Structure of Al-humic flocs and their removal at slightly acidic and neutral pH

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Abstract Using microscopic and optical monitoring techniques, the process of coagulation of humic substances was studied paying attention to the structure of flocs and their settleability and filterability with information from image analysis, and HPLC, zeta potential, TOC and UV absorbance measurements. The results show that Al-humic flocs formed at pH 5.0 appear more compact with higher fractal dimension while those formed at pH 7.0 are looser with lower fractal dimension. During growth, Al-humic flocs also undergo a decrease in their fractal dimension. The attainable removal of TOC is about 40–50% at both pH values, but the optimum Al dose at pH 7.0 is about 5 times of that at pH 5.0. Charge neutralization is believed to be the main mechanism of coagulation at pH 5.0 and sweep coagulation plays an important role at pH 7.0 as well as at pH 5.0 under an overdosing condition.

Keywords Coagulation; floc structure; fractal dimension; humic substances; optical monitoring

Introduction

Humic substances (HS) comprise most of the natural organic matter (NOM) in surface waters (Stumm and Morgan, 1996), and their removal has been a principal objective of water treatment in view of their associated water quality problems, such as color, tastes and odors, and the formation of disinfection by-product (DBP). Although many advanced technologies, including granular activated carbon adsorption, membrane filtration, ozonation etc., are applied nowadays for DBP control, the effectiveness of coagulation in removing DBP precursors is still drawing the attention of water professionals. In the USEPA Safe Drinking Water Act, enhanced coagulation, emphasizing the optimization of chemical dosing and pH adjustment in accordance with raw water TOC and alkalinity, is recommended as the best available technology for the removal of NOM from raw water (Pontius, 2000).

The chemical aspects of HS coagulation using hydrolyzing metal coagulants (alum or ferric salts) were well investigated in the past two decades. In view of the complexity of the interaction between the organic macromolecules and the coagulants, the coagulation of HS is found to be more pH-dependent than for suspended inorganic particles (Edwards and Amirtharajah, 1985; Browne and Driscoll, 1993; Najm et al., 1998). When alum is used as coagulant, slightly acidic pH between 5.0 and 6.0 is often found to be the optimum range while neutral pH up to 7.0 and above is also effective for HS coagulation. However, in different pH ranges the mechanism of coagulation is different – at lower pH charge-neutralization by soluble cationic Al species is dominant, while at higher pH sweep coagulation by Al(OH)₃ precipitates is more important (Lu et al., 1999).

In water treatment plants, coagulation/flocculation is usually followed by sedimentation and/or filtration. The settleability and filterability of flocs are related to their grown size and density. Regarding suspended particles, successful studies have been conducted on flocc structure (Vold, 1963; Sutherland, 1967), floe density (Lagvankar and Gemmell, 1968; Tambo and Watanabe, 1979) and the fractal nature of flocs (Mandelbrot, 1982; Meakin,
Image analysis has been found to be a useful method for characterizing the structure of flocs and evaluating their fractal dimension (Li and Ganczarczyk, 1989; Jiang and Logan, 1996). A completely new theoretical approach has also been made possible by introducing fractal geometry into kinetic studies of flocculation (Jiang and Logan, 1991).

Few studies have so far been concerned with the physical aspects of coagulation of NOM and little is known regarding the morphological characteristics of organic flocs and the relation between their structure and removal properties. In order to gain knowledge of the chemical, physical and morphological aspects of the coagulation/flocculation process of NOM, this paper presents an experimental study using microscopic and optical monitoring techniques and paying attention to the structure of the Al-humic flocs and their settleability and filterability.

**Materials and methods**

**Raw water**

The HS for this study were isolated from lake sediments in Xi’an, China. Firstly the collected sediment was dissolved in sodium hydroxide (NaOH) solution at pH > 12 for 24 hours, and then hydrochloric acid (HCl) was added to let the solute precipitate at pH < 1 for another 24 hours. The precipitates so obtained are humic acids (Stumm and Morgan, 1996). Raw water for the experiment was prepared by dissolving the isolated HS in distilled water. The dissolved solution was then filtered by a 0.45 µm membrane filter to remove all the suspended matters. According to liquid chromatographic analysis, the molecular weight of the dissolved organic matter in the raw water was estimated as several hundred to several thousand Dalton which is believed to be representative of natural humic matter in surface waters.

