Settling velocities of multifractal flocs formed in chemical coagulation process

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ABSTRACT
A number of different flocculation mechanisms are involved in the formation of chemical coagulation flocs. Consequently, two flocs with the same size may have been formed by different mechanisms of aggregation and therefore have different arrangement of primary particles. As a result, two flocs with the same size may have different masses or mass distributions and therefore, different settling velocities. Although the correct estimation of the floc mass and density is critical for the development of the floc settling model, none of the suggested floc settling models incorporate the information on mass distribution and variable density of flocs. A probability-based method is used to determine the floc fractal dimensions on floc images. The results demonstrated that flocs formed in lime softening coagulation are multifractal. The multifractal spectra indicated the existence of a multiple fractal dimensions as opposed to the unique box-counting dimension which is a morphology-based fractal dimensions typically introduced into the Stokes’ Law. These fractal dimensions may provide information on the flocs’ aggregation mechanism, floc’s structure, and the distribution of mass inside the floc. More research is required to investigate how to utilize the information obtained from the multifractal spectra to incorporate the variable floc density and nonhomogeneous mass distribution of flocs into the floc settling models.

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1. Introduction

In the past three decades, numerous attempts have been undertaken to incorporate floc fractal dimensions into the models describing their settling velocity (Tambo and Watanabe, 1979; Li and Ganczarczyk, 1989; Lee et al., 1996; Winterwerp, 1998; Logan 1999; Kim, 2001; Li and Yuan, 2002; Chung and Lee, 2003; Khelifa and Hill, 2006; Yang et al., 2008; Vahedi and Gorczyca, 2011; Maggi, 2013).

In this paper, the floc settling models and the assumptions used in their development are critically analyzed. Also a probability-based approach is used to investigate whether flocs formed in lime softening process are multifractals, i.e. their properties have to be characterized by multiple scaling relationships. Advanced analyses of projections of floc images are conducted to obtain multifractal spectra that provide information on other fractal dimensions that may be useful in characterizing these flocs.
In this section, the assumptions used for development of floc settling models that incorporate fractal dimensions of flocs are critically reviewed. All models developed to describe the settling of aggregates (flocs) are based on Stokes’ Law, which is derived from the force balance on an individual floc settling at the terminal velocity, \( v_{st} \). The gravitational force reduced by the buoyancy acting on a floc is given by:

\[
F_d - F_b = (M_f - M_w)g = \left( V_f \rho_f - V_f \rho_w \right) g = V_f (\rho_f - \rho_w) g 
\]

where, \( V_f \) is the floc volume, \( \rho_f \) and \( \rho_w \) are densities of the floc and water respectively, \( g \) is the gravitational acceleration, \( M_f \) is the total mass of the aggregate and \( M_f \) is the equivalent mass of water occupying the floc volume.

At the terminal velocity, the effective gravity force is equal to the drag force acting on the floc

\[
F_d = C_d \frac{1}{2} A_f \rho_w v_{st}^2 
\]

where, \( C_d \) is drag coefficient, \( A_f \) is the floc’s cross-sectional area and \( v_{st} \) is the terminal settling velocity of the floc.

### 2.1. Estimation of the mass and volume of flocs

Eq. 1 and Eq. (2) require information on floc’s volume, floc’s density and floc’s cross-sectional area. In all of the reviewed studies, the floc’s mass or volume of the aggregate can be computed by adding up masses or volumes of all primary particles composing the aggregate:

\[
M_f = V_f \rho_f = N m = NV_p \rho_p
\]

where, \( \rho_p \) and \( V_p \) are the density and volume of the primary particles forming the floc, \( N \) is the number of primary particles, and \( m \) is the mass of a primary particle.

