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Critical Conditions for High Efficiency Flocculation of Freshwater Algae with Ferric Chloride

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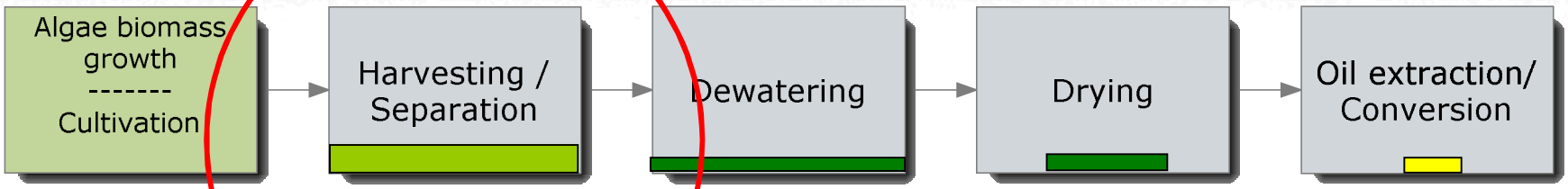
How do we make algal biofuels?

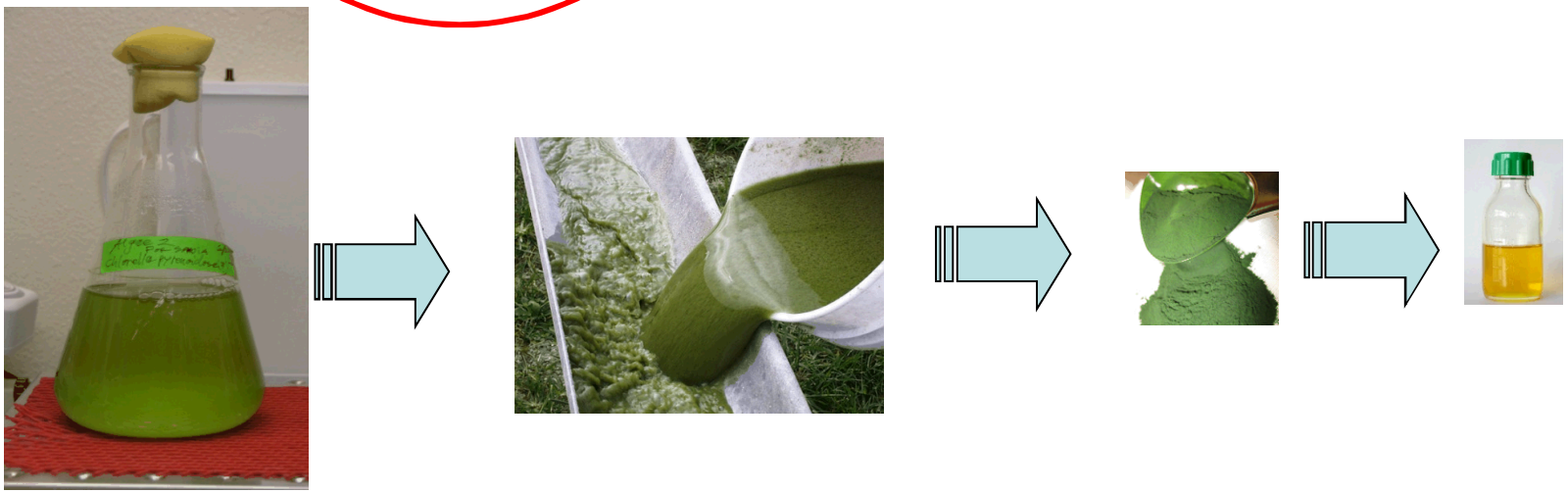
Simplified process diagram



0.1% solids

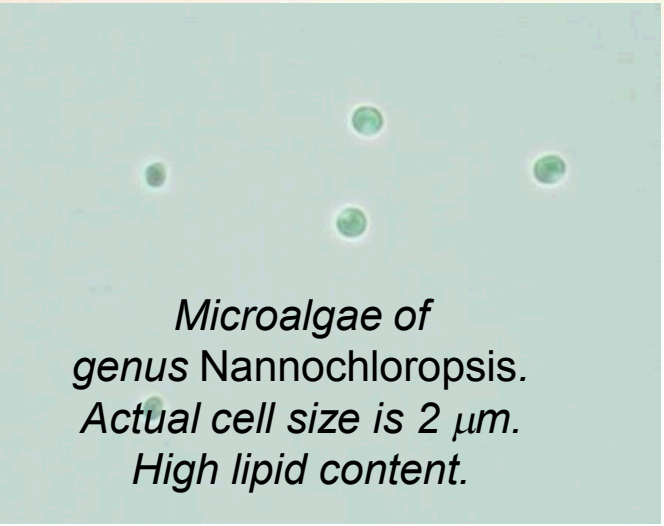
1-10% solids

to 100% solids



Need ~1000× concentration of solids

Technical challenges in harvesting/separation

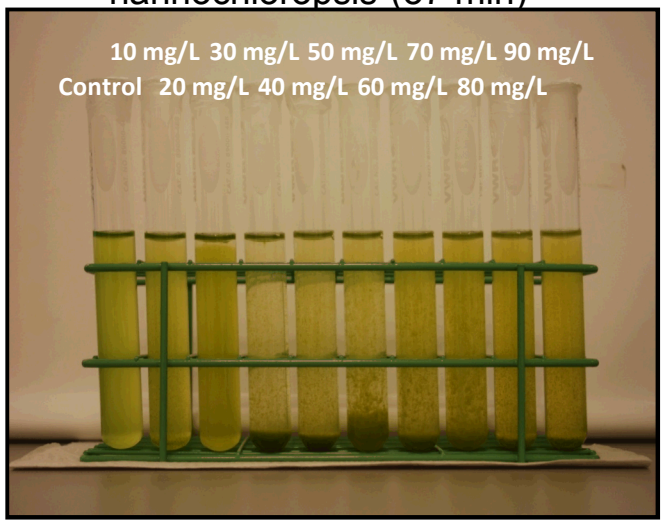


Microalgae of genus Nannochloropsis. *Actual cell size is 2 μm. High lipid content.*

