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COAGULATION IN DRINKING WATER TREATMENT: PARTICLES, ORGANICS AND COAGULANTS

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ABSTRACT

A review of coagulation in drinking water treatment is presented. The paper emphasizes the importance of raw water chemistry, natural organic matter (NOM) concentration and type, and the chemistry of coagulants. Mineral and organic particles may be stable in water due to electrostatic charge interactions, hydrophilic effects, or to steric interactions from adsorbed macromolecules. NOM rather than particles initially in water supplies can control coagulant dosages and selection. NOM consists of a mixture of various organic compounds including hydrophobic (humic and fulvic acids) and hydrophilic fractions. The negative charge and chemical structure of the hydrophobic acids affect chemical reactions with coagulants, particularly metal based coagulants. The removal of NOM with Al coagulants can involve hydrolysis, complexation, precipitation, and adsorption reactions. Specific ultraviolet absorbance (SUVA) can be used to estimate whether the NOM of a water is high or low in hydrophobic acids and to estimate removals of DOC by coagulation. Preozonation of water supplies containing algae may lead to microflocculation or impair coagulation depending on algae type, concentration and molecular weight of extracellular organic matter (EOM), and ozone dose.

KEYWORDS

Coagulation, drinking water; aluminum coagulants; natural organic matter; particle stability; algae; ozone.

INTRODUCTION

The concentration and nature of natural organic matter (NOM) 1) can control coagulant dosages and coagulant selection; 2) can influence the processes selected for water treatment plants; i.e., the coagulation and flocculation processes as well as downstream solid-liquid separation processes; and 3) can have health effects because NOM is a precursor of disinfection byproducts such as trihalomethanes, haloacetic acids, etc. The goal of the paper is to present an overview of coagulation in drinking water treatment. The emphasis is on raw water characteristics and chemistry, particularly the importance of NOM versus colloidal particles initially in the water, and the chemistry of the coagulants. Some guidelines on estimating coagulant dosages and removals of NOM as measured by UV (254 nm) absorbance, DOC, and TTHMFP (total trihalomethane formation potential) are presented. Most of the ideas are drawn from the author's research on coagulation over the last 20 years.

Traditionally, the coagulation process is described in terms of the destabilization of colloids initially present in a water supply. These colloids may include organic particulates and inorganic particulates. The role of NOM, particularly the pool of dissolved organic carbon, in exerting a coagulant demand and the need to remove this material from water supplies has become more important in the last 15 years. Fig. 1 shows that coagulants are used not only to destabilize colloidal particles, but also to remove NOM. A theme of the paper is that the chemicals used are called coagulants, but precipitation reactions occur so the removal of the dissolved NOM occurs by a phase change in which particles are produced. The removal of NOM from the bulk water can occur by direct precipitation of the NOM or by adsorption of NOM onto precipitated metal hydroxides.

PARTICLES

Particles in water supplies may be mineral (clays, aluminum and iron oxides and hydroxides, asbestos, silica, etc.) or organic (viruses, bacteria, protozoan cysts, algae). Existing primarily as colloidal suspensions, these suspensions are stable such that the particles have a slow rate of particle aggregation or flocculation. The causes of particle stability may be 1) electrostatic repulsive interactions due to diffuse electrical double layers (EDL), 2) hydrophilic effects due to bound water at particle surfaces, and 3) steric effects due to adsorbed macromolecules (Lyklema, 1978, 1985). The Verwey-Overbeek-Derjaguin-Landau (VODL) theory describing particle stability by EDL interactions for hydrophobic colloids is well known and widely cited. I begin with some simple calculations of the contribution of negative charge (EDL basis) for clean mineral surfaces and compare it to the charge associated with dissolved natural organic matter in the form of fulvic acid.

First, consider that the cation exchange capacity of a clay mineral is in the range of 0.1 to 1 $\mu\text{eq}/\text{mg}$ clay while the total charge on aquatic fulvic acids due to carboxylic and phenolic groups is about 10 to 15 $\mu\text{eq}/\text{mg}$ DOC (Thurman, 1985; Van Benschoten and Edzwald, 1990b). Using a clay cation exchange capacity of 0.5 $\mu\text{eq}/\text{mg}$, then a 10 mg/L clay suspension contains 5 $\mu\text{eq}/\text{L}$ of negative charge that needs to be neutralized by coagulants. Assume a negative charge for the fulvic acid of 10 $\mu\text{eq}/\text{mg}$ DOC for neutral pH conditions. A water supply containing 3 mg/L of aquatic fulvic acid as DOC, for example, would have a negative charge of 30 $\mu\text{eq}/\text{L}$ that would have to be neutralized by coagulants, 6 times the clay case.

