

EFFECTS OF ADSORBED ORGANIC MATTER ON SIZE, STRUCTURE AND FILTERABILITY OF IRON OXYHYDROXIDE FLOCS

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ABSTRACT

In this study, the effects of adsorbed fulvic acid, a naturally occurring organic acid, on the aggregation and filtration of hematite particles are investigated. The study of aggregate structure shows that the fractal dimensions of hematite aggregates which are partially coated with fulvic acid molecules are higher than those obtained with no adsorbed fulvic acid. The high fractal dimensions are due to restructuring within the aggregates, which only occurred at low coverage by the organic acid. In the filtration experiments, high clean filter efficiency was obtained for particles with the net charge opposite to the filter media. During ripening period, however, the particle sizes played a more important role than the surface charges. Particles of a micron size seemed to have less capture efficiency during this period, since they are controlled neither by diffusion nor interception.

KEYWORDS

Aggregation, filtration, flocculation, fulvic acid, fractal dimensions, hematite.

INTRODUCTION

The presence of natural organic acids (humic substances) in water sources impart colour and must be removed if present at excessive concentrations. The removal process typically involves addition of iron or aluminium salts to the waters under conditions at which nucleation and aggregation of the resulting particles will occur. The particles so produced are, under appropriate solution and particle surface conditions, efficient scavengers of dissolved organic and inorganic components and also act to induce aggregation (or entrapment within the floc structure) of particles that are naturally present. It is now well recognised however that the presence of organic matter may modify the nucleation and aggregation process of the oxide flocculants being used in the water treatment process. Such organic-induced modifications in floc behaviour may necessitate a variation in treatment process (e.g. addition of coagulant aids, change in pH, etc.) in order to optimally treat the water of interest, may (i) modify the scavengability of the resultant flocs for dissolved species, (ii) alter their ability to induce aggregation of other (turbidity causing) particles that are present, (iii) modify the settling characteristics of the flocs in a sedimentation process and (iv) modify the capture efficiency for the produced flocs if direct filtration is being used.

In this presentation attention is focussed on only some of these issues; namely, (i) the impact of natural organic compounds on the aggregation behaviour of iron oxyhydroxides and on the size and structure of the flocs that are produced and (ii) the impact of size, structure and surface properties of organically influenced flocs on filtration efficiency. Discussions are initiated below around the results of studies of the impact of

the natural organic acid, fulvic acid, on the aggregation kinetics and structure of a preformed, well characterised iron oxide (hematite). The implications of size and structure of organically coated flocs to the collection efficiency of such flocs on deep bed filters are then discussed.

EXPERIMENTAL METHODS

Aggregation experiments

Samples of nearly spherical hematite particles were prepared by the forced hydrolysis of a homogeneous iron (III) chloride solution under strictly controlled conditions (Penners and Koopal, 1986). Examination of the hematite particles prepared in this way using transmission electron microscopy confirmed that the particles were reasonably monodisperse with average particle diameter of $\pm 70\text{nm}$. The mean hydrodynamic diameter of hematite suspensions prior to addition of fulvic acid was on the order of 100nm suggesting the presence of some aggregated particles (mainly dimers and trimers from TEM analysis).

The hematite suspensions were mixed with different concentrations of Suwannee River fulvic acid for at least 24 hrs before each aggregation experiment was performed. The samples were prepared by mixing different concentrations of fulvic acid solution with the hematite suspension at a pH of 3 (adjusted using HCl) at 25°C for 24 hours to ensure that the adsorbed fulvic acid had reached equilibrium before the concentration of adsorbed organic, zeta potential and the aggregation kinetics were measured.

The mean hydrodynamic diameter and scattered intensity (in terms of photoncounts) of the aggregates were measured with the Malvern 4700 PCS system, utilizing a 15 mW, 633 nm He-Ne laser.

Aggregation kinetics experiments were conducted for hematite suspensions of 2.25×10^{10} particles/ml premixed with fulvic acid concentrations of 1 and 2.5 mg/l. During aggregation, the temperature was kept at 25°C . The salt (KCl) concentrations used ranged from 3mM to 50mM. For each fulvic acid and salt concentration, the variation in mean hydrodynamic diameter with time was determined by dynamic light scattering measurements every 2-3 minutes for up to 1 hr. The mean hydrodynamic diameter of the aggregates was measured at a scattering angle of 30° . Angle dependency work at low scattering angles gives a more accurate estimation of the translational mean hydrodynamic size than estimates obtained at the more typical scattering angle of 90° .

