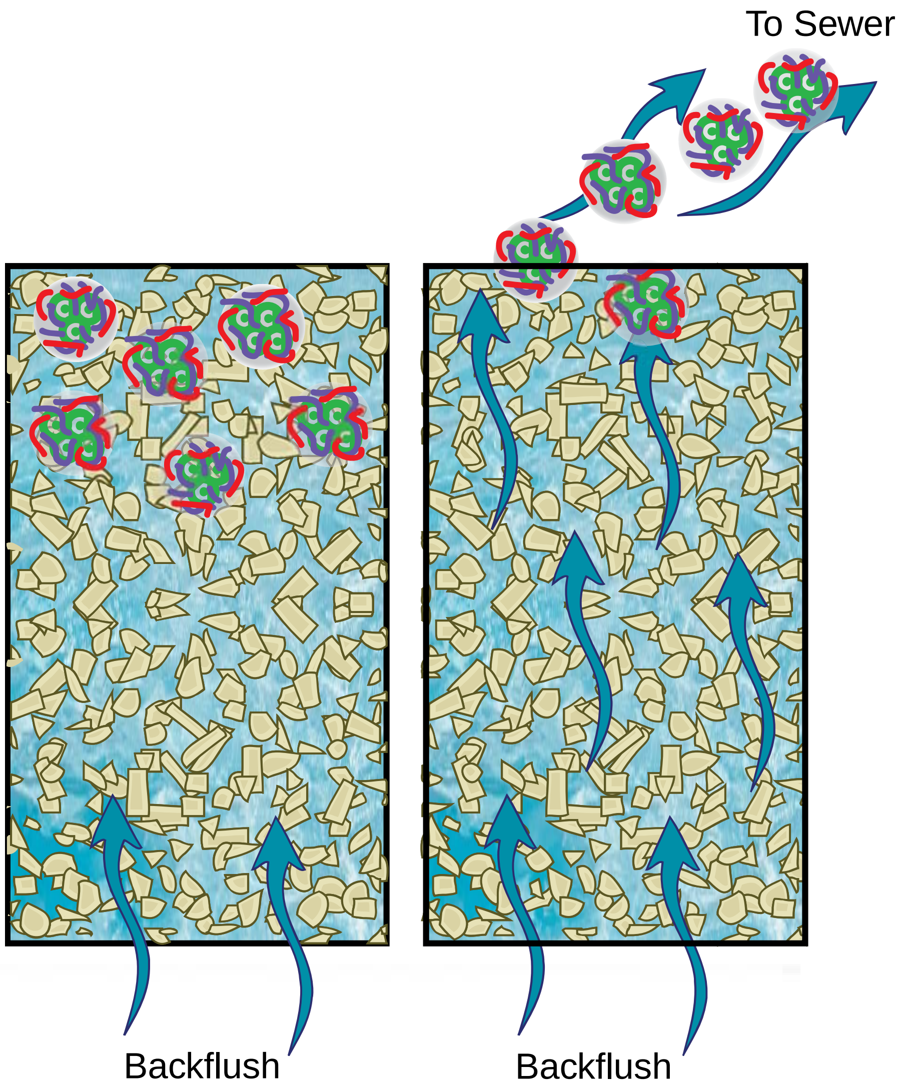
Sand bed filters can trap stable, firm floccules, and remove flocced sediment or colloidal insoluble organic phosphates from the flow of water



Backwash flushes trapped floccules into sanitary sewer system



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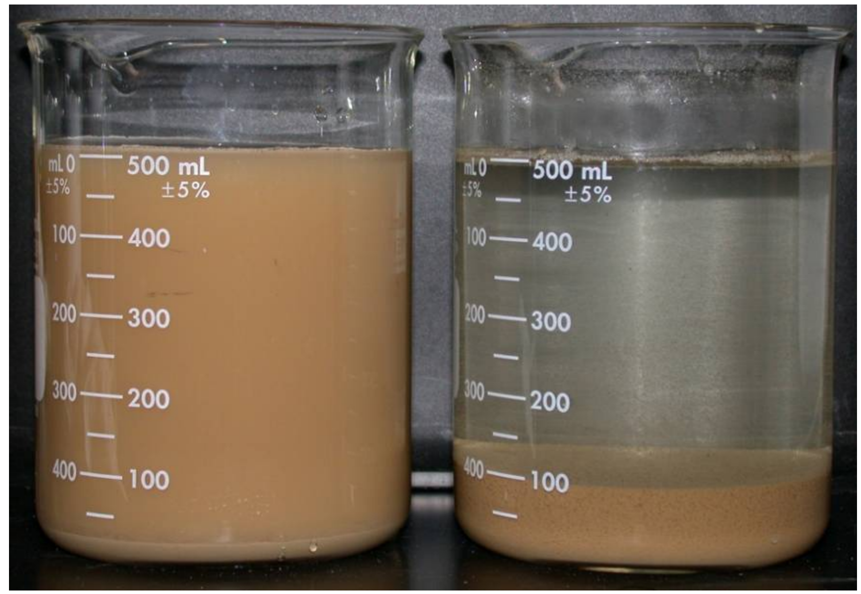
Chitosan-Mediated Flocculation of Sediment