Second, water supplies may contain mixtures of clays and aquatic humics. Aquatic humic matter can adsorb on clays and control their particle stability (Ali *et al.*, 1984). Depending on the ionic strength and Ca concentration, the stability may be due to steric effects or to EDL effects. O'Melia (1989, 1990) has described the role of adsorbed aquatic humic macromolecules in causing particle stability through steric effects. The amount of aquatic humics adsorbed and the configuration of the adsorbed macromolecules (flat layer or extending into solution) depends on solution chemistry and concentrations of clay and humics. Adsorption of negatively charged humics onto clay surfaces should be small (i.e., fraction adsorbed), however, it can also affect the particle charge as shown by the electrophoretic mobility (EPM) data in Fig. 2. The data show a great increase in the negative charge of clay particles as fulvic acid is added to a clay suspension.

Third, a simple illustration is used to demonstrate the importance of natural organic matter in controlling coagulant dosages. Jar tests were performed on two vastly different water supplies - the Missouri River at St. Louis and the Intracoastal Waterway at Myrtle Beach, South Carolina. The Missouri River is highly turbid (670 NTU), moderately hard (150 mg/L CaCO_3), and low in DOC (3 mg/L) and aquatic humics.

The Intracoastal Waterway is low in turbidity (30 NTU) and soft (< 50 mg/L CaCO_3), but high in DOC (20 mg/L) and aquatic humics. The data in Fig. 3 clearly show that alum dosages for good turbidity and DOC removals (UVC 254 nm, surrogate for DOC) are several times higher for the Intracoastal Waterway (150 to 175 mg/L) than the Missouri River (25 to 50 mg/L). This is a dramatic demonstration that DOC not turbidity controls coagulation.

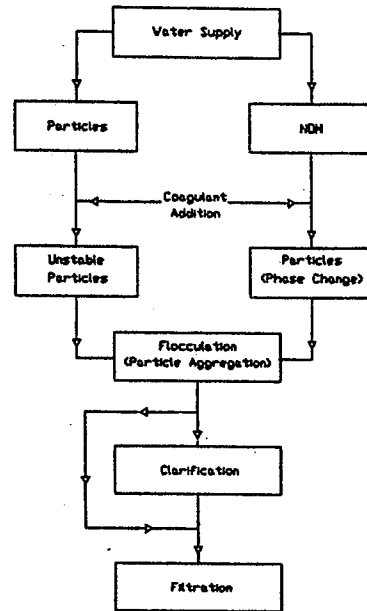


Fig. 1. Particle coagulation and removal vs. NOM removal.

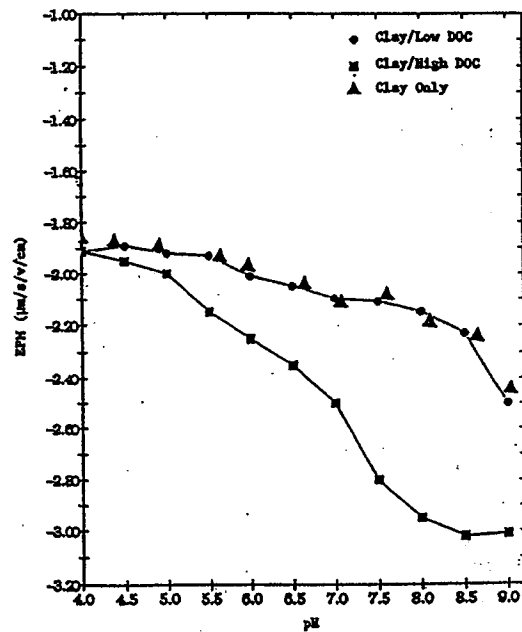


Fig. 2. Effect of DOC on particle charge (Clay only at 20 mg/L; Clay/Low DOC at 20 mg/L clay and 2 mg/L DOC; Clay/High DOC at 20 mg/L clay and 10 mg/L DOC).

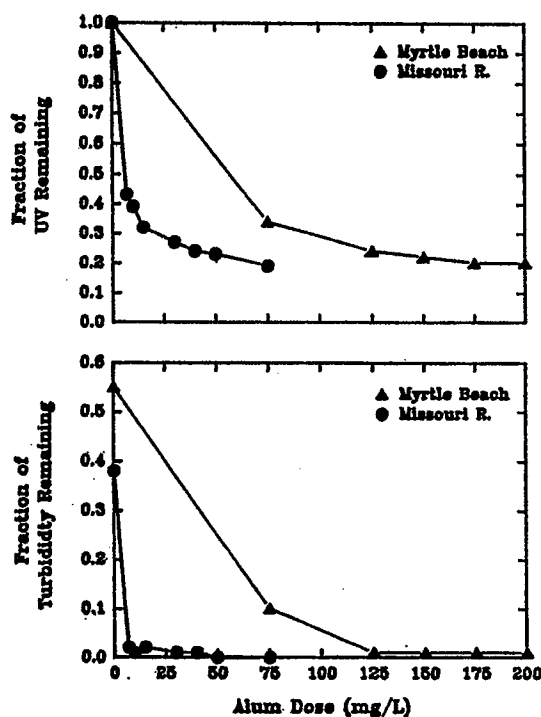


Fig. 3. Coagulation with alum at a constant pH of 7.