In studying the structure of the aggregates, the intensity (in terms of photoncounts) of scattered light was measured at angles ranging from 15° to 90° for 5 seconds at each angle. The structure information, quoted as the fractal dimension, was obtained by plotting $\log(I)$ vs $\log(Q)$. The slope of this plot is known as the scattering exponent and can be related to the fractal dimension. In order to comply with conditions governing the relationship between the scattering exponent and the fractal dimension (Amal *et al.*, 1990), these static light scattering experiments were carried out when the aggregates comprised a large number of particles and were typically about $1 \mu\text{m}$ in diameter. The static light scattering experiment was performed for hematite particles suspended in solutions containing 1, 2.5, and 10 mg/l of fulvic acid at 25°C .

Filtration experiments

Filtration experiments were conducted using a filter column of 5 cm in diameter, packed with glass beads of effective size 0.17-0.18 mm, to a depth of 6 cm. The hematite particles of 70nm diameter were filtered through the column at influent concentration of 25 ± 2 ppm and filtration velocity of approximately 1-2 cm/s. In the study of the effects of adsorbed organic matter on filtrability of iron oxyhydroxide flocs, hematite particles were first soaked in known concentration of fulvic acid for 24 hours. The pH of the suspension was kept at 3 in all of the experiments.

RESULTS AND DISCUSSION

Structure of Hematite Aggregates Formed in the Presence of Fulvic Acid

The size and structure of the aggregates formed from colloidal particles differs greatly according to the conditions prevailing in the aggregating system. As found in previous work (Amal et al., 1990a,b), tightly packed, compact structures are formed by slow aggregation which prevails at low temperatures and low salt concentrations, whilst loose tenuous aggregates are formed by rapid aggregation at higher temperatures and salt concentrations. The rate of aggregation is controlled to a large extent by the magnitude of the repulsion barrier existing between aggregates. The magnitude of this barrier is a result of the balance of inter-aggregate attractive and repulsive forces. Aggregate size and surface potential are major determinants of these forces. Both change in suspension pH and the specific adsorption of ions onto the particle surfaces will alter surface potentials and induce a change in aggregation kinetics (Liang, 1988; Tipping and Higgins, 1982; Tipping and Ohnstad, 1984).

While studies of the effects of relatively simple, well-defined organic compounds on the stability of iron oxide (Liang, 1988) and of other metal oxides (Nikologorskaya et al., 1990; Lafuma et al., 1991; Tjipangandjara and Somasundaran, 1991) have been invaluable in furthering our understanding of such surface processes, particular interest exists in the effect of more complex, naturally occurring organic compounds on the stability and the resulting aggregate structure of such oxides. The interaction of such compounds with oxides and the resultant effects on oxide aggregation behaviour are of interest in a range of areas including water and wastewater treatment, mineral extraction processes involving the nucleation and aggregation of metal oxides and the behaviour of oxides (and oxyhydroxides) in natural waters.

The effect of adsorption of negatively charged fulvic acid molecules on the surface potential of hematite at a constant pH of 3 is shown in Figure 1. Partial coverage of the hematite surface is apparent at low fulvic acid concentrations (0.5 and 1.0 mg/l), while complete coverage is apparent at higher organic concentrations with a reversal in surface charge. Not surprisingly, lower salt concentrations are required to induce rapid aggregation under conditions of partial coverage where the surface charge is significantly lower than the positive and negative extremes indicative of zero and total surface coverage respectively.