Suspended sediment-untreated

Seconds following addition of chitosan



Suspended sediment-untreated

Minutes following addition of chitosan

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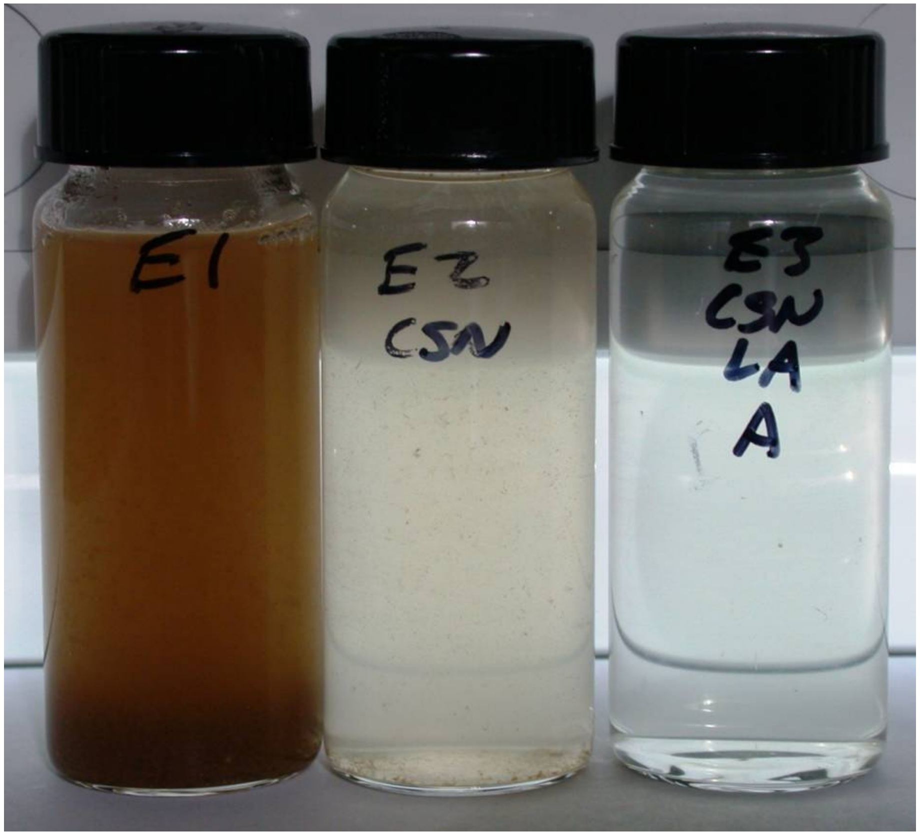
Treatment of Fish Waste with Chitosan and Lanthanum Chloride



No treatment E1

Chitosan treatment E2

Chitosan & Lanthanum chloride treatment E3

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)

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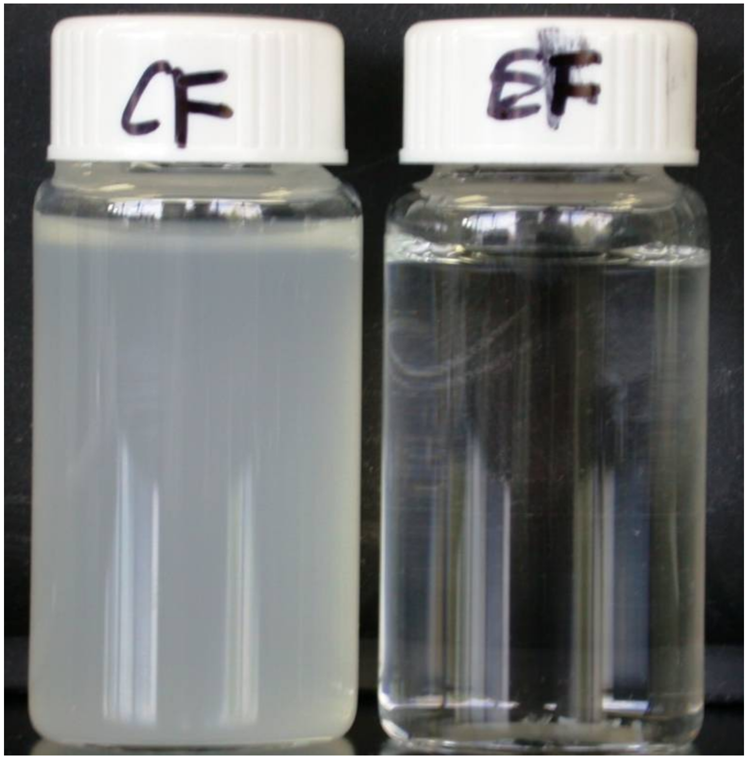
Flocculation & Filtration of Organic Phospholipid w/Chitosan

