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A Coordination Chemistry Model for Algae Autocoagulation

Key to Low Energy Algal Biofuels Processing

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Introduction

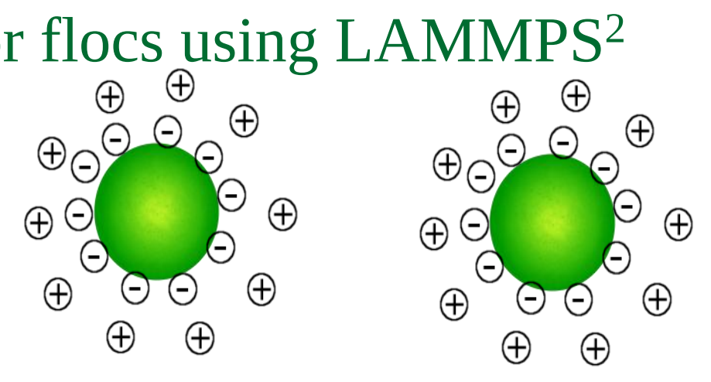
Technical challenge: Harvesting can account for 20-30% of algal biomass production cost.[1] Harvesting is difficult because of: Small particle size (2-30 μm), Low concentration of algae in water, Negative charge on algal cells. Options include centrifugation, flotation and flocculation.

A first step to identifying new coagulation strategies for dewatering algae is developing a fundamental basis for predicting the linking of algae by existing flocculants. This requires pH and ionic strength-dependent algae-water interface charge by deprotonated carboxylate, phosphate, and hydroxyl/amine groups. These algae surface groups are deprotonated above pH 4 - 6 (carboxylic groups), pH 7 - 8 (phosphoric groups), and pH 9 - 10 (hydroxyl/amine groups) and therefore able to interact electrostatically with cationic species, such as nitrogen base groups on polymers, positively charged Fe(III) and Al hydroxyl clusters, and positively charged $Mg(OH)_2$ and calcium phosphate surfaces. By compensating algae-water interface charge, coagulants are able to link individual algae which are then easier to sediment, filter, or remove by dissolved air flotation.