NATURAL ORGANIC MATTER

Organic carbon can be found in natural waters in two fractions, particulate (POC) and dissolved (DOC). Typically, the dissolved fraction is operationally defined as passing a 0.45 μm pore filter. The pool of POC may include bacteria, algae, zooplankton, and organic detritus, but usually it is a small fraction of the TOC compared to DOC, less than 10% except for highly eutrophic supplies.

Later some discussion of POC in the form of algae is given. Below, the emphasis is on dissolved natural organic matter, its nature and properties. Some arguments can be made, however, that humic acids which are high molecular weight (MW) negatively charged macromolecules, have colloidal properties.

Nature and Properties

NOM contains organic compounds that are both hydrophobic and hydrophilic in nature. Most attention in the past has been paid to the strong hydrophobic acid fractions of humic and fulvic acids (aquatic humics) that cause natural color. It has been estimated that on an average basis about 45% of the DOC in rivers is composed of hydrophobic aquatic humics (Thurman, 1985). This fraction of aquatic humics can vary widely from perhaps 10 to 90% with waters of high natural color being at the high end such as bogs, swamps, or supplies draining these systems.

Table 1 is a compilation of NOM hydrophobic and hydrophilic fractions with general chemical groups and compounds associated with each fraction. Generally, coagulants should be more effective in removing hydrophobic material over hydrophilic, and higher MW compounds over low MW. Additional insight into the fractions and their

TABLE 1 Natural Organic Matter Fractions and Chemical Groups *

Fraction	Chemical Groups
<u>Hydrophobic</u>	
<u>Acids</u>	
Strong	humic and fulvic acids, high MW alkyl monocarboxylic and dicarboxylic acids, aromatic acids
Weak	Phenols, tannins, intermediate MW alkyl monocarboxylic and dicarboxylic acids
<u>Bases</u>	Proteins, aromatic amines, high MW alkyl amines
<u>Neutrals</u>	Hydrocarbons, aldehydes, high MW methyl ketones and alkyl alcohols, ethers, furans, pyrrole
<u>Hydrophilic</u>	
<u>Acids</u>	Hydroxy acids, sugars, sulfonics, low MW alkyl monocarboxylic and dicarboxylic acids
<u>Bases</u>	Amino acids, purines, pyrimidines, low MW alkyl amines
<u>Neutrals</u>	Polysaccharides; low MW alkyl alcohols, aldehydes, and ketones

* (Based on: Leenheer *et al.*, 1982; Leenheer and Noyes, 1984; and Reckhow *et al.*, 1992).

characteristics is given in Table 2. The Forge Pond supply contains NOM in which 45% of the DOC is aquatic humics with a split of 59% hydrophobics and 33% hydrophilics. The aquatic humics, weak hydrophobic acids, and hydrophilic neutrals constitute 71% of the total DOC. These fractions also contain 30% of the DOC with AMW > 1000 and dominate the negative charge contributing at least 60% of it. This supply exhibits primary productivity so the hydrophilic neutral fraction (polysaccharides) may be typical of reservoirs and lakes, but higher than what would be found in streams and rivers.

Specific UV Absorbance Concept

Organic compounds that are aromatic in structure or that have conjugated double bonds absorb ultraviolet (UV) light. UV absorbance (UVA) at 254 nm is often used as a simple surrogate measurement for DOC that is especially effective for waters containing aquatic humics (Edzwald *et al.*, 1985). The specific UV absorbance (SUVA) defined as the UV absorbance expressed as per meter of absorbance per unit concentration of DOC in mg/L can be an instructive measurement for water supplies. As shown by the data in Table 2, the hydrophobic acids (particularly, humic and fulvic acids) have high SUVA values. The hydrophilic neutrals also have moderately high SUVA values (hydrophilic bases constitute only 3% of the DOC and are ignored). For Forge Pond, Reckhow *et al.* (1992) found DOC removals of 70 to 80% for the aquatic humic fractions (high SUVA values), only 10% DOC removals for the hydrophobic neutrals (low SUVA), and 30 to 50% DOC removals for the other fractions. These DOC removals with regard to SUVA agree with the following.

TABLE 2 Characteristics of NOM from Forge Pond*

Fraction	% of DOC [†]	AMW [#]	Charge ^{**} μeq/mg C	SUVA m ⁻¹ /mg C
<u>Hydrophobic</u>				
Humic Acid	7	70	5 - 10	6 - 6.5
Fulvic Acid	38	30	10 - 15	4 - 4.5
Weak	4	65	5	3.5
Bases	1.5	ND	-	< 1
Neutrals	8	35	-	< 1
<u>Hydrophilic</u>				
Acids	8	40	45 ⁺⁺	1
Bases	3	60	-	3
Neutrals	22	40	-	3.5 - 4

* Compiled from Reckhow et al. (1992);

† Initial DOC of 6.6 mg/L; lost 8% in processing;

Apparent molecular weight (ultrafiltration) as % of DOC in this fraction > 1000;

** Negative charge density at pH 8.

++ may be in doubt

Edzwald and Van Benschoten (1990) have made a case using SUVA data for several sources of aquatic humics, aquatic fulvics, and for several water supplies. Their data included DOC and THM precursor removals from bench-scale, pilot-scale, and full-scale plant studies for several coagulants. They proposed the following guidelines.