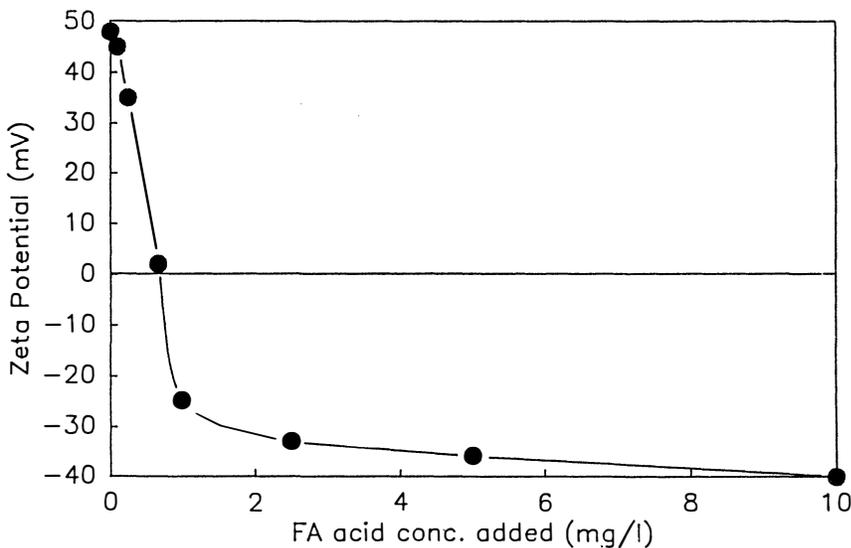


Fig. 1. Effect of fulvic acid adsorption on zeta potential of hematite particles at pH of 3.

Fractal dimensions of the hematite aggregates formed in the presence of 1 and 2.5 mg/l fulvic acid and measured by static light scattering are summarized in Table 1. The scattering exponents ranged from 2.83 ± 0.08 to 3.42 ± 0.09 . During rapid aggregation of these coated particles, the aggregate structure formed is much more compact than that formed during rapid aggregation of the uncoated particles. However, these compact aggregates can still be characterised as mass fractals (where light is still scattered from the bulk of the aggregates and not the surface). During slow aggregation, however, the scattering exponents obtained are greater than 3. These values cannot be quantified as mass fractal dimensions (d_f), since $1 \leq d_f \leq 3$. Scattering exponents of greater than 3 indicate that scattering results from objects that have pores which are bounded by surfaces with a fractal structure (surface fractals). The scattering intensity of surface fractals is related to the surface fractal dimension by (Feder, 1988),

$$I(Q) \propto Q^{d_s-6} \quad (1)$$

where $2 \leq d_s \leq 3$.

Table 1 The scattering exponent and the appropriate mass or surface fractal dimension of the aggregates obtained at different fulvic acid and KCl concentrations.

FA conc. (ppm)	KCl conc. (mM)	SE	d_f	d_s
0	50	2.86 ± 0.05	2.86	
	60	2.55 ± 0.06	2.55	
	80	2.33 ± 0.06	2.33	
1	3	3.42 ± 0.09		2.58
	5	3.24 ± 0.08		2.76
	10	2.93 ± 0.08	2.93	
2.5	20	3.17 ± 0.07		2.83
	30	3.05 ± 0.09		2.95
	50	2.83 ± 0.08	2.83	
20	30	2.72 ± 0.08	2.72	
	50	2.41 ± 0.07	2.41	
	70	2.07 ± 0.05	2.07	

Restructuring (i.e. a change in structure over time) did not appear to be important in the case of the uncoated hematite aggregates. The results for the uncoated particles showed that once the aggregate diameters had reached approximately $1 \mu\text{m}$ size, the scattering exponents obtained did not vary with time. However, the scattering exponents obtained for partially coated aggregates, when the aggregate sizes are greater than $1 \mu\text{m}$ (i.e. the sizes are large enough for the scattering power law equation to hold) still vary with time. The exponents vary from ~ 2.3 to ~ 2.8 for fast aggregation and ~ 2.8 to ~ 3.4 for slow aggregation. The scattering exponents presented in Table 1 are the exponents that have reached the equilibrium values. The increase of the scattering exponents with time indicates that the aggregates restructure to a more compact form. The restructuring process observed here is most likely attributable to the presence of oppositely charged surface sites within the aggregate structures resulting in strong intra-aggregate attractive forces inducing continuing rearrangement until an even charge distribution is attained.

As found in the absence of fulvic acid, slow aggregation yields more compact structures than those obtained for aggregates formed rapidly (Amal et al., 1990). For fulvic acid coated hematite aggregates formed slowly, the particles become solid-cored rough-surfaced aggregates due to the restructuring process. The scattering exponents of these aggregates are greater than 3, and can be related to the surface fractal dimensions (d_s), by $d_s = 6 - \text{scattering exponent}$ (i.e. d_s ranging from 2.58 to 3 for scattering exponents of 3.42 to 3).

The difference in aggregate structure formed with and without the presence of fulvic acid in the diffusion limited regime (Amal et al., 1991) is illustrated below.