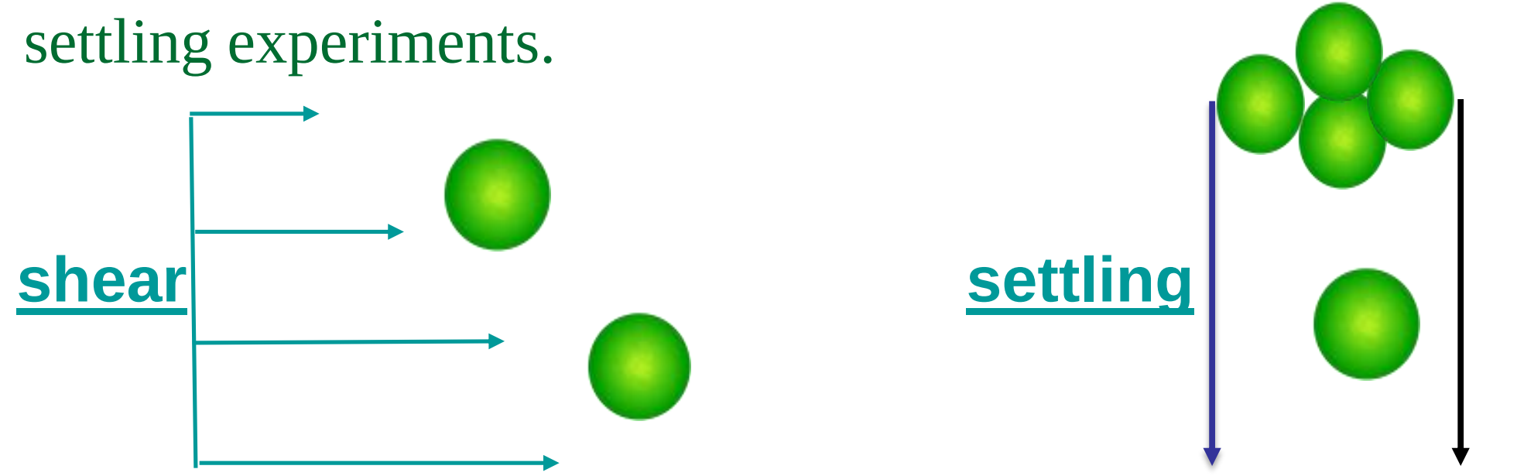
Flocculation dynamics

Flocculation rates are determined by

1. Sticking affinity measured for pairs of cells using laser tweezers[2]; for flocs using LAMMPS[2]



2. Algae collision frequency determined by shear and settling experiments.

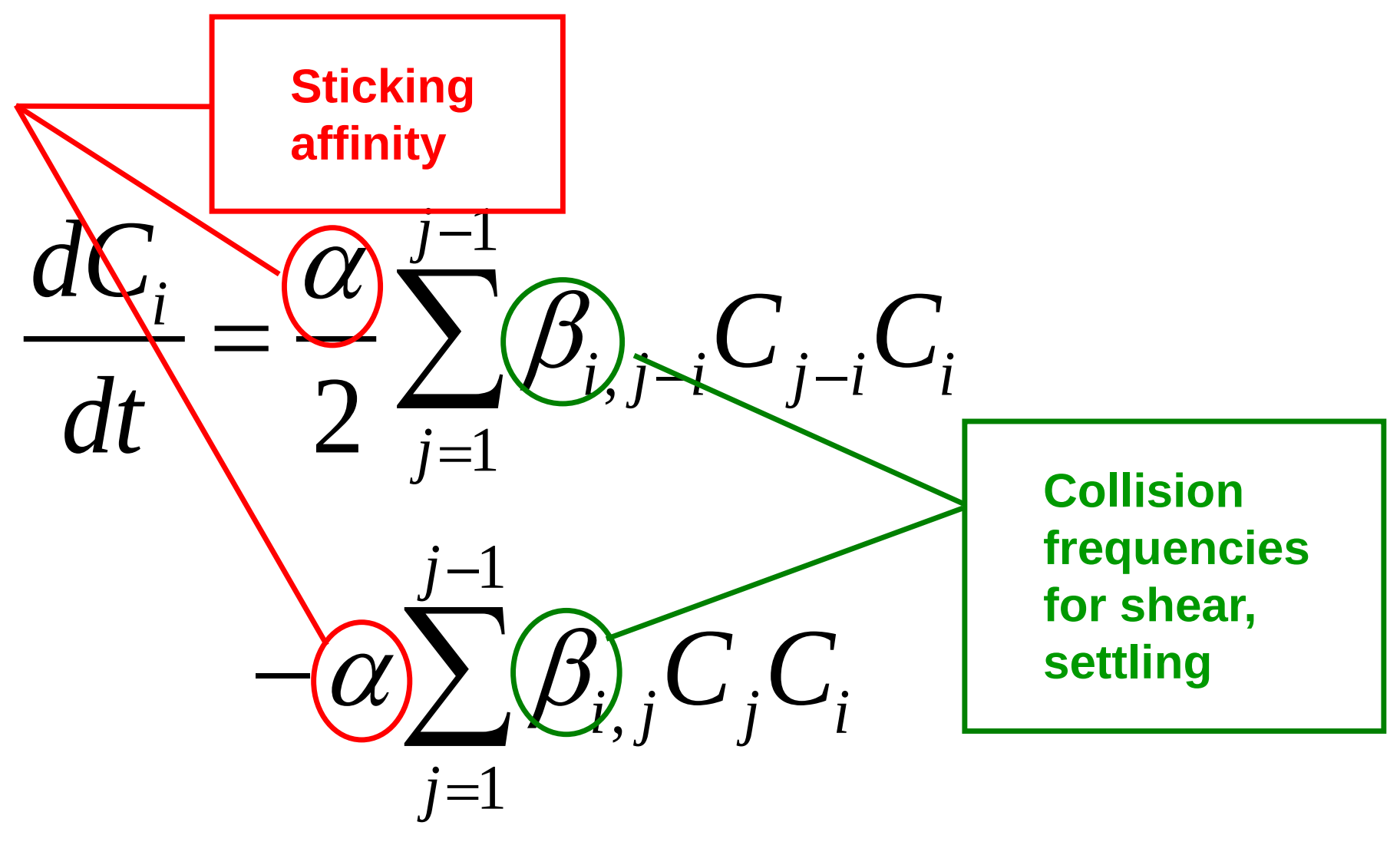


$$\beta_{i,j,sh} = \frac{4}{3}\gamma\left(r_i + r_j\right)^3$$

$$\beta_{i,j,ds} = \frac{2}{9}\frac{\pi g}{\nu}\frac{\Delta\rho}{\rho}\left(r_i + r_j\right)^2 \left|r_i - r_j\right|^2$$

Macro-scale floc evolution predicted using

population dynamics model w/differential settling, turbulent shear



$$\frac{dC_i}{dt} = \frac{\alpha}{2}\sum_{j=1}^{j-1}\beta_{i,j-i}C_{j-i}C_i - \alpha\sum_{j=1}^{j-1}\beta_{i,j}C_jC_i$$

$$- \text{settling} + \text{reproduction}$$

Sticking affinity

Collision frequencies for shear, settling

Factors which complicate electrostatic mapping of coagulant-algae interaction include:

- Coagulant loads depend upon the algal surface area, which increases during the algae growth phase,
- Extracellular organic material is secreted by the algae surface, particularly in the later stages of growth,
- Algae surface charge is distributed across a gel-like interface, resulting in both interior/external potential,
- Solution chemistry often changes due to algae growth or process steps, affecting surface charge, polymer unfolding/shielding, and the reactivity of inorganic coagulating agents,
