Ozone Effects on Algae Flocculation Kinetics

Experimental Design

Flocculation kinetic experiments were used to measure the effect of ozone on algal particle stability by determining alpha values. Singer and Chang (1989) used this approach in their studies of the effect of ozone as an aid to coagulation. Experiments were conducted in which algae were added at a known (measured) cell number concentration. Over time, the algal suspension was mixed at a known velocity gradient of 10 or $50s^{-1}$, and samples were withdrawn for particle size and number measurements. Ozone algae removal

Flocculation kinetic experiments were conducted for Chlorella for a calcium concentration of 30 mg/L as $CaCO_3$. The water also contained $10^{-3}M$ $NaHCO_3$ and the pH was 7. Three experiments were done for the following ozonation conditions: (1) no ozone, (2) ozone at an absorbed dose of 1mg/L, and (3) ozone at an absorbed dose of 3 mg/L. No coagulant was used so that the direct effect of ozone on algal particle stability could be compared against the no-ozone case. Flocculation kinetic experiments with Scenedesmus were first performed for the standard calcium concentration case of 30 mg/L as $CaCo_3$. This yielded a total of nine experiments.

The kSmoluchowski for orthokinetic flocculation was used as a basis to calculate alpha, the stability factor, from the measurements. When waters are ozonated, the particle volume concentration f may not remain constant. It may increase following ozonation due to production of particles through precipitation (e.g., oxidation of Fe or Mn producing $Fe(OH)_3$ or MnO_2 particles) or it may decrease due to breakup or shrinkage of organic part such as algae. In the controlled experiments with synthetic waters, precipitation from Fe or Mn would not occur; however shrinkage or breakup of the algal cells can occur. Alpha values indicate the stability of the particles, low values, e.g., 0.01, indicate stable particles that flocculate very slowly, whereas higher alpha values approaching 1 indicate destabilized particles that flocculate rapidly.

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Results and Discussion

The kinetic experiments for *Chlorella* were run in duplicate. The data show that no measurable flocculation for *Chlorella* occurred with or without preozonation (i.e., little, if any, change in the cell concentration *N* time). Alpha values in most cases approach zero, so any computation of alpha would be highly inaccurate. Nevertheless, it can be concluded from these results that *Chlorella* is stable and that ozone has no positive effect on the flocculation kinetics of *Chlorell*. Based on these results and the jar test data, no additional kinetic experiments were done with *Chlorella*.

Unlike *Chlorella, Scenedesmus* did undergo flocculation; consequently, alpha values were computed and then normalized or put on a relative basis with respect to an ozone effect as presented below.

Kinetic flocculation experiments with algae are difficult to perform because living organisms are used. The particle volume concentration (f) may change upon ozonation affecting rates of particle flocculation. Therefore, absolute alpha values cannot be determined accurately. What is more important is the relative effect of ozone on alpha. For these reasons, the relative effect of ozone on alpha, not absolute alpha values, are present. Relative alpha a_{rel} is defined as follows.

$a_{rel} = a_{(test)} / a_{(ref)}$

Where $a_{(test)}$ = the alpha value for any test case

$a_{(ref)}$ = the alpha value for the reference condition of no preozone

Ozone increases the flocculation kinetics of *Scenedesmus* for all calcium cases as indicated by the increase in a_{rel}. When Ca is low (0 and 30 mg/L [$CaCO_3$]), the effect of ozone on the algae particles is about the same as that indicated by the approximately equal a_{rel} values. At the highest Ca concentration tested, ozone has a great effect at 1mg/L (a_{rel} of 10), while increasing ozone to 3 mg/L decreases a_{rel} to 5. This increase in a_{rel} at 1 mg/L and then decrease at higher ozone may be due to interacting effects between ozone and calcium.