Harvesting is a challenge because of:

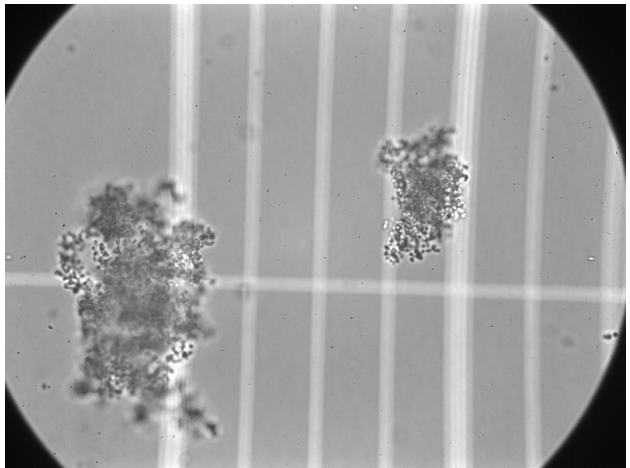
1. **Small particle size (2-30 μm)**
2. **Low concentration of algae in water (0.1%)**
3. **Negative charge on algal cells**

Chemically (FeCl3) flocculating nannochloropsis (37 min)



Flocculation

- **Increases effective particle size.**
- **Allows rapid settling or flotation.**



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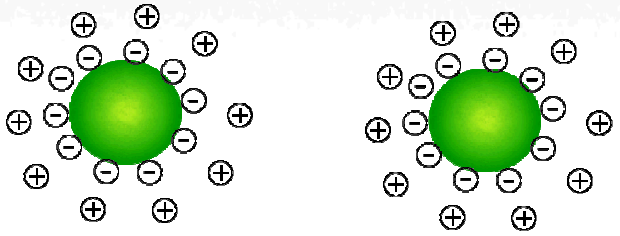
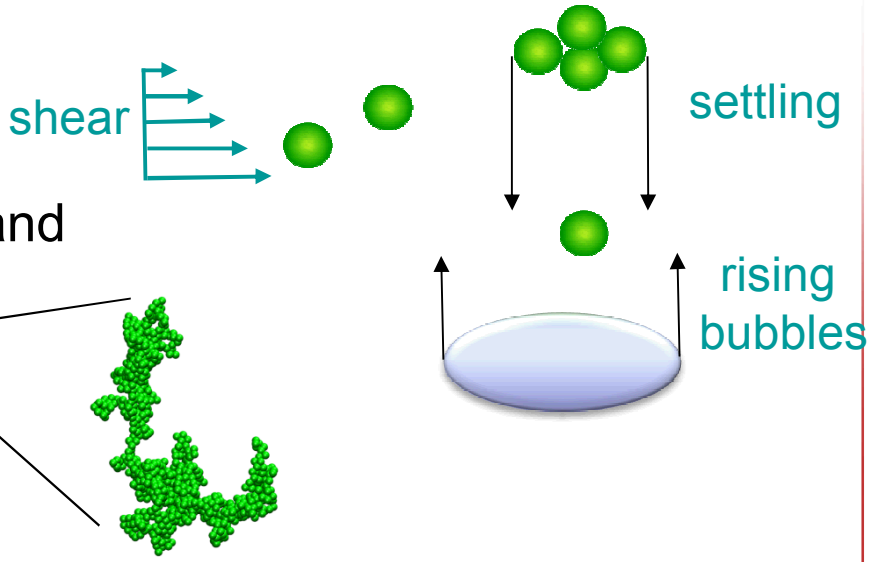
Key factors that control flocculation

1. **Sticking affinity:** overcoming negative surface charge depends on water/surface chemistry interaction.

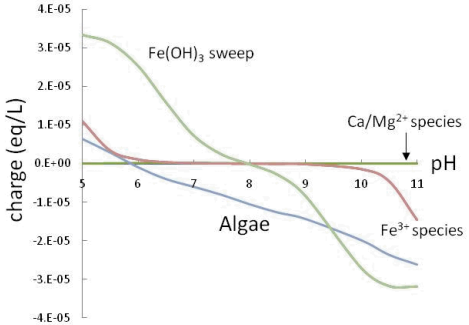


2. **Algae collision frequency:**
   - Algae concentration
   - Relative motion: fluid mixing and settling velocity.
   - Interaction cross section

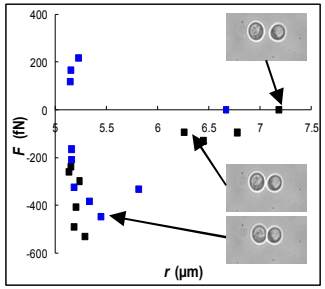


Understanding algae floc formation
From nano scale to field scale

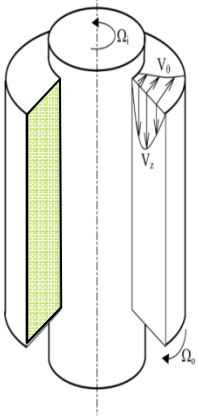
Surface potential measurements



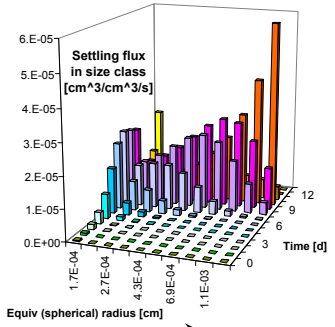
Surface interaction force measurements



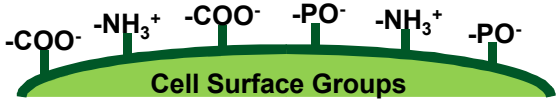
Controlled flow population dynamics measurements



