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# Water Technology

## Stoichiometric Relationship Between Humic and Fulvic Acids and Flocculants

Nava Narkis and Menahem Rebhun

**The investigation of the flocculation of humic and fulvic acids has shown that the sodium salts of these acids, which are anionic polyelectrolytes, react chemically with the flocculants, such as cationic polyelectrolytes, and aluminum sulfate through carboxylate and phenolate groups. A stoichiometric relationship has been found between humic and fulvic acids content in solution and the cationic polyelectrolyte or alum dose required for effective flocculation of the humic substances. As the pH value becomes lower, flocculation is better; the degree of dissociation of the organic molecule is lower, and the flocculant requirement is lower.**

In addition to mineral turbidity, surface waters, lakes, and rivers contain organic matter responsible for the yellow-brown color and for taste and odor. The organic matter poses special problems for water-treatment processes. Black<sup>1,2</sup> isolated these organics by low pressure evaporation of colored surface waters and subsequent separation, based on solubility differences at various pH levels. Black found that various sources of water contained from 15–50 mg/l of naturally occurring organic matter, of which the main constituents have been defined as fulvic acids—87 per cent, together with humic acids—11 per cent, and humic acids—2 per cent. Similar compositions have been found in rivers by Packham<sup>3</sup> who isolated 8 mg/l of humic substances. These organics are composed of high molecular weight aromatic substances that display polyanionic characteristics in neutral or alkaline solutions.

Humic substances isolated from various soils have similar characteristics, although they differ in small details.<sup>4</sup> Up to now, no specific chemical formula has been proposed that describes the molecular structure with complete confidence. General types or frames of structures have been proposed, fitting the general known characteristics.<sup>5</sup> Degradation of humic substances has shown that their molecules contain alcoholic-OH, phenolic-OH, carboxylic, methoxylic, and chinoidic groups as the main functional constituents. Amino acids and polypeptides also were isolated among decomposition by-products, indicating that the nitrogenous groups are not a part of the basic chain structure.<sup>6</sup>

The typical color of surface waters is between 5 and 200 color units (CU).<sup>7</sup> Drinking water standards permit up to 5 CU. At pH 8.0, a solution of 1 mg/l of humic acids has 26.5 CU, while a solution of 1 mg/l of fulvic acids is ten times less colored and has 2.8 CU.

The organics inhibit removal of iron and manganese from groundwaters during aeration and sedimentation<sup>8</sup> and interfere with demineralization processes, since fouling of the resin or membrane occurs, diminishing exchange and desorption efficiencies.<sup>9</sup> Humic substances absorb light and interfere with the normal growth of aquatic life.

From the public health point of view, humic and fulvic acids are harmless as pure compounds, but their ability to form stable complexes with heavy metals, such as lead, and to adsorb pesticides and insecticides may cause health hazards. Recently their chlorinated by-products were said to be harmful to fish. For these reasons, water-treatment techniques include methods for the removal of fulvic and humic acids.

In some places, oxidation by ozone or chlorine is used. The oxidation processes have some disadvantages:

1. They are expensive.
2. The organic matter is not completely oxidized to CO<sub>2</sub> but remains in solution as colorless, stable, dissolved organic molecules that may still interfere with water use.<sup>1,10</sup> Therefore, separation techniques, such as flocculation, should be used for complete removal of the organics from solution.

### Behavior of Humic Substances in Flocculation

Humic substances are the end products of the decay of vegetable matter and can be expected to remain stable in natural waters. Their interference in flocculation processes has been shown to be related to their activity as protective colloids. Previous research<sup>11-13</sup> on flocculation processes in the presence of organic matter has shown that humic and fulvic acids stabilize mineral suspensions and cause changes in flocculation processes. When a cationic flocculant is added to a clay or an organo-clay complex suspension dispersed in humate or fulvate solution, colloids and organic matter compete for reaction with the flocculant.<sup>12</sup> The organic acids were found to react first. Only after complete reaction of the flocculant with the organic matter does flocculation of the suspension begin. The removal of the humates or fulvates from solution is essentially the result of charge neutralization, with bridging leading to flocculation and subsequent settling of the reaction product. Therefore, large doses of flocculant are necessary for good clarification of turbid water that contains organic matter.

As a result of previous study<sup>14</sup> on flocculation conditions of natural surface waters, a stoichiometric reaction between cationic flocculants and organic matter was suggested.

The work reported here confirms this hypothesis and demonstrates the existence of a quantitative relationship between humic or fulvic acids and cationic flocculants.