* SUVA values of 4 to 5. The DOC of a water is composed largely of aquatic humics. The DOC is relatively hydrophobic, aromatic, and of high molecular weight compared to waters with lower SUVA values. The DOC controls coagulant dosages, but due to its nature, relatively high removals of DOC are expected by coagulation.

* SUVA values of less than 3. The DOC is composed largely of non-humic materials. The organic matter is relatively hydrophilic, less aromatic, and of lower molecular weight compared to waters with higher SUVA values. For these type waters, the DOC will have a small, if any effect, on coagulant dosages and relatively low removals of DOC are expected.

COAGULANTS

Table 3 lists numerous aluminum based, ferric based, and cationic organic polyelectrolytes available for water treatment. The focus of the discussion is on aluminum based coagulants. Alum is the most widely used water treatment coagulant. Over the last ten years there has been great interest and some use of prehydrolyzed aluminum chemicals sold as polyaluminum chlorides. The chemistry of the Al species formed depends on the solution strength (total aluminum concentration, Al_T), ligand number (OH_{added}/Al_T) or basicity, mixing conditions, and the anions present.

Specialty formulations of PACls can be prepared with low (about 1) to high (about 2 to 2.5) ligand numbers, small amounts of sulfate, as well as adding certain base cations.

TABLE 3 Primary Coagulants Used in Water Treatment

Name	Comments
Alum	Widely used
Sodium aluminate	Used with alum; provide alkalinity and pH control
Aluminum Chloride	Used in blends with organic polymers
Polyaluminum Chloride (PACl)	Several formulations based on Al strength, $[\text{OH}^-]/[\text{Al}_T]$, and anions and cations added
Polyaluminum Sulfate	Produced on-site
Ferric Chloride	Widely used
Ferric Sulfate	Widely used
Ferric Chlorosulfate	Used
Polyiron Chloride	Produced on-site
Cationic Organic Polymers	Wide variety of formulations with different charge densities and molecular weights; Poly (DADMAC)* and Epi/DMA† types are common

* Poly (DADMAC): polydiallyldimethylammonium chloride; molecular weights 10^4 to 10^5 with charge densities up to 6 meq/g active polymer.

† Epi/DMA: polyquaternary amine polymers prepared from epichlorohydrin and dimethylamine; molecular weights 10^4 to 10^5 with charge densities up to 8 meq/g active polymer.

Three advantages often cited for PACl are 1) high charge, moderate MW species such as $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ exist for coagulation, 2) unlike alum where Al hydrolysis products are formed in situ, the Al species already exist and are available for coagulation, and 3) it is less temperature dependent than alum.

Alum and PACl Solubility and Temperature Effects

Much of the following was taken from a paper by Van Benschoten and Edzwald (1990a). The solubility of Al for alum and PACl additions to deionized water is shown in Fig. 4 for water temperatures of 4 and 25°C. Experiments were done for about a two hour reaction or detention time. The soluble species used in Fig. 4a (alum case) to construct the theoretical curves included only Al^{+3} , $\text{Al}(\text{OH})^{2+}$, and $\text{Al}(\text{OH})_4^-$.

Amorphous $\text{Al}(\text{OH})_3$ was assumed as the solid phase controlling solubility and no polymeric species of Al were included. Pretty good agreement is found between theoretical predictions and experimental data. It is frequently cited that cationic polymeric forms of Al exist under certain acidic pH conditions and are available to