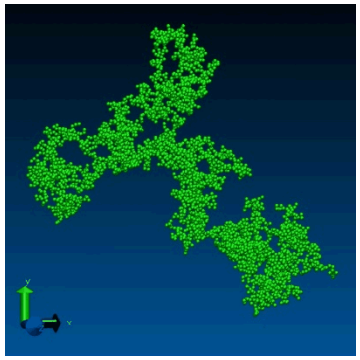
Predicting and optimizing floc dynamics at scale



Surface complexation models



Floc aggregation simulations



Predict size and flux distributions

nanometer | micrometer | millimeter | meter

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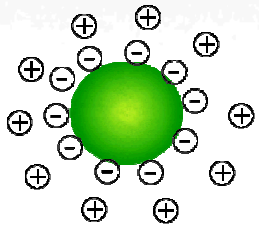
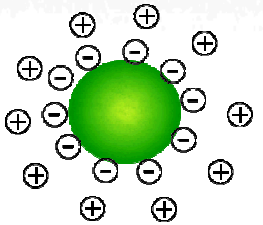
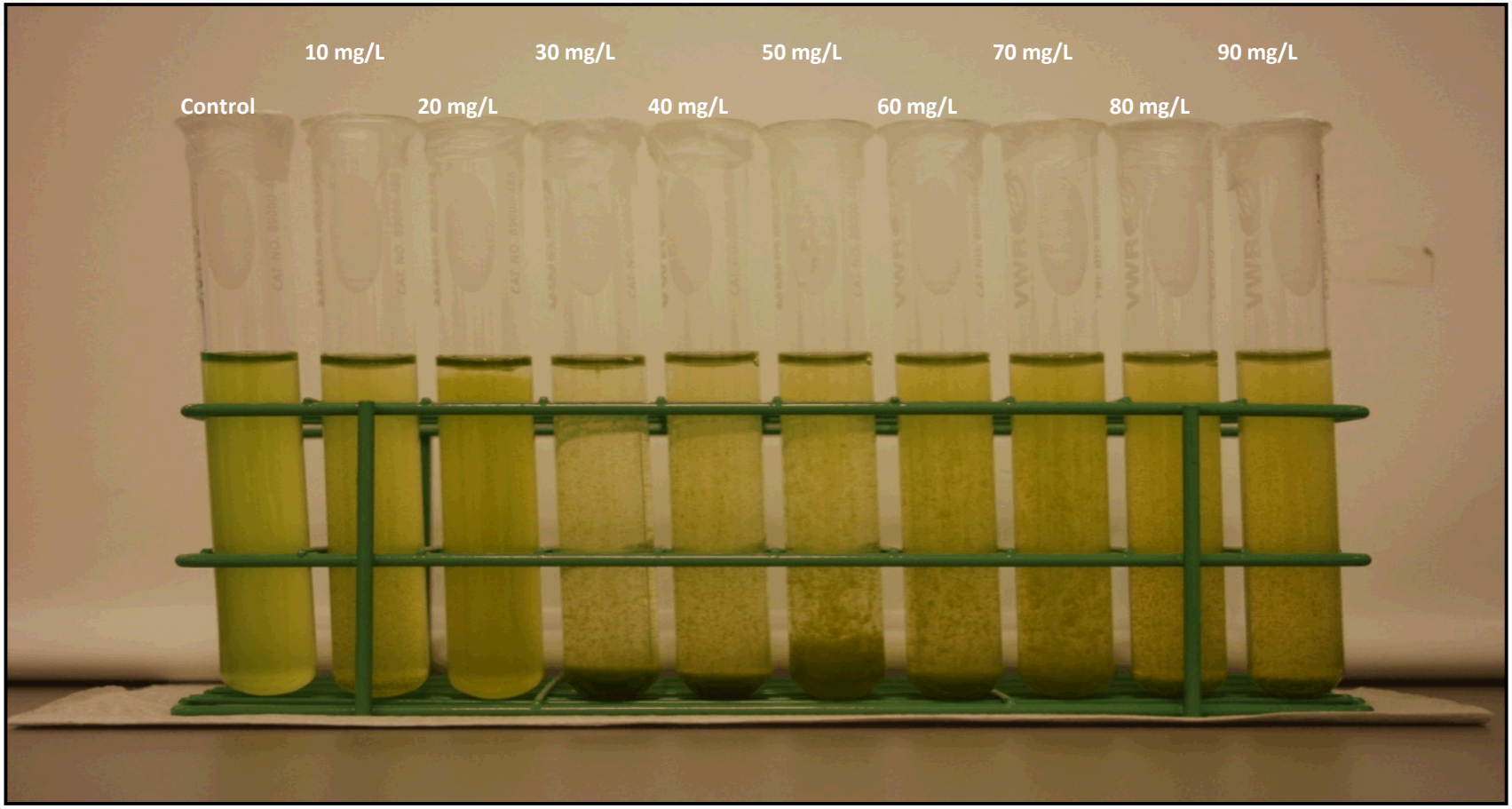
Means to induce flocculation

- Double layer compression.
- Inorganic flocculants.
  - Ferric chloride, Alum, etc.
- Organic polymers, bridging.
  - Chitosan.
  - Natural algae or bacterially produced polymers?
- Salt precipitation through pH adjustment.
- Clays, etc.
- Bubbles.