- Algae surface charge changes during coagulation, increasing coagulant demand and/or slowing the process,
- Algae morphology can decrease coagulation effectiveness, particularly if algae are non-spherical or large,
- Algae coagulation is often a combination of two different processes – charge compensation and sweep flocculation, the first tends to prevail at pH ~ 5, the second at higher pHs; both often in parallel.

Surface Chemistry via Potentiometric Titrations

For titration measurements, a 400-mL aliquot of *C. zofingiensis* in growth media was used. The concentrated algae sample was titrated on a Mettler model G20 auto-titration apparatus with 0.095 N NaOH, and repeated twice with algae samples from the same culture. Surface charge results were modeled as arising from deprotonation of carboxyl, phosphoryl, and amine groups present at the algae-water interface (Reactions 1-3 from [3]). Algal surface area was assumed to be 1000 m^2/g, consistent with [4].

$$-COOH \leftrightarrow -COO^- + H^+ \quad K_{COOH} = [-COO^-]e^{(F\Psi/RT)}a_{H+}/[-COOH] \qquad [1]$$

$$-POH \leftrightarrow -PO^- + H^+ \quad K_{POOH} = [-PO^-]e^{(F\Psi/RT)}a_{H+}/[-POH] \qquad [2]$$

$$-NH_2^+ \leftrightarrow -NH + H^+ \quad K_{NH} = [-NH]e^{(F\Psi/RT)}a_{H+}/[-NH_2^+] \qquad [3]$$