J Chang and Singer (1991) have reported on a study in which they measured a values before and after ozone addition for waters collected form seven locations throughout the United Stated. They found that ozone reduction of particle stability (i.e., increased alpha) depended on both the ozone dose and the water hardness, which they expressed in terms of the raw-water hardness to total organic carbon (TOC) ratio. Specifically, they found increases in alpha for ozone doses of 0.4 to 0.8 mg O_3/mg TOC and hardness-to-TOC ratios of at lease 25 mg $CaCO_3$/mg TOC. While they did not address the role of algae, at least on a seasonal basis: Los Angeles (Owens River Aqueduct), Monroe, Mich. (Lake Erie), and Bay City, Mich. (Saginaw Bay of Lake Huron). Chang and Singer (1991) found for all three of these supplies that ozone at low doses increased alpha, while at higher ozone doses alpha decreased, in some cases approaching the alpha for no preozonation. For Monroe, alpha increased for ozone doses up to 1 mg/L and then decreased at a dose of 2 mg/L. For Bay City, for a water sample collected during the summer, alpha increased with ozone up to a dose of 2 mg/L and then decreased at an ozone dose of 3 mg/L. For Los Angeles, the results were similar but at lower ozone doses. In the work of Chang and Singer, all three supplies had higher hardness (70 to 144 mg/L $CaCO_3$) values than the hardness used in the algae work of this project (0 to 50 mg/L $CaCO_3$), but the hardness-to-TOC ratios are comparable --- 35 to 60 mg $CaCO_3$/mg TOC for the three supplies in the Chang and Singer work versus 15 to 30 mg $CaCO_3$/mg TOC for the two calcium cases of this project. Independent DOC measurements for the algae experiments indicated values of about 2 mg/L with little particulate carbon. IN summary, the results for Scenedesmus and Chlorella show the effect of ozone on alpha depends on ozone dose, calcium and hardness and algae type.

Reference: American Water Works Association

Research Foundation

"Ozone as a Aid to Coagulation and Filtration"

ELIMINATION OF ALGAE WITH OZONE

People involved in water treatment speak generally of an "algae " problem. In fact, it is more accurate to use the term "plankton". This term includes all the micro-algae that under favorable conditions (the presence of ideal amounts of nutrients, heat, and sunlight in the environment) can undergo periods of explosive growth. It also includes animal plankton (zooplankton), which belong to a higher level in the food chain, as well as actinomycetes. All these organisms are sized within a range of a few microns to a few millimeters.

The following table presents a list of plankton species generally predominant in water and the effects they produce (Krauter 1974; Palmer 1980)