### Experimental Materials

The following materials were used for the experiments:

1. Humic acids, available from a chemical company\*
2. Fulvic acids, prepared from peat from the Huleh Valley, Israel, as reported by Narkis and Rebhun<sup>12</sup>
3. Cationic polyelectrolyte—a polyethylene imine† with a molecular weight of 30,000
4. Aluminium sulfate: Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 18H<sub>2</sub>O

\*Aldrich Chemical Co. Inc., Milwaukee, Wis.  
†Purifloc C-31, The Dow Chemical Co., Midland, Mich.

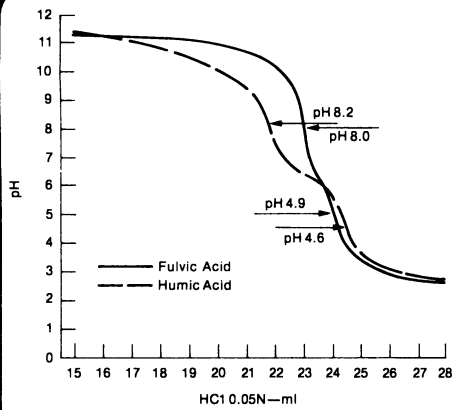


Fig. 1. Potentiometric Titration Curve of Fulvic and Humic Acids

TABLE 1  
Phenolic-OH and -COOH Groups in Humic and Fulvic Acids

Acids	Anionic Groups		
	-OH me/100 g	-COOH me Ca <sup>++</sup> /100 g	Σ -COOH + -OH me Ba <sup>++</sup> /100 g
Fulvic	308	164	472
Humic	425	445	870

TABLE 2  
Cationic Polyelectrolyte and Alum Required for Reaction With Humic and Fulvic Acids Solutions as a Function of the Anionic Groups

Acids	Concentration mg/l	Σ-COO- + -O- μe/l	-COO- μe/l	-O- μe/l	Cationic Poly- electrolyte* Optimal Dose at pH 8.0 μe/l	Alum Optimal Dose	
						μe/l	pH
Humic	5	43.5	22.2	21.3	43.1	27	6.7
Humic	10	87.0	44.5	42.5	79.5	45	6.6
Humic	25	218	111	107	190		
Humic	50	435	222	213	342	97.7	6.0
Fulvic	25	118	41.0	77	101		
Fulvic	50	236	82	154	228	90	5.8
Fulvic	100	472	164	308	380		

\*Purifloc C-31, The Dow Chemical Co., Midland, Mich.

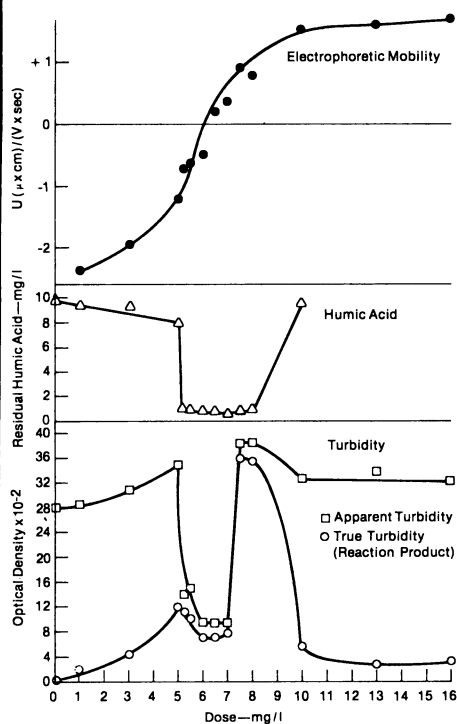


Fig. 2. Effect of Cationic Polyelectrolyte on Na-Humate Solution 10 mg/l humic acid. pH of 8.0

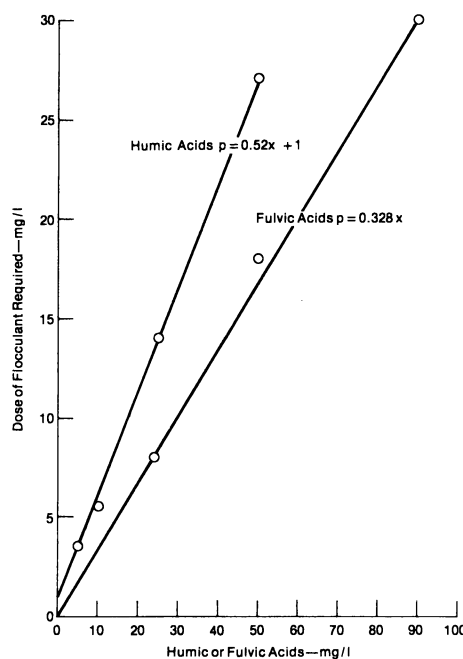


Fig. 3. Optimal Dose of Cationic Polyelectrolyte Required As a Function of Na-Fulvate and Na-Humate Solutions pH = 8.0

### Electrically Charged Groups

Humic and fulvic acids are anionic polyelectrolytes. Their degree of ionization depends on pH.