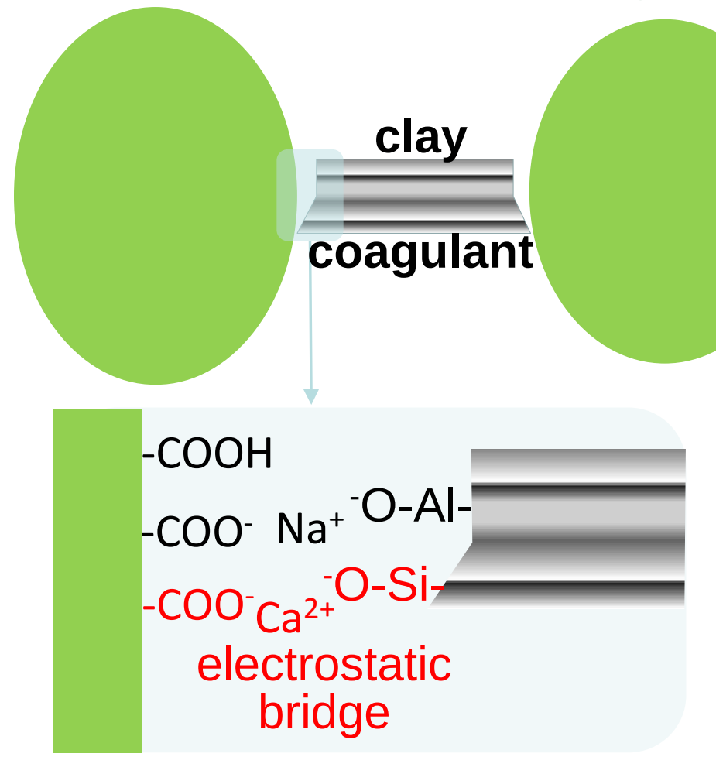
Titration results were fit using ProtoFit 2[5].1 to calculate surface group acidity constants and site densities (Table 1). A diffuse layer model of surface electrostatics was used in the analysis because of its simplicity and its wide use in examining colloid surface chemistry[6]. As such, it is expected that the model presented here will apply to freshwater algae generally rather than being confined to a specific species.

Table 1. pKa values and associated functional groups for *C. zofingiensis*

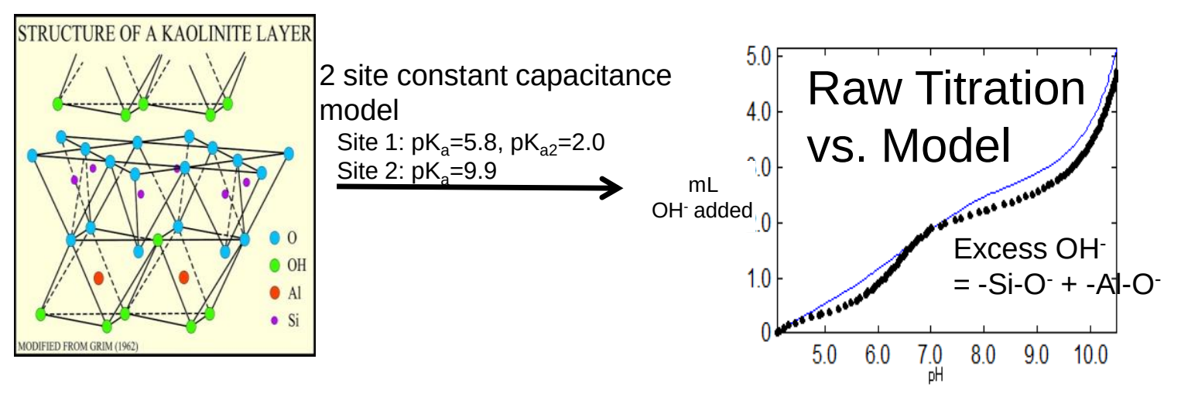
Group	pKa	Density (mmol/g)
-COOH	3.6	.36
-POH	6.0	.15
-NH	8.7	.31

Algae-Coagulant-Water Electrostatics

Goal: Develop surface complexation models to predict electrostatics of algae and candidate coagulants (e.g. clays, low cost cationic polymers-lccps*) as *f*(pH, Ca^{2+}, Na^+, Cl^-, EOM…)



Kaolinite electrostatics model



Amino Acid	pK_a	Isoelect Pt
Histidine	6.04	7.60
Glutamic Acid	4.07	3.15
Cysteine	8.18	5.05

Done:
Kaolinite vs. salinity
Kaolinite vs. Ca^{2+}, T

In progress
Algae vs. salinity, Ca^{2+}

In planning:
Lccps vs. salinity, Ca^{2+}

**Lccps = cation-doped starches and clays*

Surface Complexation Model

Using titration results (Table 1), the dependence of algae surface charge, $Mg(OH)_2$ and calcite in seawater as a function of pH was calculated (Fig. 1). Calculations were performed using PHREEQC[7] and surface complexation constants for the inorganics were taken from the WATEQ database.