Chlorella flocculation with ferric chloride



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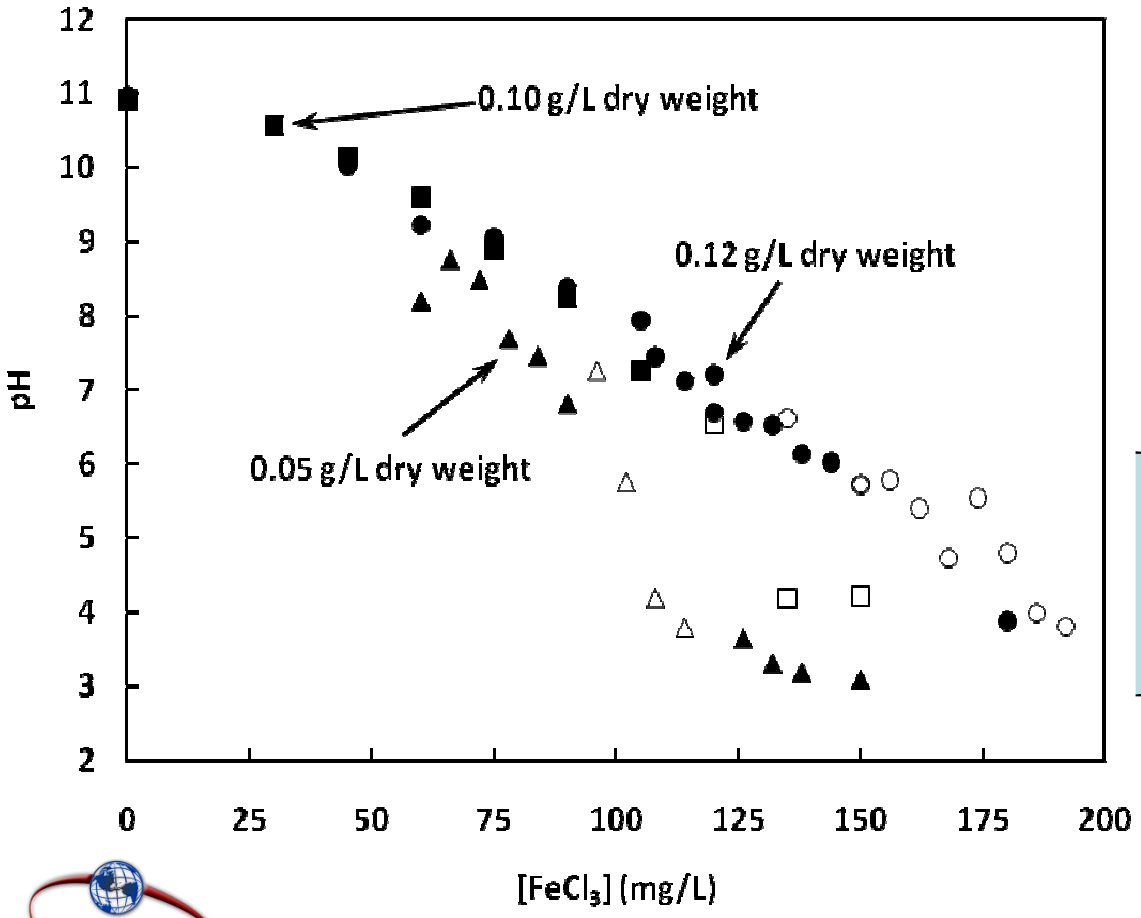
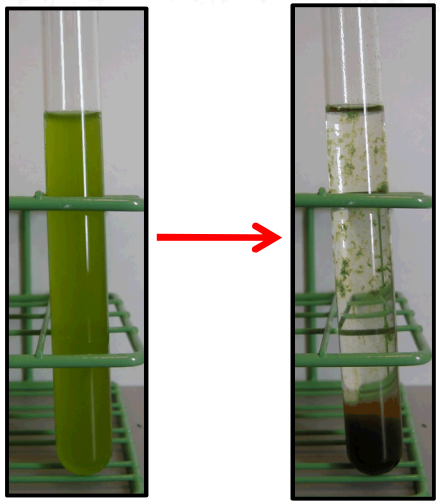
Flocculant addition effects linked with pH

pH as function of added $FeCl_3$ concentration for three different algae concentrations



Adjust pH from 2.88 to 4.5 and flocculate



Open symbols indicate solutions that flocculated with >90% efficiency.