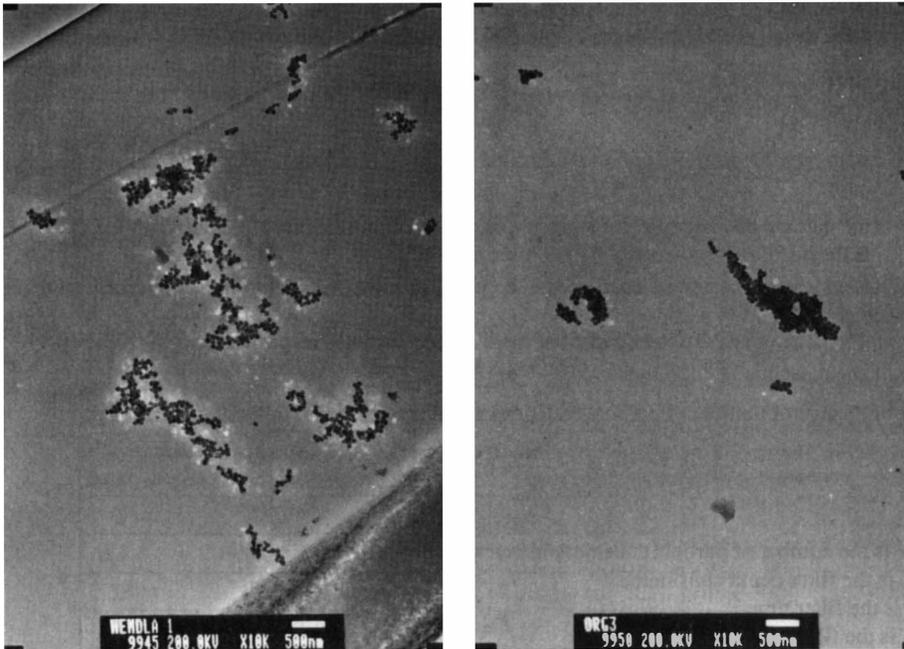


Plate 1 Transmission Electron Microscope plates of hematite aggregates formed (i) without fulvic acid, and (ii) with fulvic acid presence, under the diffusion limited aggregation.

At fulvic acid concentrations for which complete surface coverage is expected (20 mg/l), the scattering exponents obtained are much lower than those obtained from lower fulvic acid concentrations (1, 2.5 mg/l). Aggregates formed under such conditions can all be characterized as mass fractal structures. These fractal dimensions are even lower than the fractal dimensions obtained from the uncoated hematite aggregates.

Implication to Filtration

The importance of chemical effects in filtration has long been recognised (O'Melia and Crapps, 1964; Ives and Gregory, 1966). The use of DLVO theory in coagulation and bed filtration studies of inorganic particles is well reported in the recent literatures of both environmental and colloid chemistry (Tobiason and O'Melia, 1988; Elimelech and O'Melia, 1990). However, in natural aqueous systems particles are typically coated with organic matter yet the study of deposition of such coated particles (Warzynski, 1989; Tadros *et al.*, 1989; Van de Ven, 1989) has only recently commenced and not yet been extensively reported. In this section we report preliminary observations on the deposition of hematite particles coated with naturally occurring fulvic acid on columns packed with 0.17-0.18 mm diameter glass beads.

The attachment of a suspended particle to filter medium or to another particle which has been retained on the filter medium is mainly controlled by the surface properties of the particles and the filter media. In this study, as an initial attempt, efficiency of clean bed, ripening stage and breakthrough period are related to particle-filter medium attachment coefficient (α), particle-particle attachment coefficient (α_p) and breakthrough constant (β_2) in the mathematical model proposed by Vigneswaran and Chang (1989). A brief summary of the above model which is an extension of the O'Melia and Ali model is presented below,

$$\eta_{ri} = \eta\alpha + N\alpha_p\eta_p\left(\frac{d_p}{d_c}\right)^2 - \beta_2\frac{J_{i-1}}{n}[\sum(\eta_r n)_{i-1}] \quad (2)$$

where d_p and d_c are diameters of particles and filter medium (glass bead) respectively.

n is the particle concentration at a given time (t) and depth L .

J_{i-1} is the headloss gradient at $(i-1)$ th time step ($=\Delta H/2$).

α and α_p are attachment coefficients between particle and filter media, particle and particle respectively.

η and η_p are contact efficiency of filter medium and particles respectively.

β_2 is the detachment coefficient.