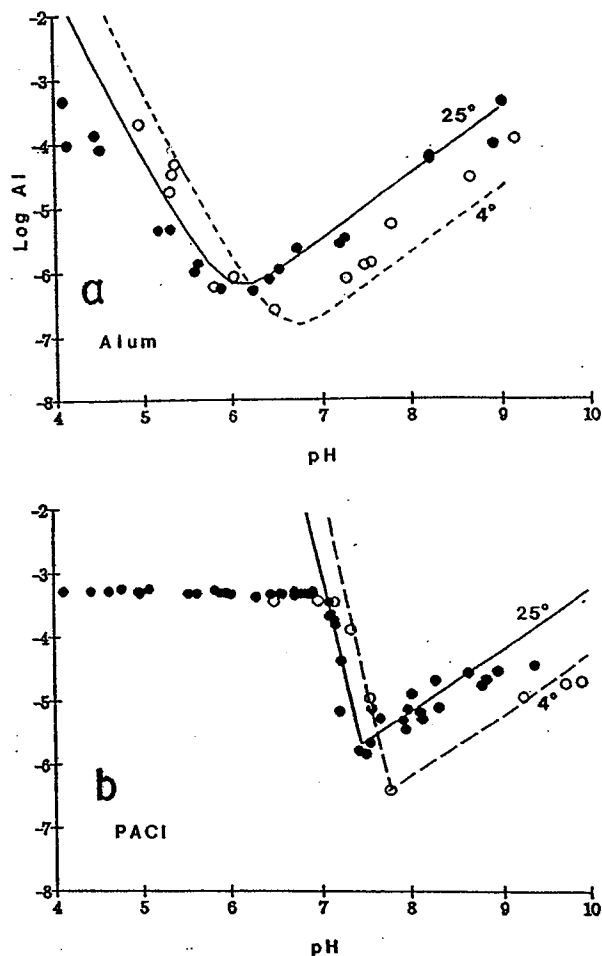


Fig. 4. Solubility plots of dissolved aluminum for alum and PACl in deionized water at 25°C and 4°C versus experimental data. (a) Alum: solid and dashed lines are theoretical solubility of aluminum in equilibrium with $\text{Al}(\text{OH})_3(\text{am})$ ($\text{pK}_{\text{so}} = 31.5$). (b) PACl: solid and dashed lines drawn to show data trends and do not represent theoretical solubility curves.

adsorb on negatively charged particle surfaces producing charge neutralization. While the agreement between experiment and theory to construct the solubility diagram does not prove the absence of Al polymers, other Al characterization data of Van Benschoten and Edzwald (1990a) showed only Al monomers present for alum.

The effect of low temperature on Al solubility for the alum case (Fig. 4a) is twofold. First, the pH of minimum solubility is shifted about a one-half pH unit higher - from pH 6.2 to about pH 6.7. Second, the solubility of Al decreases for pH above 6.2 and increases below pH 6.2. Clearly, water temperature affects Al behavior in coagulation and can affect residual Al leaving water plants.

The PACl data are presented in Fig. 4b. The lines are drawn to show data trends; they do not represent theoretical solubility curves. The data show that PACl is stable below about pH 7, and is much less affected by temperature than alum. It does not precipitate and polymeric Al species exist for adsorption and charge neutralization. Above pH 7, it does precipitate so that its soluble concentration is similar to alum.

HYDROPHILIC PARTICLES

Electrical double layer (EDL) interactions between charged particles can explain particle stability for hydrophobic particles, but hydrophilic effects due to adsorbed or chemically bound water at particle surfaces also affects particle stability (e.g., silica particles are stable at pH conditions of zero charge). Aluminum hydroxide precipitated in deionized water with alum forms an amorphous solid phase that contains adsorbed or bound water giving it a jelly type appearance.

The flotation of freshly precipitated aluminum hydroxide particles was examined as a function of pH (Edzwald *et al.*, 1990). The results are presented in Fig. 5. The EPM data show an isoelectric point at about pH 8 (pH_{iep} of zero charge). At 20°C (middle panel) the turbidity following flotation improves as you increase the pH and reduce the charge of the particles (EDL effects are between positively charged $Al(OH)_3$ particles and positively charged microbubbles), but the residual turbidity is between 1 to 2 NTU indicating some particle-bubble stability. This is clearly shown at 4°C (top panel) where poor turbidity removal occurs at all pH conditions including the pH_{iep} . These results suggest that when alum is used to treat waters of low turbidity and low DOC, the particles formed should be largely amorphous $Al(OH)_3$ and their stability is due in large part to hydrophilic effects.

COAGULATION OF NATURAL ORGANIC MATTER

General

This presentation is directed at the coagulation of NOM with aluminum coagulants; similar chemical reactions should apply to other coagulants. Material presented above on the nature and characterization of NOM identified hydrophobic acid fractions as the primary fractions of NOM subject to removal by coagulation. To remove this material requires neutralization of the negative charge which is estimated at 5 to 15 $\mu eq/mg$ DOC depending on pH - say about 10 $\mu eq/mg$ DOC for an average number.

Fig. 1 portrays the removal of NOM by coagulation through a phase change; i.e., the NOM must be either directly precipitated into particles or the NOM must be adsorbed onto particles. The precipitation reaction would follow complexation reactions between the metal (Al) and the organic ligands constituting the NOM. The organic ligands that are negatively charged cause strong electrostatic based complexation reactions with positively charged Al species. When the negative charge is satisfied, precipitation occurs. Even under conditions when adsorption of NOM onto amorphous $Al(OH)_3$ occurs, the adsorption reactions can involve NOM that is complexed to some degree with aluminum. To summarize, the removal of NOM from solution by Al coagulants may involve several chemical reactions including:

- 1) Al complexation reactions with NOM, particularly reactions with humic and fulvic acids acting as strong organic ligands for Al;
- 2) Al hydrolysis reactions where the inorganic ligand, OH^- , competes with organic ligands;
- 3) Direct precipitation of Al-NOM particles (or Al-Humates) following complexation and charge neutralization;
- 4) Adsorption of NOM, may be complexed Al-NOM species, on amorphous $Al(OH)_3$ particles which precipitate following coagulant addition.

It is argued that under neutral or acidic pH conditions, humic and fulvic acid organic ligands would complex Al creating a demand for Al that must be satisfied before precipitation of $Al(OH)_3$ can occur producing removal of NOM by adsorption per #4.