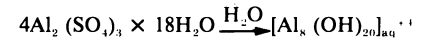
Figures 1 shows potentiometric curves of humic and fulvic acids. Two inflection points can be observed on the titration curves. The first, at pH 8.0 for humic acids and pH 8.2 for fulvic acids, corresponds to the phenolic-OH groups. The second, at pH 4.9 for humic acids and pH 4.6 for fulvic acids, corresponds to the carboxylic (-COOH) groups. The amount of the anionic functional groups expressed in me/100 g of humic or fulvic acids has been determined by the method recommended by Kononova<sup>13</sup> and is summarized in Table 1. This table shows the exchange adsorption capacity of phenolate and carboxylate ionic groups in humic and fulvic acids. These anionic groups are responsible for the reaction of fulvic and humic acids with the chemicals used as flocculants in water treatment. Thus, it can be assumed that in waters investigated at pH 8.0 or above the organic materials underwent complete dissociation. At a pH below 8.0, the dissociation was only partial.

The amount of effective positive charge in the flocculant molecules can be calculated also. In the cationic polyelectrolyte, which is a polyethylene imine, the amino group is charged positively because of the reaction with HCl.

The authors postulated that the positive-charge-carrying unit structure has an average empirical formula  $-CH_2-CH_2-NH^+HCl^-$  with a molecular weight of 79.5.

Alum, the inorganic flocculant, is hydrolyzed very easily. There is a step-wise conversion of the positive aluminium hydrated ion to the negative aluminate ion.<sup>16,17</sup>

Different aluminium hydrolysis products are known to be formed at different pH values. Matijevic and coworkers<sup>16,18</sup> showed that hydrolysis of aluminium salts in the pH range between 4 and 7.0 leads to the formation of a soluble polynuclear tetravalent aluminium hydroxo complex, with the empirical formula  $[Al_8(OH)_{20}]_{aq}^{++}$ , as the main hydrolysis product. One molecule of the tetravalent aluminium hydroxo complex  $[Al_8(OH)_{20}]_{aq}^{++}$  is formed from four molecules of alum, according to the equation



Thus, at the conditions of the experiments, it can be approximated that each molecule of alum develops a unit positive charge, or one equivalent.

Alum is an effective flocculant at pH range 4 and 7.0 in which the tetravalent aluminium hydroxo complex is dominant.<sup>16,20</sup>

### Flocculation of Humic and Fulvic Acids

The effect of the cationic polyelectrolyte on 10 mg/l sodium humate solution at pH

8.0 is shown in Fig. 2. The curves are also typical of what is obtained for sodium fulvate solutions. Three curves are shown, optical density of true turbidity, residual humate concentration, and electrophoretic mobility, each as a function of flocculant dose. Both sodium humate and fulvate solutions react chemically with the cationic flocculant and form a colloidal precipitate, observed as turbidity. This turbidity increases with increasing polymer dose up to a maximum. If the flocculant dose is increased further, the reaction product flocculates and settles. At higher doses, flocculant is adsorbed on the reaction product and a stable dispersion is produced once more.

The turbid reaction product can be removed by centrifuging. Determination of residual sodium humate and fulvate in the supernatant liquid shows that the maximum turbidity is produced at precisely the optimum flocculant dose required for precipitation, which is not necessarily a dose for good flocculation. This dose is slightly lower than that at which the isoelectric point is reached.

The amount of flocculant required for removal of fulvic or humic acids depends on the concentration of organic matter in solution.

In Fig. 3, a linear relationship between the concentration of humic and fulvic acids and the dose of flocculant required for the removal of these organics from solution is seen.

As regards alum, a linear relationship also exists only at low concentrations of humic acids—up to 10 mg/l (Fig. 4). The linear relationship shows that the chemical reaction between two polyelectrolytes of opposite charge is stoichiometric in nature.

Table 2 shows the optimal doses of cationic polyelectrolyte required for complete reaction with humate and fulvate solutions as a function of the anionic groups.

Given the quantities of  $-COOH$  carboxylic and  $-OH$  phenolic groups in fulvic and humic acids, the relationship is  $\mu e/l$  between organic matter and flocculants can be calculated.