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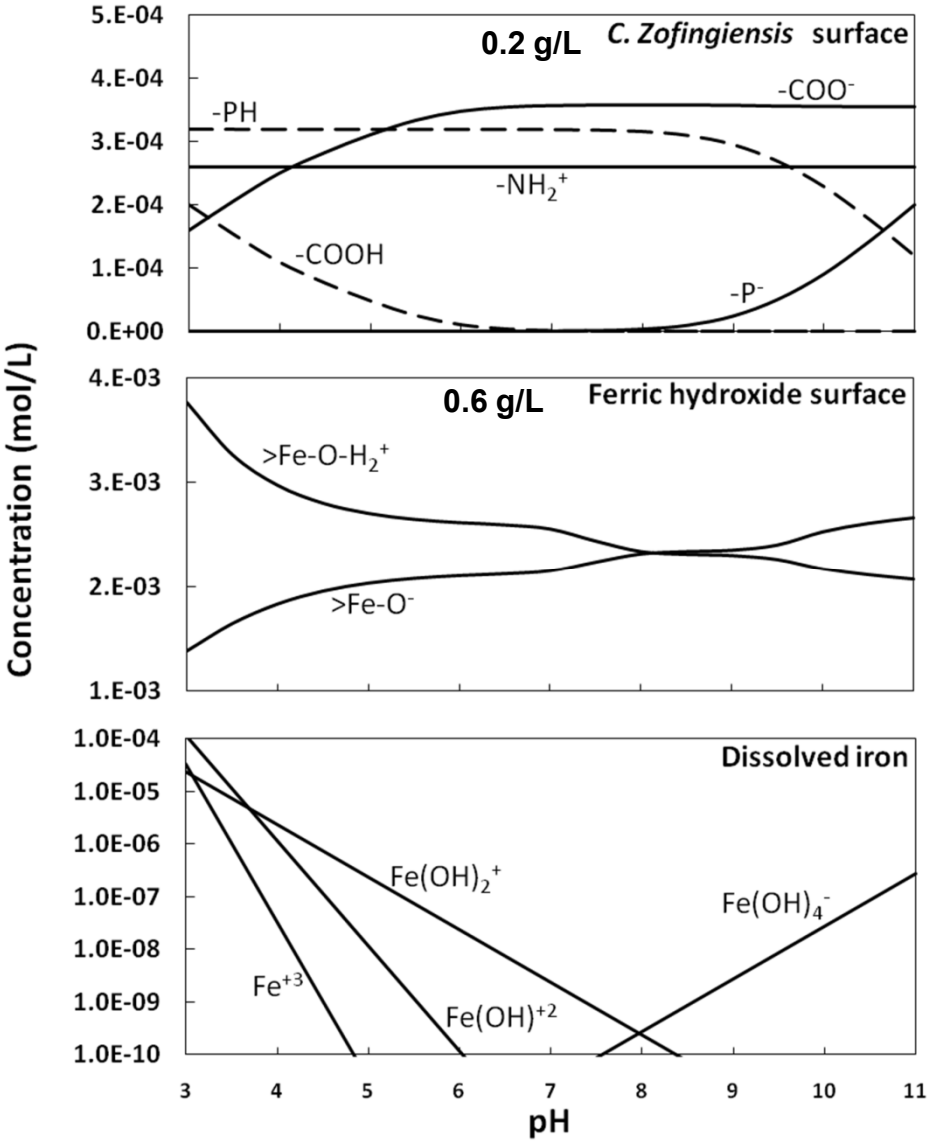
Predicted abundance of surface groups and ions



Measured functional groups

Functional Group	pKa	Density (mmol/g dry weight)
-COOH	3.7	1.8
-POH	9.1	1.6
-NH	[a]9.9	1.3

Solvated species, algae and precipitate functional groups modeled using PHREEQC

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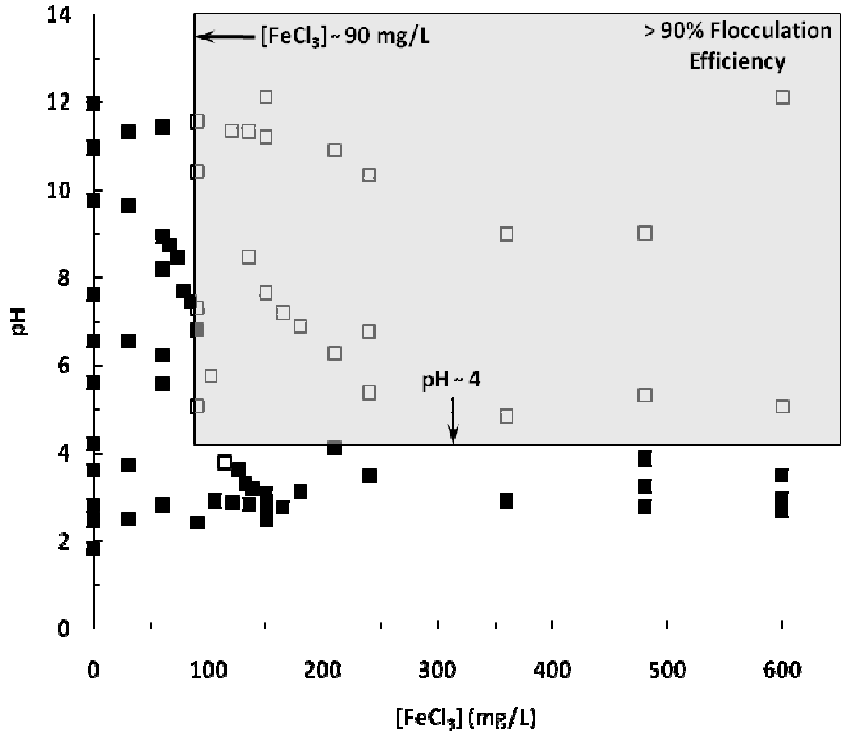
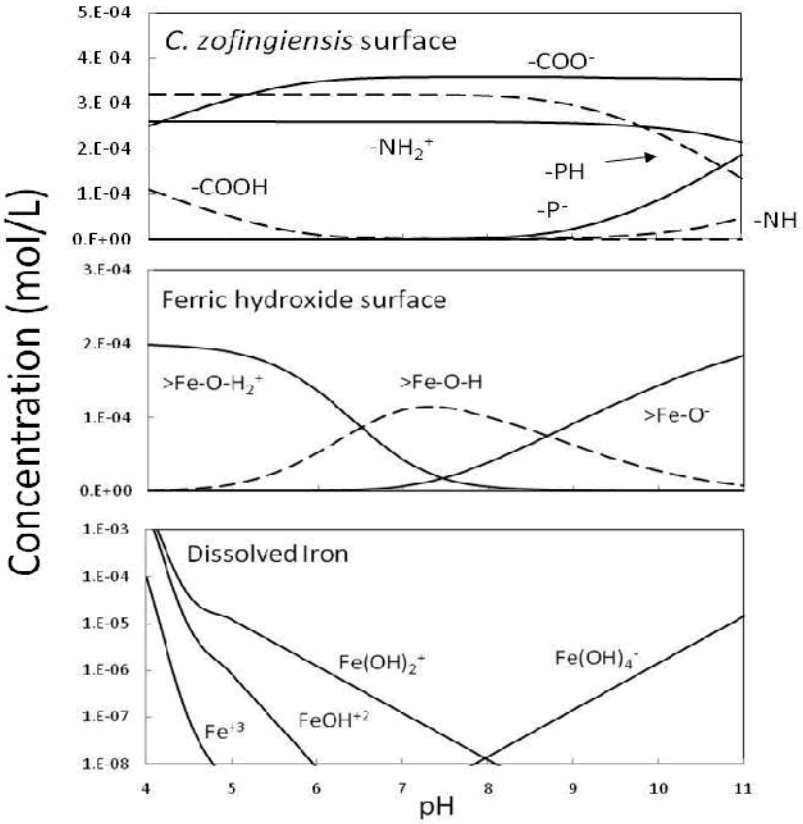
Models for algae-water interface help map effective flocculation regimes

Phase diagrams for effective algae flocculation: $FeCl_3$ plus 0.05 g algae/L



- Comparison with surface state and precipitation models shows where charge neutralization and sweep flocculation are significant.