When Al coagulants are used in practice, we refer to a coagulation process, but we are actually relying on chemical precipitation processes for removal of the NOM. The particles produced (Fig. 1) may be unstable or stable depending on the coagulant used

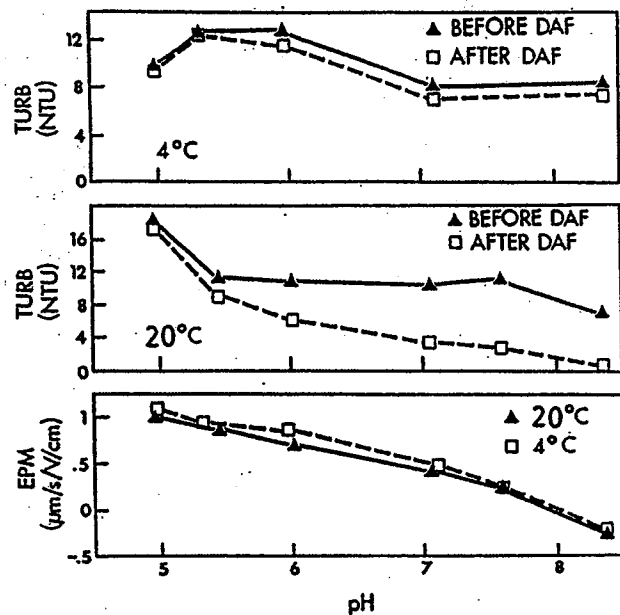


Fig. 5. Precipitated $\text{Al}(\text{OH})_3$ particles from alum addition ($5 \times 10^{-4} \text{ M}$) to demineralized water: EPM data and residual turbidity after flotation.

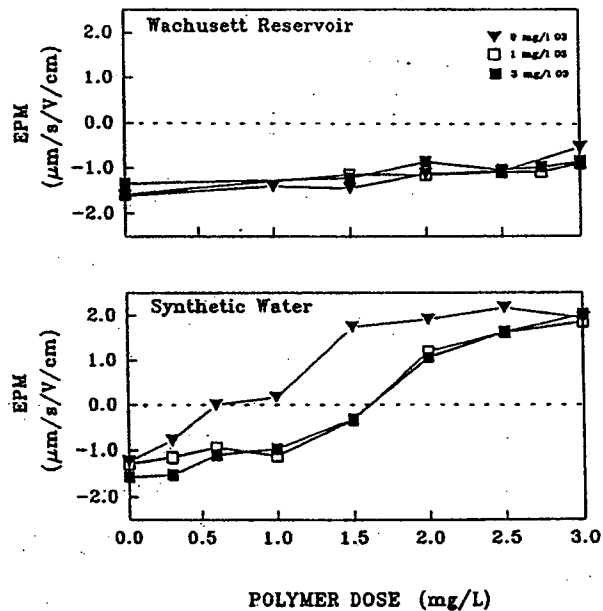


Fig. 6. Effect of preozonation on the surface charge of *Cyclotella* sp. in Wachusett Reservoir water and a synthetic water (2×10^4 cells/mL; synthetic water at pH 7, $10^{-3} \text{ M NaHCO}_3$, 30 mg/L Ca as CaCO_3).

(e.g., stable particles from overdosing with PACl or alum at low pH) and pH conditions (charged particles depending on pH vs. isoelectric pH of solids).

Modelling Aluminum-Fulvate Complexation

Van Benschoten and Edzwald (1990b) have presented complexation models for alum and PACl reactions with fulvic acid (FA). They accounted for Al speciation and measured Al fractions for FA of known concentration in terms of $\mu\text{eq}/\text{mg}$ DOC. The PACl used in their experiments had been prehydrolyzed to a ligand number of 2.5 ($n = 2.5$, OH/Al_T).

From pH 5 to 7, they found for typical coagulant dosages the following. When alum is used, Al complexed with FA is hydrolyzed to a ligand number of 2.7. For the PACl used, the results indicated that the preformed Al polymers underwent slight additional hydrolysis and complexing with FA. For the complexed species, $n = 2.8$ was found, very close to the alum results.

For the alum and PACl results, a hydrolysis ligand number of about 2.7, $\text{Al}(\text{OH})_{2.7}^{+0.3}$ was found when Al complexed with FA. The data also showed the average mass of complexed Al per unit mass of DOC was 0.61 mg Al/mg DOC. A water containing 1 mg/L DOC would require 0.61 mg/L Al, which supplies a positive charge from $\text{Al}(\text{OH})_{2.7}^{+0.3}$ of about 10 $\mu\text{eq}/\text{L}$. This agrees with the expected negative charge for 1 mg/L DOC of aquatic fulvic acid, i.e., about 10 $\mu\text{eq}/\text{mg}$ of DOC (Table 2). The above analysis suggests that PACl coagulants, especially those prehydrolyzed to high ligand numbers, would not be good choices for waters with high concentrations of NOM containing aquatic humics. Minimizing hydrolysis of the aluminum, means less Al is needed for complexation and charge neutralization. In other words, with no hydrolysis Al^{+3} has a charge of +3 per Al atom which is more effective than AlOH^{+2} or the Al_{13} polymer ($\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{+13}$) in $\frac{+13}{24} \approx +0.54$ +7 PACl which has a charge of +0.54 per Al atom. The vast experience with alum and iron coagulation of natural color verifies this analysis and has shown less coagulant is needed at lower pH conditions. The pH at which coagulation is actually carried out depends also on water buffering, temperature, residual coagulant considerations, and particle stability of the precipitated particles.