The experiments with the cationic polyelectrolyte were carried out at pH 8.0, in which both functional groups are in anionic form. The flocculant demand corresponds well with the equivalent anionic groups available in fulvate and humate solutions. A stoichiometric reaction expressed in  $\mu e/l$  exists between the cationic polyelectrolyte and the sum of phenolate and carboxylate groups. A solution of 5 mg/l of humic acid containing a total of 43.5  $\mu e/l$  of carboxylate and phenolate groups, reacts with 43.1  $\mu e/l$  cationic polyelectrolyte. Or, a solution of 50 mg/l fulvic acids containing a total of 236  $\mu e/l$  carboxylate and phenolates reacts with 228  $\mu e/l$  of the cationic polyelectrolyte.

The experiments show that this is a charge-neutralization reaction between the

polycation and phenolate and carboxylate group in the molecule of humic and fulvic acids.

At high concentrations of humic and fulvic acids there is a deviation from strict stoichiometry, which may be caused by screening of charged groups during the formation of the reaction product.

### Effect of pH

Figure 5 shows flocculation of a 10-mg/l humic acids solution with the cationic polyelectrolyte at various initial pH levels.

The reaction of humic and fulvic acids with flocculants is sensitive to the pH of the solution, affecting the degree of dissociation and the type of groups that are ionized. At low pH, the flocculant demand is reduced, and the dose range for good clarification is narrowed. This is because less anionic groups in the organic molecule take part in the reaction.

Table 3 shows the quantities of the polycationic flocculant in  $\mu e/l$  that react with 10 mg/l humic acids at various levels of pH.

The inorganic flocculant alum also removes humic and fulvic acids from solution by chemical reaction between the positively charged chains of the tetravalent aluminium hydroxo complexes and the organic polyanions. During hydrolysis of alum, protons are released. At the optimal dose range the pH decreases to within the range 5.8–6.7.

At this pH range, the assumption that only the carboxylic groups are dissociated can be made. Table 2 shows that a stoichiometric reaction occurs between carboxylate groups and alum. In solution of 10 mg/l of humic acids at pH 6.6, 44.5  $\mu e/l$  of carboxylate ions react with 45  $\mu e/l$  of alum, while 82  $\mu e/l$  carboxylate ions in a solution of 50 mg/l fulvic acids at pH 5.8 react with 90  $\mu e/l$  of alum. In this case, there is also a deviation from stoichiometry at high concentrations of humic acids.

### Discussion

Humic and fulvic acids solutions react chemically with cationic flocculants by means of charge neutralization.<sup>12</sup> The interactions between polyelectrolytes of opposite charge usually give rise to strong association complexes that form precipitation. The respective distribution of charge in solution of a simple electrolyte and a polyelectrolyte are not the same.<sup>19,20</sup> In the solution of a simple electrolyte, charge distribution is uniform, whereas the structure of polyelectrolyte molecules leads to the formation of localized regions of high charge density in the vicinity of each polymer molecule. This leads to strong electrostatic interactions between polyanion and polycation.

In a solution of the sodium salt of humic or fulvic acids, every segment of the molecule containing an anionic group is naturally surrounded by  $Na^+$  ions. Upon the addition of a solution of cationic polyelectrolyte to a solution of humate or fulvate,

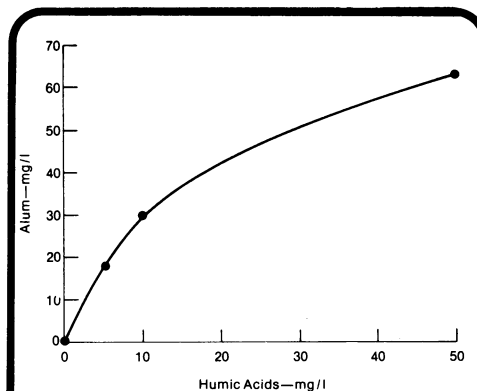


Fig. 4. Optimal Dose of Alum Required As a Function of Humic Acids Initial Concentration in Humate Solutions