List of Species Generally Predominant in Water and the Effects They Produce

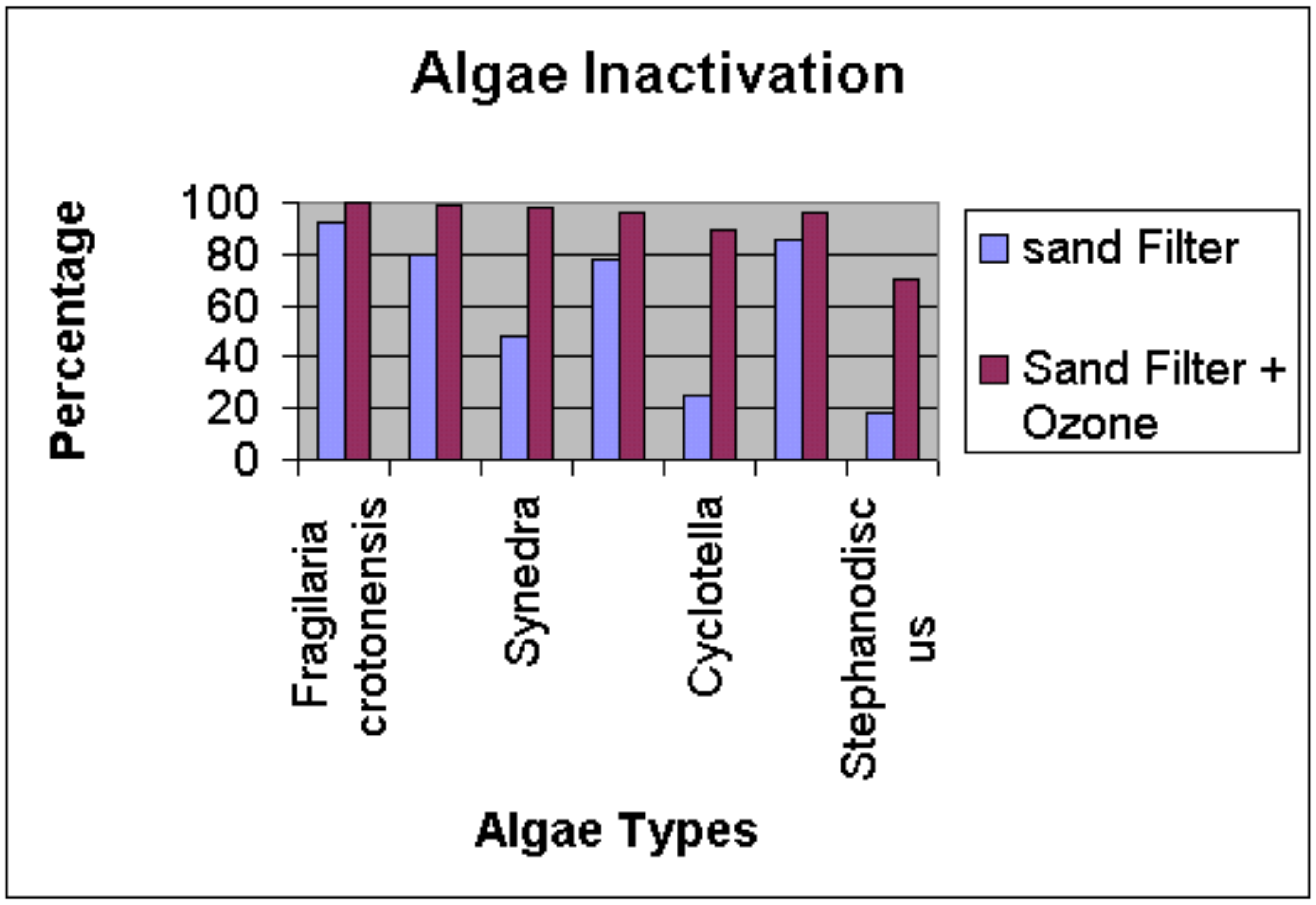
Algae	***Type***				***Dimension***	***Interference in Water Treatment***	
						Biochemical	***Morphological***
Name	Circular/Oval	Filamentous	Rectangular	Irregular	Average	Taste and Odor Problems	Effect Indefinite
Cyanophyceae							
Aphanizomenon	0	1	0	0	5	1	1
Microcystis	1	0	0	0	5	1	1
Oscillatoria	0	1	0	0	10	1	0
Chorophyceae							
Chlamydomonas	1	0	0	0	20	1	0
Chlorella	1	0	0	0	8	1	0
Coelastrum	1	0	0	0	20	0	1
Mougeotia	0	1	0	0	35	0	0
Pandorina	1	0	0	00	10(30)	1	1
Pediastrum	0	0	0	1	30	1	0
Scenedesmus	1	0	0	0	15	1	1

Ulothrix	0	1	0	0	10	0	0
Volvox	1	0	0	0	5 (500)	1	1
Cryptomonas	1	0	0	0	20(40)	0	1
Euglenophyceae							
Euglena	1	0	0	0	70	1	0
Crysophyceae							
Dinobryon	0	0	0	1	40	1	0
Bacillariophyceae							
Asterionella	0	0	0	1	80	1	0
Coscinodiscus	1	0	0	0	200	0	1
Cyclotella	1	0	0	0	30	1	0
Diatoma sp.	0	0	0	1	60	0	0
Melosira	0	1	0	0	25	1	0
Nitzschia	0	0	1	0	40	0	0
Synedra	0	0	1	0	200	1	0

Ozone has been used for algae elimination for years with very good results. In the following table you can compare ozone with some other very strong oxidants and you will see that ozone obtains very good results in a short amounts of time.

Oxidant Used	***Oxidation Conditions***		**% Inactivation**
Name	**Dose (mg/l)**	**Reaction Time (min)**	**%**
Potassium Permanganate	1	30	9.5
	2	30	68
	3	30	89
	1	60	68
	2	60	98
	3	60	100
Hydrogen Peroxide	100	30	50
	100	60	75
Ozone	1	1	14
	2	1	64
	3	1	70
	1	5	26
	2	5	72
	3	5	76

With the following graph you can compare a system which has only filtration, with a system which has added ozone to do the algae control. For almost all kind of algae, ozone can reduce it more than 95%.



As you can see, the correct installation is crucial for getting the best results from your system. If the ozone system is not well designed and installed, you will not get the desired benefits.

Bibliografic References: Ozone in Water Treatment - Bruno Laglis, David A. Reckhow, Deborah R. Brink, Ozone in Water Treatment - International Ozone Association - San Francisco 1993