Coagulant Dosages and Removals of NOM

The specific UV absorbance (SUVA) concept was presented above. Guidelines were presented that for waters with SUVA values of 4 or higher, then the DOC of these supplies is composed largely of hydrophobic aquatic humic and fulvic acids. For these waters, a stoichiometry between Al and the NOM should exist. The exact stoichiometry depends on the concentration of humic and fulvic acid fractions relative to the total DOC, pH, coagulant (alum vs. PACl), and sequence of coagulant addition with regard to acid or base addition for pH adjustment.

In the section prior to this, data from Van Benschoten and Edzwald (1990b) indicated a stoichiometry based on complexation and charge neutralization of about 0.6 mg Al per mg FA as DOC. This figure is an average. Specific data indicated pH dependence with lower values with decreasing pH and higher values with increasing pH. Edzwald and Van Benschoten (1990) used this aluminum complexation data and data from the literature for model aquatic humics and for natural waters high in color to propose the following coagulant dosage guidelines for alum and PACl.

pH about 5.5: 0.5 mg Al per mg DOC
pH about 7: 1 mg Al per mg DOC

As an example, the Intracoastal Waterway (Myrtle Beach water supply) had a UV (254 nm) absorbance of 0.87 cm^{-1} , a DOC of 20.7 mg/L yielding a SUVA of $4.2 \text{ m}^{-1}/\text{mg}/\text{L}$. The SUVA indicates that this supply is high in aquatic humics. The estimated alum dosage at pH

7 based on 1 mg Al per mg DOC would be about 175 mg/L (as alum) which is in agreement with Fig. 3.

I have examined the removals of UV, DOC, and THM precursors (based on TTHMFP) for many different type water supplies. The data base includes laboratory, pilot plant, and full-scale plant studies. The following guidelines are offered.

- * For waters high in aquatic humics (relatively high SUVA values), removals of 50 percent or greater should be expected; for SUVA values of 4 to 5, DOC removals of about 70 percent should be achieved.
- * For waters low in aquatic humics (relatively low SUVA values), removals should be less than 50 percent; for SUVA less than 3, DOC removals of 30 percent or lower should be expected.

Generally speaking UV removals are higher than DOC, and TTHMFP removals depend on the formation potential test conditions. Table 4 illustrates this for four water supplies; two with NOM high in aquatic humics (high SUVA) and two with NOM low in aquatic humics.

TABLE 4 Removals of UV, DOC and TTHMFP

Water Supply	SUVA $\text{m}^{-1}/\text{mg/L}$	Percent Removals			Data Base
		UV	DOC	TTHMFP	
Middleton Pond (Danvers, MA)	4.5	90	70	NM	Full-Scale Plant Data
Grasse River (Canton, NY)	4.6	80	70	72	Bench, Pilot, and Full-Scale
Lake Champlain (Burlington, VT)	2.5	56	23	NM	Full-Scale
Wachusett Reservoir (Boston, MA)	2.1	30-60	22	45	Bench and Pilot-Scale

NM - Not measured

COAGULATION OF ALGAE AND OZONE EFFECTS

How ozone causes a reduction in the coagulant dose or induces flocculation is not well understood. Several mechanisms have been proposed. These include: 1) increased Al complexation with natural organic matter (NOM), 2) increased Ca complexation with NOM, 3) reduction in particle stability due to loss of adsorbed organic matter from particles, 4) polymerization of NOM, 5) break-up of metal-organic complexes such as iron yielding in situ production of metal coagulant, and 6) reactions with algae. Most studies of preozonation effects on coagulation and flocculation have been directed at the role of humic substances (Farvardin and Collins, 1989) and the effects of ozone on the interaction of humic substances with various mineral particles (Grasso and Weber, 1988; Dowbiggin and Singer, 1989; Jekel, 1990). Less research has been done on the role of algae in ozone induced coagulation and flocculation. Algae during growth excrete polysaccharides, pectins, lipoproteins, and polyamino acids. The amount and structure of this extracellular organic matter (EOM) attached to the algae cell surfaces and released to the bulk water phase depends on algae type and algal physiological growth phase (Lüsse et al., 1985; Bernhardt et al., 1986; Bernhardt and Clasen, 1991). The EOM may cause steric stability or depending on the structure of

the adsorbed material and the ionic strength or Ca concentration may flocculate particles via interparticle bridging.