Autocoagulation of algae by $Mg(OH)_2$ or calcite requires binding of the respective surfaces, presumably through electrostatic bridges formed by oppositely charged surface groups (Obviously, the autocoagulating mineral also needs to be stable, for $CaCO_3$ in seawater this means pHs > 8, for $Mg(OH)_2$ this means pHs > 9.5). Autocoagulation by $Mg(OH)_2$ is likely to be caused by a linkage between $>MgOH_2^+$ and –COO- groups at pHs < 11; at pH > 11 autocoagulation by $Mg(OH)_2$ is likely by electrostatic attraction between $>MgO^-$ and $–COOCa^+$ and/or $–COOMg^+$.

Autocoagulation of algae by calcite should be favored over a wide range of pHs because the two primary groups on the algae and calcite surface, $-COO^-$ and $>OH_2Ca^+$, are oppositely charged and abundant at all pHs. A complication to this prediction is the possibility that sulfate sorption might lower the calcite surface charge. Again, uncertainty in the magnitude of the sulfate-calcite sorption constant makes accurate prediction of any sulfate effect difficult.

The model described above provides a mechanistic explanation for observations of autocoagulation. Knuckey et al. [8] showed that increasing pH flocculated algae (*T. pseudonana*) from seawater. Flocculation efficiencies exceeded 50% at pH 6 and 90% at pH 10 - 13 (The non-ionic polyelectrolyte LT-25 was used to enhance floccing). Because neither calcite nor $Mg(OH)_2$ forms from seawater below pH 8, electrostatic bridging must be between individual algae. Figure 1 points to the potential importance of electrostatic bridges formed between $–POMg^+$ and $–COOCa^+$ and $–COO^-$ groups at pH < 9. Equivalently, the process can be visualized as a charge neutralization in the algae double layer by Mg^{2+} sorption. At pH > 9 calcite and $Mg(OH)_2$ are both predicted to form from seawater. Flocculation effectiveness is pH independent from pH 10 – 13 and is probably driven by interaction between $>OH_2Ca^+$ and $–COO^-$ groups for calcite autocoagulation, and $>MgOH_2^+$ and $–COO^-$ groups for $Mg(OH)_2$ autocoagulation.