**Experiment**

Figure 1 shows the experimental setup for this study. The system consists of a cubic jar equipped with a speed-adjustable stirrer, a flocculation monitor (PDA2000, Rank Brothers, UK) with a peristaltic pump, a microscopic camera, and a personal computer with data acquisition units. In each experimental run, the jar stirrer was filled with 800 mL of raw water with an initial dissolved organic carbon (DOC) concentration of 10 mg/L or UV absorbance at 254 nm (UV254) of 0.15 cm⁻¹. Sodium bicarbonate (NaHCO₃) solution was pre-injected at a dose of 10 mg/L for adding alkalinity. Aluminium sulfate (Al₂(SO₄)₃·18H₂O) was added at the required dose, together with a predetermined amount of NaOH solution to restore the pH to the required value. The stirrer was operated at preset conditions of: rapid mixing (200 rpm) for 1 min, slow stirring (20 rpm) for 30 min and quiescent settling for 60 min. Water temperature was kept at about 25°C.

During slow stirring, samples were continuously taken from the jar through a tube of 3 mm inner diameter by means of the peristaltic pump at a rate of 20 mL/min. The sample passed through the PDA detector where the light transmitted through the flowing suspension was directly monitored and then flowed back to the jar. The root mean square value of

![Figure 1 Schematic diagram of experimental setup](https://iwaponline.com/ws/article-pdf/2/2/99/408197/99.pdf)
the fluctuating component of the transmitted light was derived by the PDA, and the ratio of the root mean square value to the mean (d.c.) value of the transmitted light intensity was obtained and recorded by the connected PC to give a sensitive indication of the degree of aggregation of the suspension (Gregory, 1985). The ratio is called the flocculation index (FI) in this paper. At given intervals, a small amount of the suspension was gently collected from the jar using a glass tube of 3.5 mm inner diameter, and then moved on to a cell mounted on the microscopic camera for image analysis of the particles in the suspension. Because the sampling tube was sufficiently large and the cell was previously filled with an amount of distilled water, no breakage or further growth would happen with the sampled particles during image analysis under careful operation.

Water quality analysis was conducted for (i) zeta potential of the destabilized suspension at the end of rapid mixing using a ZC-2000 zeta potential analyzer (Microtech Nichion Co., Japan); (ii) TOC of the supernatant after settling without and with 0.45 µm membrane filtration using a TOC-5000A organic carbon analyzer (Shimadzu Co., Japan); (iii) UV$_{254}$ of the supernatant before and after passing through a paper filter; (iv) evaluation of the molecular weight distribution of the organic matter in the raw water and the supernatant by means of high performance liquid chromatographic (HPLC) analysis using a LC-9A unit (Shimadzu Co., Japan) with a W520 gel column and UV detector.

Image analysis

With the picture of flocs captured by the microscopic camera connected to the PC, the diameter and fractal dimension of the flocs were obtained by image analysis using a computer program. Firstly the projected area of each floc was measured, and then the diameter of the equal-circle-area was calculated. For evaluating the fractal dimension at each sampling time, the maximum length of each particle appearing in the picture was also measured. According to the theory of fractal geometry (Chakraborti et al., 2000), there exists a relation between the projected area $A$ and the maximum length $L$ of $A = \alpha L^{D_f}$, where $\alpha$ is a proportional coefficient and $D_f$ is the two-dimensional fractal dimension ($D_f = 2$ for non-fractal objects). By plotting $A$ against $L$ on a logarithmic paper, $D_f$ was thus evaluated from the slope of the linear relationship.

Results and discussion

PDA outputs – FI curves

Figure 2 and Figure 3 show the FI curves as the outputs of the PDA online monitor under different alum doses at slightly acidic (pH 5.0) and neutral (pH 7.0) conditions, respectively. The time on the figures was counted from the start of rapid mixing after alum dosing. The variation of the FI value with time shows the condition of particle growth during flocculation (Gregory, 1985). At both pH values, a low alum dose of 0.07 mg-Al/mg-TOC did not result in significant change of the FI value, indicating that almost no flocs could grow within the given period of floculation time. As alum dose increased, the FI curves began to rise from the start or after a certain period of lag time and then in most cases reached a
plateau, indicating an equilibrium state of floc growth. However, the pattern of variation of the FI curves with alum dose is noticeably different between the two pH values. At pH 5.0, the height of the FI curve reached the maximum at a dose about 0.17 mg-Al/mg-TOC but decreased as alum dose further increased. No apparent growth of flocs was detected at 0.27 and 0.41 mg-Al/mg-TOC. At still higher alum doses, fast growth of flocs was noticed again after several minutes of lag time though the FI curves tended to be unstable. In contrast to this, at pH 7.0 the height of the FI curve simply increased with alum dose and kept an almost unchanged shape at 0.27 mg-Al/mg-TOC and above.