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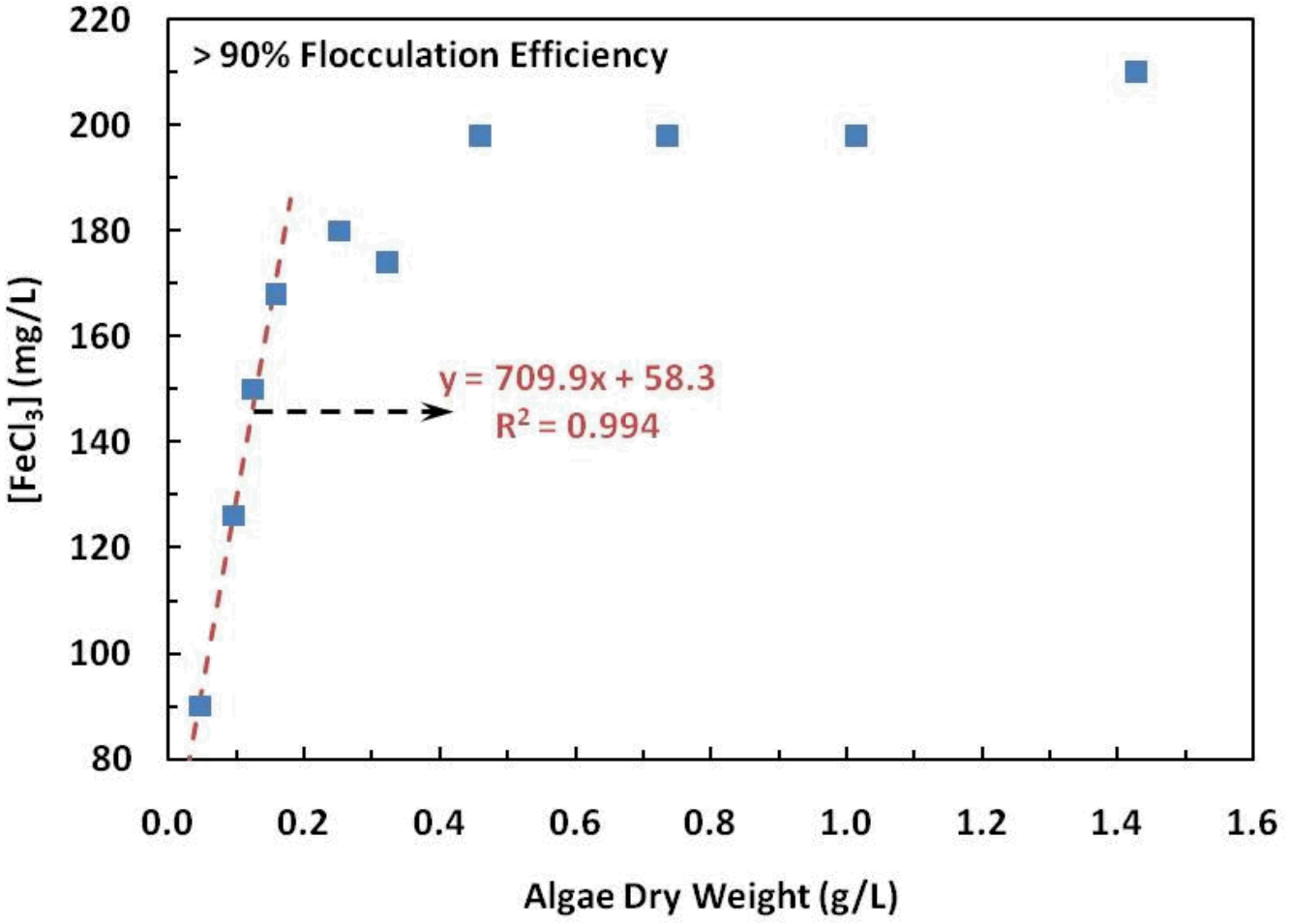
Minimum flocculant required: stoichiometric and then constant



Flocculant requirements are large

Measured functional groups

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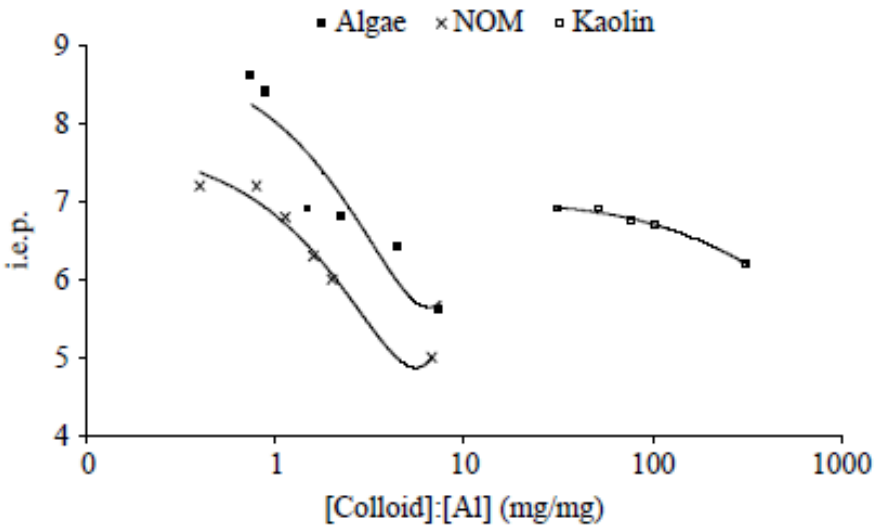
-COOH	3.7	1.8
-POH	9.1	1.6
-NH	[a]9.9	1.3

Algae surface areas separately measured 100-10,000x geometric area: Wang, X., et al. (1997)Chemosphere **1997**: 1131-1141.