The rate of change of number of particle collectors can be given by the following equation,

$$\frac{\partial N}{\partial t} = \beta\eta\alpha n v \frac{\pi}{4} d_c^2 \quad (3)$$

where

N is the number of particle collectors in unit volume

L is the filter depth considered

t is the filter time

v is the filtration velocity, and

β is the fraction of retained particles acting as particle collectors.

The mass balance of a small element of the filter yields the following equation,

$$\frac{\partial n}{\partial t} + v \frac{\partial n}{\partial L} + \frac{3}{2}\eta_r v n \frac{1-f_0}{d_c} = 0 \quad (4)$$

where

f_0 is the porosity of clean filter bed

η_r is the removal efficiency of a collector (filter medium or retained particle) at a given time and depth.

Combining equations (2), (3), and (4) and considering n and η_r as stepfunctions, one can obtain the removal efficiency of i th time step as follows,

$$\eta_i = \eta\alpha \left\{ 1 + \beta\eta_p \alpha_p v \frac{\pi}{4} d_p^2 \left(\sum n_0 \Delta t \exp \left(-\frac{3}{2} (1-f_0) \eta_{r(i-1)} \frac{\Delta L}{d_c} \right) \right) \right\} - \beta_2 \frac{J_i}{n_0} \sum (\eta_{r,n})_{i-1} \quad (5)$$

where i and $i-1$ represent the i th and $i-1$ th time steps.

The head loss is calculated from the following equation which is a modified form of Kozeny's equation (Vigneswaran and Chang, 1986)

$$\frac{h_f}{L} = 36K \frac{\mu v (1-f_0)^2}{\rho g f_0^3} \frac{1}{d_c^2} \times \left\{ \frac{1 + \beta'(N_p/N_C)(d_p/d_c)^2 (S_2/S_1)^2}{1 + (N_p/N_C)(d_p/d_c)^3 (S_2/S_1)^3} \right\} \quad (6)$$

h_f is the headloss across a filter depth L at a given time

K is Kozeny's constant

N_C and N_p are number of filter grains and retained particles in a unit volume at a given time in a particular filter layer, and

S_1 and S_2 are shape factors of particles and filter grain respectively.

The value of $\alpha\eta$ is calculated from the initial effluent concentration value using the following equation:

$$\ln \frac{n}{n_0} = -\frac{3}{2} (1-f_0) \alpha\eta \frac{L}{d_c} \quad (7)$$

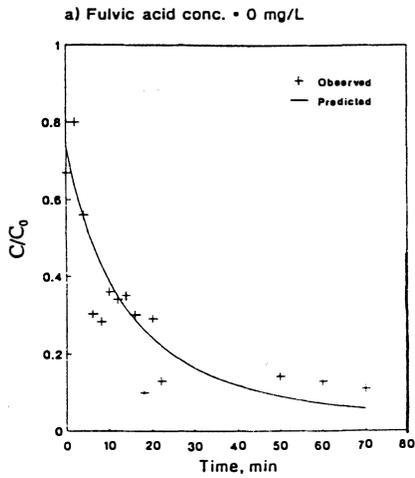
The values of $\alpha\eta$, α_p , and β_2 calculated from the model for different conditions of filtration are presented in the following table.

Table 2 Filtration model coefficients for different fulvic acid concentrations.

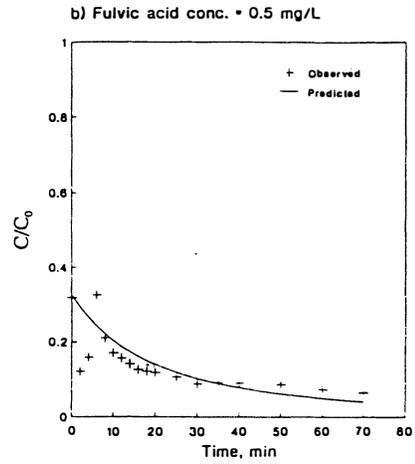
Fulvic acid conc. (mg/l)	$\alpha\eta \times 10^4$	$\alpha_p\beta$
0	-	-
0.5	29.7	0.40
1	11.65	0.30
3	1.08	0.75

The C/C_0 (ratio of effluent to influent concentration) profile of hematite particles in different concentrations of fulvic acid is presented in Figure 2. It is clear from these figures that the presence of fulvic acid significantly modifies the particle capture efficiency of the filter. Effect of fulvic acid on (i) surface charge of particles and filter media, and (ii) size of particles must be taken into account in interpreting the obtained data. In addition, conditions initially ("clean" bed filter conditions) may be expected to be somewhat different to conditions eventually after the filter has "ripened".