**Image of flocs and their fractal dimension**

Figure 4 shows the images of typical flocs at different stirring time under the condition of pH 5.0 and alum dose 0.17 mg-Al/mg-TOC, and Figure 5 shows the relation of projected area $A$ of the flocs with their maximum length $L$ on logarithmic coordinates where the fractal dimension of the flocs at each time was derived. Apparently flocs underwent growth with prolonged stirring time and reached the maximum size after 20 min. At the beginning, the flocs were small but appeared more compact, while growing larger they became more porous and more irregularly shaped. The derived fractal dimension showed a similar tendency of variation – the estimated $D_f$ was about 1.66 at 1 min and gradually decreased to 1.43 at 30 min.

The difference of floc structure at pH 5.0 and pH 7.0 was also noticed. Figure 6 shows the images of typical flocs after 30 min stirring under the two conditions. (The alum dose was 0.17 mg-Al/mg-TOC at pH 5.0 and 0.27 mg-Al/mg-TOC at pH 7.0, both resulting in the formation of flocs of similar size.) The flocs formed at pH 5.0 appeared more compact with a fractal dimension of 1.43, while that at pH 7.0 appeared looser and more porous with a lower fractal dimension of 1.17.

**HS removal**

TOC and UV$_{254}$ were used to measure HS removal by coagulation/flocculation followed by sedimentation and filtration. The TOC was measured in two ways: (i) direct measurement

![Figure 4 Images of typical Al-humic flocs at different stirring time (pH = 5.0, alum dose: 0.17 mg-Al/mg-TOC)](image)

![Figure 5 Evaluation of the fractal dimension of flocs (pH = 5.0, alum dose: 0.17 mg-Al/mg-TOC)](image)
of the supernatant which represents the total amount of the residual organic matter after setting and (ii) measurement after passing the supernatant through a 0.45 µm filter which represents the amount of uncoagulated dissolved organic matter (DOC). For UV$_{254}$ measurement, a paper filter was used to fractionate the filterable and unfilterable parts in the supernatant. Figure 7 shows the results in comparison with zeta potential of the particles. At pH 5.0, the optimum alum dose to bring about the best removal corresponds to nearly zero zeta potential (or $|\zeta|<5$ mV) as can be judged from Figure 7a considering TOC and UV$_{254}$ before filtration. Overdosing resulted in charge reversal and poor removal of TOC and UV$_{254}$ before filtration, but significant removal was achieved again at still higher alum dose. However, regarding DOC and UV$_{254}$ after filtration, higher removal was achieved even under the condition of overdosing, indicating that most of the coagulable organic matters were in fact coagulated but did not grow to a settleable size. At pH 7.0, the measured zeta potential became close to zero at sufficient alum dose but charge reversal did not happen even at very high alum dose (Figure 7b). The optimum alum dose was not as apparent as that in the case of pH 5.0, and there was little difference between the values of TOC and DOC, or between UV$_{254}$ values before and after filtration.

**HPLC analysis results**

By liquid chromatographic method using a gel column, aquatic organic matter can be effectively fractionated according to molecular weight, in accordance with the elution time (Amy et al., 1987). Figure 8 compares the liquid chromatograms of the raw water used in this study and the supernatant after treatment under the condition of pH 5.0 with the optimum alum dose. The approximate molecular weight range is given in the figure following Tambo and Kamei (1978). As can be seen clearly from the figure, almost all the significant peaks with elution time less than 50 min on the chromatogram of the raw water have disappeared after coagulation. This shows that HS with higher MW can be effectively removed by coagulation, while those with lower MW (<500 Dalton), will remain in the supernatant. There is little difference between the chromatograms at pH 5.0 and pH 7.0 under the optimum conditions.
Comparison of characteristic parameters

As shown in Figure 2 and Figure 3, the process of floc growth in the jar stirrer has been well monitored by the PDA device and the FI curve is a good record of the flocculation process. A typical FI curve is of sigmoid shape and can be characterized by the parameters $s$, $h$, and $t$ shown in Figure 9, where $s$ represents the maximum rate of flocculation, $h$ the equilibrium floc size and $t$ the time to reach the maximum flocculation rate. Detailed discussion of these parameters is beyond the scope of this paper, but correlations are found between $s$, $h$, floc diameter and TOC removal. Figure 10 is an example at pH 5.0. The parameters $s$ and $h$ tend to increase as alum dose increases to bring about charge neutralization (Figure 7a), and then decrease as alum dose further increases to give charge reversal. Finally $s$ and $h$ tend to increase again at very high alum dose. The average diameter of flocs and percent TOC removal show a similar tendency. This shows that the optical monitoring is a simple but very useful method to provide on-line information on floc growth. A quick prediction of the removal efficiency could also be made possible.