It is often stated that ozone causes algal cell lysis releasing intracellular organic matter (IOM) to solution. If the IOM were of sufficient molecular weight and structure, it could flocculate mineral particles but obviously not the destroyed algae. Cell lysis and release of IOM is probably not a likely mechanism since ozone does not destroy (lyse) most algae cells at ozone dosages frequently used to aid coagulation and flocculation such as 3 mg/L or less (Edzwald and Paralkar, 1992). In fact, high concentrations of released intracellular or extracellular organic matter are more likely to impair coagulation by increasing the coagulant demand or by adsorbing and stabilizing mineral particles (Bernhardt *et al.*, 1985, 1986). This may occur at high ozone dosages or for eutrophic lake conditions where high concentrations of EOM in solution may exist.

Some interesting data on the effects of ozone on algae are presented next (Edzwald and Paralkar, 1992). First, Fig. 6 shows the effect of ozone dose on the cationic polymer dose required for charge neutralization (EPM of zero) of *Cyclotella*, a diatom. The required polymer dose is about 0.6 mg/L in a synthetic water while a charge of zero is not obtained for a natural water for polymer dosages up to 3 mg/L. The hypothesis is that the presence of natural organic matter in Wachusett Reservoir water, particularly DOC, exerts a demand for cationic polymer. The second point is that ozone had more of an effect on EPM data for the experiments done in a synthetic water in contrast to the experiments done in natural waters. Ozone causes more polymer to be needed for charge neutralization for the synthetic water. On the other hand, in the natural water (top part of Fig.) ozone has little effect on the EPM data. It is noted that ozone was applied under batch conditions so the reported ozone dosages are both applied and absorbed dosages. Other data not shown for residual turbidity and algae number indicated that the algae flocculated at polymer dosages less than needed for charge neutralization indicating that the stability of the algae was not due solely to charge.

Other experiments were conducted on the effect of ozone on the flocculation rate of algae for three different algae; *Chlorella vulgaris* (green alga), *Scenedesmus quadricauda* (green alga), and *Cyclotella sp.* (diatom). These experiments were all done under log growth phase conditions. The flocculation rates were measured in terms of α , particle stability factor where higher values of α indicate a faster rate of flocculation and less stable particles. The results showed that ozone at absorbed doses of 1 to 3 mg/L increased the flocculation rate (higher α) for *Scenedesmus* and *Cyclotella*, but not for *Chlorella*. Lower α values following ozone addition were found for *Chlorella*. The study showed that 1) Ca concentration and 2) concentration and molecular weight (MW) of the EOM were important factors in determining whether ozone increased α . *Scenedesmus*, for example, at 1 mg/L ozone flocculated more rapidly as Ca increased from 0 to 50 mg/L CaCO₃. At higher ozone (3 mg/L), however, the highest α values were observed in the absence of Ca.

Significant findings of the study had to do with the production of EOM and the MW distribution. *Chlorella* produced very little EOM. Most of the EOM was transformed upon ozonation to low MW material (< 3000 daltons). *Scenedesmus* produced 10 times more EOM than *Chlorella* and about 70 percent of the EOM prior to ozone was of a high MW (> 30000 daltons). Ozone shifted the MW distribution to lower MW materials. After ozonation, about 40 to 50 percent of the EOM was of intermediate (3000 to 30000 daltons) or high MW corresponding to approximately 1 μg DOC/10⁶ cells. *Cyclotella* underwent microfloculation. It produced 36 times more EOM than *Chlorella* and about 90 percent of the EOM prior to ozone was of a high MW. Ozone shifted the MW distribution to lower MW materials; however, after ozonation about 40 to 50 percent of the EOM was still present as intermediate or high MW material corresponding to approximately 3 μg DOC/10⁶ cells.

CONCLUDING REMARKS

The traditional view of coagulation is to describe destabilization of colloids, particularly mineral particles. A case is made that for many waters natural organic matter (NOM) controls coagulant dosages, not turbidity causing particles initially present in a water supply. NOM consists of a mixture of organic compounds with different chemical structures and properties. Classification according to hydrophobic and hydrophilic fractions is instructive. On average, about 45% of the DOC in rivers is composed of hydrophobic humic and fulvic acids. Higher fractions of these hydrophobic acids would be found in bogs, swamps, and supplies draining these systems; the NOM in lakes and reservoirs would contain lower fractions. The negative charge and chemical structure of the hydrophobic acids affect reactions with metal based coagulants. The removal of NOM from solution by Al coagulants may involve several chemical reactions including 1) Al complexation reactions with NOM, 2) Al hydrolysis reactions, 3) direct precipitation of Al-NOM particles, and 4) adsorption of NOM or complexed Al-NOM species to amorphous $\text{Al}(\text{OH})_3$.

Specific ultraviolet absorbance (SUVA) can be used to estimate whether the NOM of a water is high or low in hydrophobic acids and to estimate removals of DOC by coagulation. Preozonation of water supplies containing algae may lead to microflocculation or impair coagulation depending on algae type, concentration and molecular weight of extracellular organic matter (EOM), and ozone dose.

ACKNOWLEDGMENTS

The subject of coagulation has been of great professional interest to the author for about twenty five years. The author has learned much during this time from Charles R. O'Melia and continues to benefit from his wisdom. The author is also grateful to all my former graduate students; they taught me well.

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