Algae and NOM require 100x flocculant relative to clays, silica



Henderson R, et al. 2006. Water Sci Technol: Water Supply 6(1):31-38.

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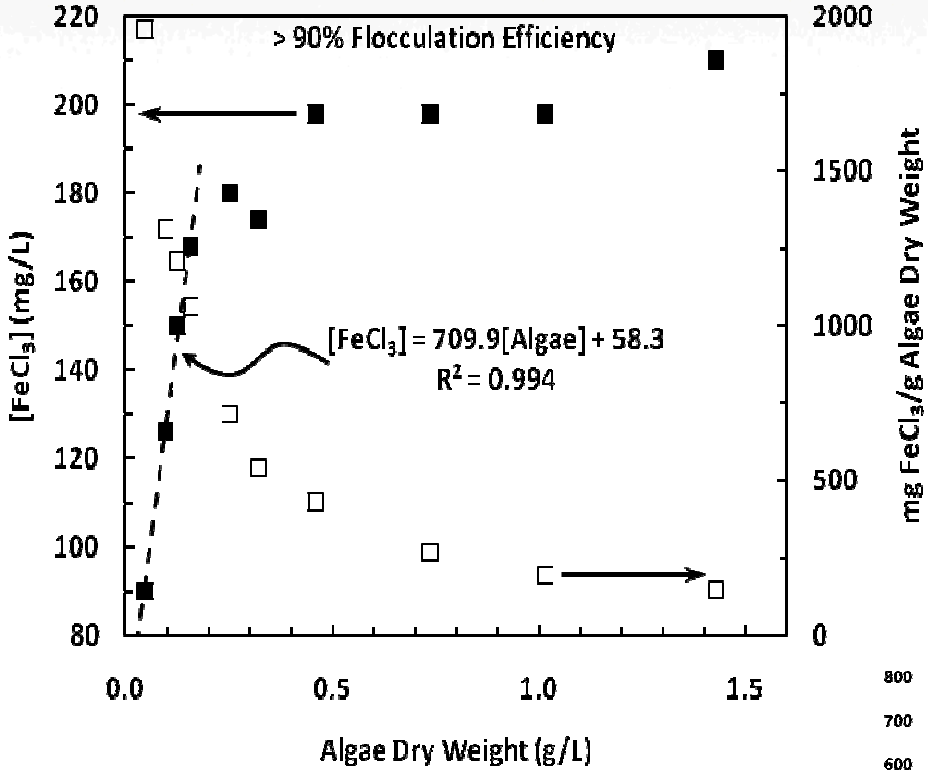
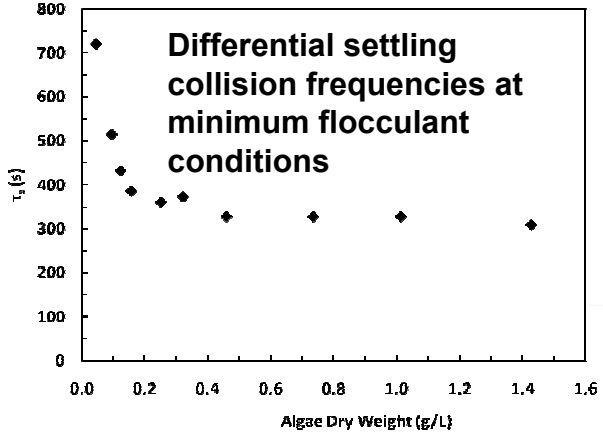
Linking algae concentrations to flocculant requirements



Measured functional groups

Functional Group	pKa	Density (mmol/g dry weight)
-COOH	3.7	1.8
-POH	9.1	1.6
-NH	[a]9.9	1.3

$$\tau_s = \frac{\mu N_0^{1/3}}{\Delta\rho g \phi^{4/3}} = \frac{\mu}{\Delta\rho g \phi r_0}$$