untreated

Chitosan treated



Untreated- sand filtered

Chitosan treated & sand filtered

CF-total Phosphorus- 33 ppm

CF-total Phosphorus- 6.0 ppm

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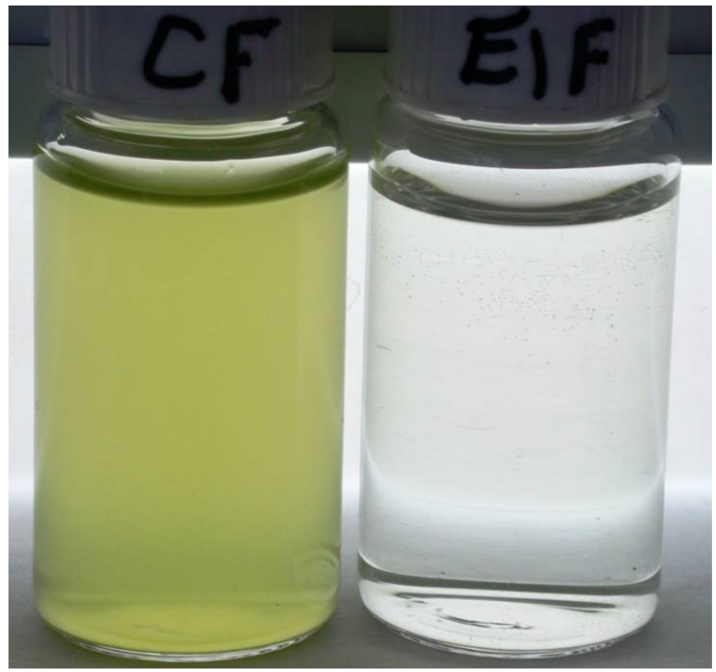
Flocculation & Filtration of Green Algae w/Chitosan

Algae non-treated

Algae chitosan-treated



Algae non-treated & sand filtered

Algae chitosan-treated & sand filtered

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Chemical Treatment Options for Orthophosphate Removal

Alum - $Al_2(SO_4)_3$ – most common

$$Al_2(SO_4)_3 + 6\,H_2O \xrightarrow{pH>5} 2Al(OH)_3 + H_2SO_4$$

$$HCO_3^- + H^+ \longrightarrow H_2CO_3 \longrightarrow CO_2 + H_2O$$

$$Al_2(SO_4)_3 + 3\,Ca(HCO_3)_2 \longrightarrow 2Al(OH)_3 + 3CaSO_4 + 6\,CO_2$$

Ferric Sulfate - $Fe_2(SO_4)_3$ – similar chemistry to alum

$$Fe_2(SO_4)_3 + 3Ca(HCO_3)_2 \longrightarrow 2Fe(OH)_3 + 3\,CaSO_4 + 6\,CO_2$$

Removal of orthophosphate w/ alum and ferric sulfate is a sorption process

$Al(OH)_3$ sorbs orthophosphates $\longrightarrow$ $Al(OH)_3 \cdot H_2PO4$

Advantages

- Low cost

Disadvantages

- Reduction of alkalinity (acid neutralization of HCO_3^-)
- Gelatinous precipitates
- Large quantities required to reduce PO_4^{-3} to low levels
- Toxicity concerns have been raised (Al^{+3})
- Potential for staining (iron)
- Increased CO_2 – photosynthesis & algae growth

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Lanthanides (trivalent rare earth metals)

1. **Anion Substitution/Ion Exchange**
   Lanthanum carbonate

2. **Direct Precipitation**
   Lanthanum chloride

Anion Substitution - exchange of carbonate for phosphate

Lanthanum carbonate $La_2(CO_3)_3$ *(insoluble)*

$$La_2(CO_3)_3 + 2\ PO_4^{-3} \xrightarrow{\textit{Slow}} 2\ LaPO_4^{-3} + 3\ CO_3^{-2}$$

$$CO_3^{-2} + H_2O \longrightarrow HCO_3^{-3} + OH^-$$

$$Ca^{+3} + CO_3^{-2} \longrightarrow CaCO_3$$

Direct Precipitation of Orthophosphate

Lanthanum chloride $LaCl_3$ *(soluble)*

$$La^{+3} + 3\ Cl^- + PO_4^{-3} \xrightarrow{\textit{VeryFast}} La\ PO_4 + 3\ Cl^-$$

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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

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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 <u>both</u> 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.

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Acknowledgements

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Questions

For Additional Information

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