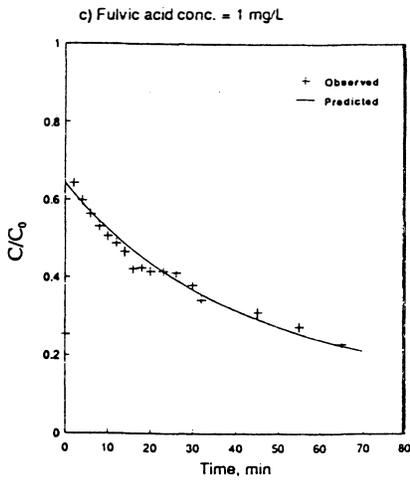
Consider firstly, conditions under clean bed conditions. For 0.5 mg/l the net charge on the particles is significantly lower than in the uncoated case but is still positive compared to the 1.0 mg/l case where the charge is again low but is now reversed. In the 0.5 mg/l case, strong initial interaction between the positively charged particles and the negatively charged filter medium is thus to be expected compared to that likely in the 1.0 mg/l fulvic acid case. Indeed a significantly higher C/C_0 is observed (i.e. less retention) in the 1.0 mg/l fulvic acid case. This is also reflected in the values computed for $\alpha\eta$ from the initial effluent concentration (29.7×10^4 and 11.65×10^4 for 0.5 and 1.0 mg/l fulvic acid concentrations respectively). At higher fulvic acid concentrations where the hematite particles exhibit more negative surface charge (and are thus repelled more by the negatively charged medium) the initial filtration efficiencies (and the corresponding $\alpha\eta$ values) are significantly lower (higher C/C_0 values).



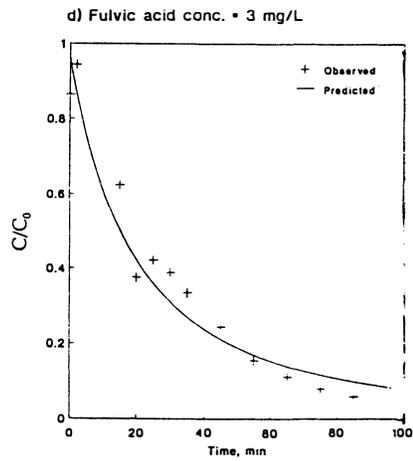
(Particle size = 70 nm; $v = 1.56$ cm/min; $d_c = 0.175$ mm; $L = 6$ cm; influent Fe conc. = 18.07 mg/L)



(Particle size = 1500 nm; $v = 2.22$ cm/min; $d_c = 0.175$ mm; $L = 6$ cm; influent Fe conc. = 16.33 mg/L)



(Particle size = 1250 nm; $v = 1.80$ cm/min; $d_c = 0.175$ mm; $L = 6$ cm; influent Fe conc. = 17.07 mg/L)



(Particle size = 200 nm; $v = 2.28$ cm/min; $d_c = 0.175$ mm; $L = 6$ cm; influent Fe conc. = 18.32 mg/L)

Fig. 2 Effect of fulvic acid on filter efficiency.

Particle sizes (as indicated by both aggregate size and the particle-particle attachment coefficient, α_p) appear to be strong determinants of capture efficiency during and following ripening of the filter. Values of α_p are significantly lower for fulvic acid concentrations of 0.5 and 1.0 mg/l where surface charge is low and particles are of micron sizes. Consistent with the results of previous studies (Vigneswaran and Chan, 1989), the lowest capture efficiency is observed for particles in the near micron size range (1.0 mg/l fulvic acid concentration) where neither diffusion nor interception controls deposition.

Continuing studies are underway of the effects of aggregate size and structure on particle deposition on the filter.

CONCLUSION

From the above discussions, it is clear that the structure of the aggregates formed in the presence of fulvic acid depends on the aggregation kinetics and the amount of the fulvic acid. The presence of fulvic acid also greatly affects the filter efficiency due in part to the reversal of charge on the particles but particle size and structure are obviously also important variables. Since the filtration and the removal of these particles undoubtedly depends on their characteristics (size, shape and chemical nature), the studies of the aggregation kinetics and the resulting structure of organic influenced particles have important implications for the removal of pollutants from the surface waters.

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