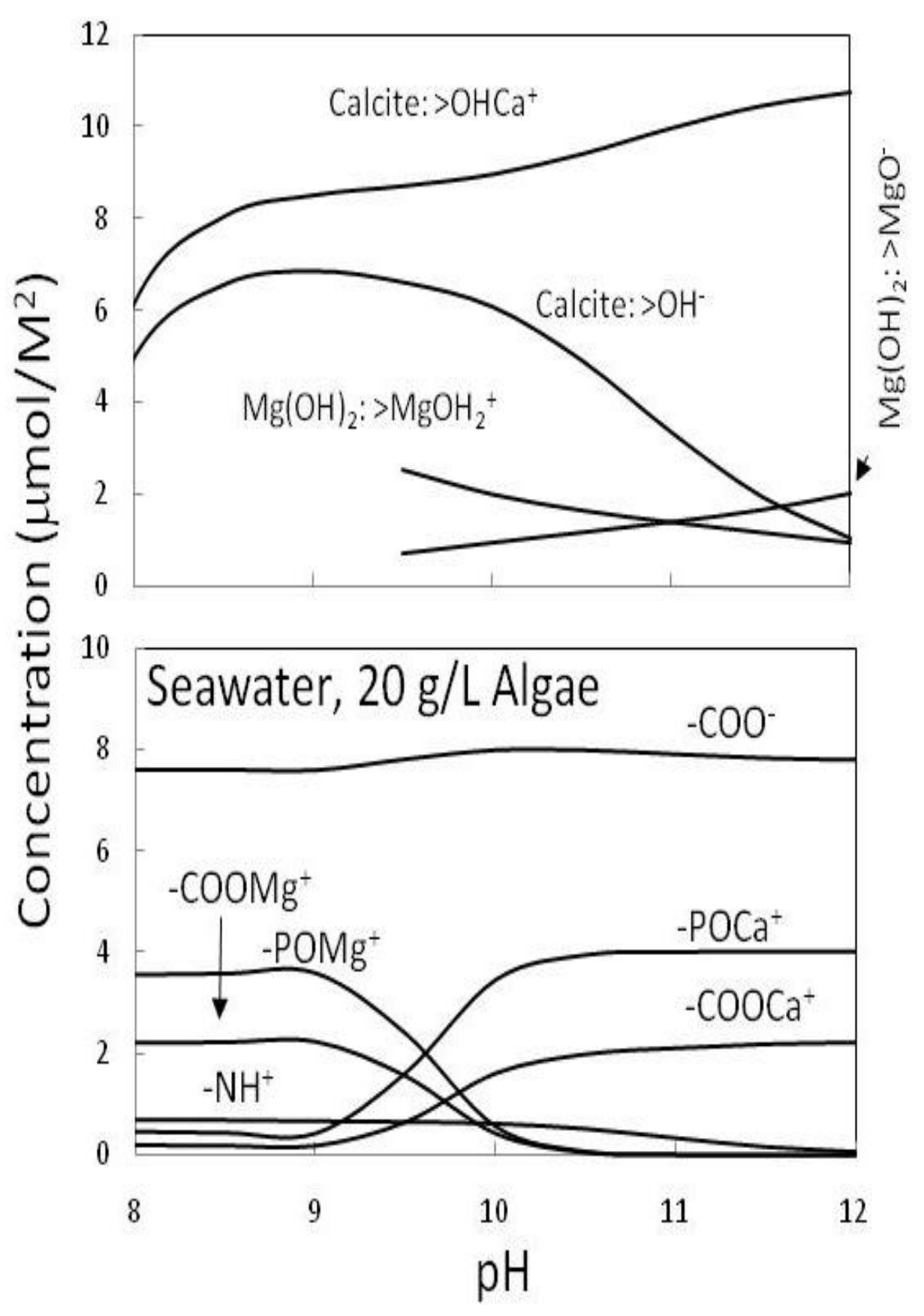


Figure 1. Comparison of algae, $Mg(OH)_2$, and calcite surface chemistry as a function of pH in seawater. Calcite is unstable below pH ~ 8; $Mg(OH)_2$ is unstable at pH < 9.5. The calculation assumes a sulfate coordination log K_{25oC} of 0.7.

Conclusions and Future Work

The experiments cited confirm the model and lay the framework for further effort in the area of autocoagulation, which has been demonstrated by [8-11] for different purposes. The model developed above allows us to meet one goal of this work, prediction of autocoagulation conditions. Because the trends can be calculated numerically, the model might lend itself to optimizing strategies for autocoagulation. For example, target pHs can be predicted for autocoagulation. Similarly, the tradeoff between pH shifts and additions of Ca, Mg, and P on autoflocculation can be numerically assessed. Deflocculation requirements (e.g. needed acid additions) can be estimated. The approach should also lend itself to predictive testing of flocculation by addition of clay minerals to form electrostatic bridges. Predictive autoflocculation will become more precise as surface complexation models of algae and mineral precipitates are improved. Future work includes:

- Use of clay and other precipitates (e.g. calcium phosphate, calcite, etc.) as a flocculant will be tested with the model above and through experimental verification.
- Finally, as a potential valuable application, the flocculation strategy developed here should also be evaluated with multiple water types such as wastewater, desalination concentrate and inland brines.

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