As stirring time increases, flocs continue to grow until an equilibrium state is reached. The relation between the average diameter of the flocs and their fractal dimension can be seen more clearly from Figure 11. The apparent tendency of decrease of $D_f$ with increasing floc diameter indicates that the structure of flocs becomes looser and more irregular as they grow larger. Generally speaking, at the initial stage of coagulation of HS using aluminium coagulant, interactions occur between hydrolyzed AI species and humic molecules forming insoluble AI-humic complexes (Thomas and O’Melia, 1988) especially under slightly
acidic conditions with moderate alum dose. Random collision and aggregation then occur among these insoluble micro particles as long as suitable agitation conditions are provided, thus bringing about floc growth. In this process, more and more void water will be involved in a growing floc among the micro particles as well as the constituent smaller aggregates. This makes the floc structure more and more open before the final equilibrium state is reached, thus resulting in a decrease of the fractal dimension.

**Mechanism of coagulation/flocculation at pH 5.0 and pH 7.0**

The flocs formed at pH 5.0 and pH 7.0 are noticeably different in their structure and fractal dimension (Figure 6) – the former being more compact with higher \( D_f \) value and the latter being more porous with lower \( D_f \) value. From the zeta potential measurement results (Figure 7), it is understood that at pH 5.0 the degree of charge neutralization is very sensitive to alum dose and greatly affects floc growth and TOC or UV\(_{254}\) removal, while at pH 7.0 zeta potential is less sensitive to alum dose and good flocculation is achieved at a much broader range as long as the alum dose is sufficient. As alum is added to a solution, the Al\(^{3+}\) ions will be hydrolyzed to form various species (Amirtharahah and O’Melia, 1990). This process depends on Al\(^{3+}\) concentration and pH of the solution. At lower values of pH, the dominant soluble species are cationic monomers such as Al\(^{3+}\) and Al(OH)\(_2^+\). Because the cationic monomers are very effective in charge neutralizing with the charge of HS molecules, adsorption-charge neutralization plays a leading role in HS coagulation at slightly acidic pH. At higher pH, the amorphous aluminum hydroxide Al(OH)\(_3\)(am) becomes dominant and sweep coagulation of HS by aluminum precipitates is believed to be the main mechanism of flocculation. This is also the condition at pH 5.0 at the highest alum doses.

**Conclusion**

From the experimental results explained in the former sections, conclusions can be drawn as follows.

- Al-humic flocs are shown to be of fractal nature and the two-dimensional fractal dimension \( D_f \) derived from image analysis characterizes their morphological properties. At different pH values, there exists noticeable difference in floc structure – flocs formed at pH 5.0 appear to be more compact with higher fractal dimension, and those formed at pH 7.0 are looser in structure with lower fractal dimension. And during growth, Al-humic flocs undergo a decrease in the \( D_f \) value with the increase of their size because of the addition of void water among the constituent small aggregates, which makes the flocs more porous and of more irregular shape.

- At pH 5.0, the optimum coagulation condition corresponds to charge neutralization to near zero zeta potential, with charge reversal being observed at higher alum dose and giving worse removal of TOC, but at still higher alum dose, high removal of TOC can be achieved again. At pH 7.0, charge reversal never happens and steady removal of TOC is achievable if alum dose is above a required minimum. Sweep coagulation by aluminum hydroxide precipitates is believed to be the main mechanism of floc formation at pH 7.0 as well as at pH 5.0 under an overdosing condition, but charge neutralization caused by Al-humic complexation plays the most important role at pH 5.0 under moderate alum dose.

- The attainable removal of TOC is about 40–50% at both pH 5.0 and pH 7.0, but the optimum alum dose at pH 7.0 is about 5 times that at pH 5.0 to achieve the maximum TOC removal. pH adjustment is important in the coagulation of humic substances from the viewpoint of effective coagulant use and the structure of flocs formed – more compact flocs with higher fractal dimension are favorable to solid/liquid separation.

- On-line optical monitoring is very useful in providing direct information on floc growth.
and makes it possible to predict the removal efficiency. The characteristic parameters of the FI curve have good correlations with floc diameter, as well as TOC removal.

**References**