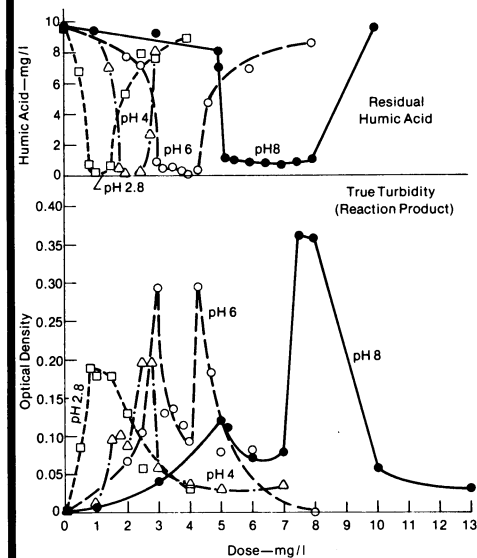


Fig. 5. Effect of Cationic Polyelectrolyte on 10 mg/l Sodium Humate Solution at Various pH Levels

the attraction between the oppositely charged electrostatic fields draws the molecules together, and many  $Na^+$  ions are replaced by the polycation species. In the same way  $Cl^-$  ions, accompanying the cationic polyelectrolyte molecule or  $SO_4^{=}$  of the aluminum hydroxo complexes, are replaced by polyanion. Cross-linking occurs, and the resulting product is insoluble.<sup>21</sup> At high concentrations of humic acids solutions, the interaction may not be complete, and surplus charges on the polyelectrolyte molecules are accompanied at high concentrations by  $Na^+$  or  $Cl^-$  ions, possibly resulting in a deviation from stoichiometry.

The removal of polyanionic organic matter from solutions by the use of oppositely charged cationic flocculants is essentially the result of charge neutralization. Bridging then leads to flocculation and subsequent removal of the reaction product that has already been neutralized.<sup>12</sup> In this work the occurrence of the flocculation of humic substances through charge neutralization and, thus, a stoichiometric relationship between the concentration of anionic groups and the flocculant demand have

TABLE 3  
Amount of Cationic Polyelectrolyte Required for Reaction With 10 mg/l Humic Acids Solution As a Function of Anionic Groups Present at Various pH Values

pH	Dissociated Anionic Groups			Cationic Polyelectrolyte	
	-COO- μe/l	-O- μe/l	Σ-COO- + -O- μe/l	mg/l	μe/l
2.8	—	—	—	0.8	10.1
4.0	< 44.5	—	—	1.8	22.8
6.0	44.5	—	44.5	3	38
8.0	44.5	42.5	87	6.25	79.5

been postulated. The reaction of flocculation is sensitive to the pH of solution. At low pH, flocculation is improved. Decreasing pH leads to a decrease in the degree of dissociation of the organic molecules of humic and fulvic acids, and the flocculant demand is reduced correspondingly. Generally, lower pH means a higher degree of ionization of the cationic polyelectrolyte, although in this work the authors postulated that below pH 8.0, the cationic polyelectrolyte is completely in cationic form.

In addition, a reduction in degree of dissociation of humic acids leads to lower its solubility and an increase in the hydrophobic character of the molecule, and there is an increase in its tendency to leave solution.

### Conclusions

Humic and fulvic acids are anionic polyelectrolytes because of the presence of carboxylate and phenolates groups. Their degree of ionization depends on pH.

Humic and fulvic acids react chemically with cationic polyelectrolytes by means of a charge neutralization reaction.

There is a stoichiometric relationship between the concentration of the anionic groups and the flocculant demand.

As the pH values go down, better flocculation is achieved. At low pH, the degree of dissociation in the organic molecules is decreased, and the flocculant demand correspondingly is reduced.

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## Viruses in Water Supply

James D. Fenters and Josephine M. Reed

**In comparison with information concerning bacterial contamination of water supplies, much less is known about viruses in water because few water systems determine the presence of viral pollutants in their supplies, although various techniques exist for delineating the presence of viruses. A summary of the advantages and disadvantages of the various techniques is given along with the recommendations of APHA concerning detection and control of waterborne viruses.**

The necessity to develop and to improve water resources to meet the demands of an ever growing population is well recognized throughout the world. In the US most of the laws passed over the years concerning water are directed primarily toward protection of

health. City, state, and federal governments have taken appropriate steps to keep the water consumed by humans pure in terms of bacterial and chemical pollution. Yet there has been little concern about viruses as water pollutants.

A considerable amount of information is available relating to the presence of bacteria in water supplies and to waterborne bacterial diseases. Much less is known, however, about diseases of viral origin transmitted by water. Pathogenic viruses found in sewage and water include poliomyelitis virus and various coxsackieviruses and echoviruses. Furthermore, the spread of infectious hepatitis has been proven in many instances to be waterborne.<sup>1</sup> While classical virological studies of water supplies are rather scarce, sufficient epidemiological proof is available to link outbreaks of viral diseases to water supplies. In this respect, the interrelationship between the viral contamination of