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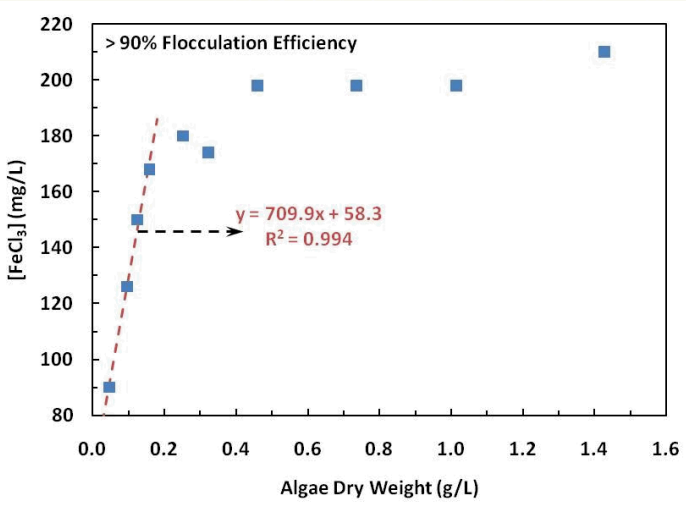
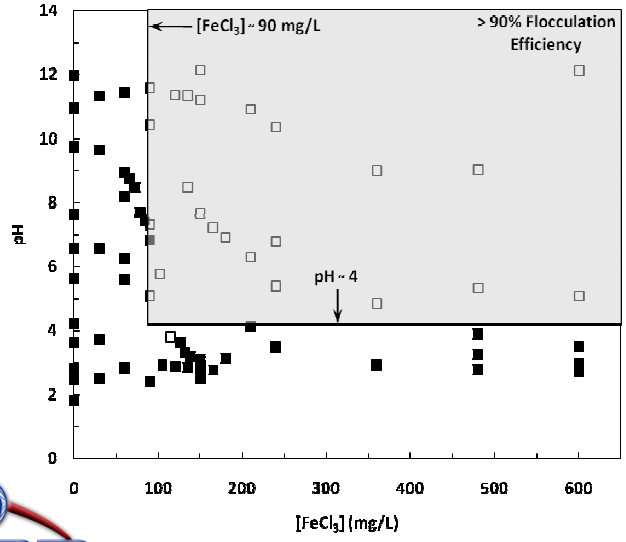
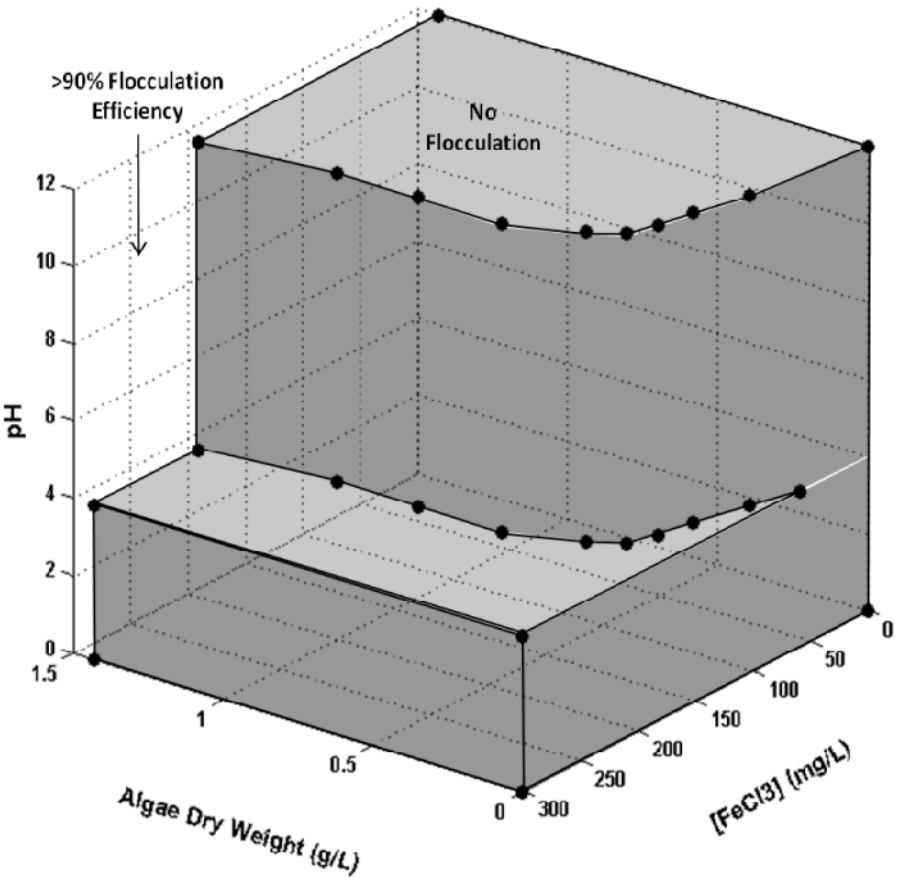
Mapping effective flocculation: pH, algae concentration, flocculant added







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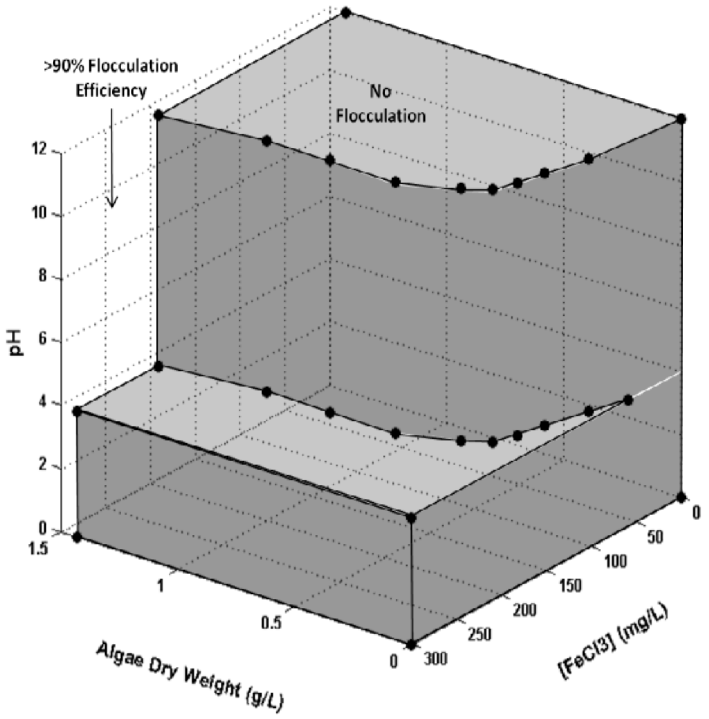
Summary

- A multiscale approach to a fundamentals of flocculation:
  - Sticking affinities and interaction frequencies.
  - Measurements and modeling.
- Linking measurements and modeling to map reliable flocculation space.
  - Relate algae concentration, flocculant dosage, pH, efficiency.
  - Targeting open source tools.
- Flocculant requirements for algae are large:
  - Functional group concentrations.
  - Suggests natural flocculants.



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