An important assumption in Eq. (3) is that all primary particles have the same mass. This is incorrect for aggregates formed in water and wastewater which are composed of a variety of particles of different sizes. All of the reviewed studies use the assumption in Eq. (3) to rewrite Eq. (1) as:

\[
V_f (\rho_f - \rho_w) = N V_p (\rho_p - \rho_w)
\]

It is important to note that, analogically to the floc mass, the floc volume in Eq. (4) is computed by adding up the volumes of primary particles only. The flocs contain significant amounts of chemical coagulant species and/or microbial by-products such as extracellular polymers. Both the coagulant and the extracellular polymers have very low densities, therefore, their contribution to the total mass of the aggregate may be small but they can occupy a significant part of the floc volume and create low density regions within the floc. Therefore, computing the floc mass by adding volumes of the primary particles alone totally ignores the presence of the hydrolyzed coagulant species. In summary, the mass and volume of a floc formed in chemical coagulation cannot be computed by adding up the masses or volumes of primary particles alone.

### 2.2. Floc density and floc aggregation mechanisms

All equations presented so far assume constant density of the primary particle (\( \rho_p \)). As mentioned before, flocs in water treatment are aggregates of a variety of different primary particles that not only have different sizes but also have very different densities. For instance, the density of calcium carbonate primary particles is about 2700 kg/m\(^3\) (Vahedi and Gorczyca, 2011), whereas the primary particles of coagulant hydrolysis products have densities very close to the water density, i.e. about 1000 kg/m\(^3\). These different primary particles with different densities aggregate into fioculi, which assemble themselves into microflocs. Microflocs bind together to form floc aggregates. Therefore, the floccule is a “primary particle” for microflocs and microflocs are the primary particles for floc aggregates. The important feature of flocs formed in chemical coagulation is that each level of floc aggregation (fioculi, microflocs, floc aggregate) may be formed according to a different mechanism. Therefore, different primary particles arrangements may be present inside the floccule, the microfloc or the floc aggregate. The consequence of these complex aggregation mechanisms is that the densities of the floccule, the microfloc and the floc aggregate will be different (Gorczyca and Ganczarczyk, 2002). This mechanism of floc formation results in a floc with a multilevel structure and a nonhomogeneous density (mass distribution).

Eq. 4 requires an estimation of the number of primary particles forming the floc, \( N \). The following equation has been...
widely used to describe the relationship between the number of primary particles within a floc and the fractal dimension of the floc in a flocculation process (Kranenburg, 1994):

\[ N \sim \left( \frac{d}{d_f} \right)^{D_f} \]  

(5)

where, \( d \) and \( d_f \) are the floc size and primary particle size respectively. A very important assumption in Eq. (5) is the representation of flocculation process by a unique scaling factor (\( D_f \)). This assumption which indicates that \( D_f \) is constant for different flocs is also incorrect. The number of primary particles in flocs representing different levels of aggregation can be described by the same fractal relationship only if the flocule, the microfloc and the floc aggregate are formed by an identical mechanism of aggregation and this is not correct for flocs formed in water coagulation. For instance, in an earlier study (Vahedi and Gorczyca, 2011) we identified at least two different mechanisms for chemical (lime) coagulation flocs. Two different relationships between the floc fractal dimensions and floc size were identified: one for small flocs (<60 \( \mu m \)) and another one for large flocs (>60 \( \mu m \)) (Fig. 1).

Note that, Eq. (5) is a fundamental equation for “ideal” fractals formed by a single mechanism of aggregation and mono sized building blocks (mono fractals). Even though, it may not be correct for many types of flocs, all reviewed studies have used Eq. (5) to estimate the number of primary particles in the aggregate (\( N \)) to derive the following equation:

\[ V_f (\rho_f - \rho_w) = V_p (\rho_p - \rho_w) \left( \frac{d}{d_f} \right)^{D_f} \]  

(6)

Considering all of the above, using the drag coefficient for a sphere, \( C_d = (24/Re)(1 + 0.15Re^{0.687}) \) (Clift et al., 1978) where, \( \mu \) is the water viscosity and Reynolds number is \( Re = (\rho_p d v_s)/\mu \), the balance of forces acting on the floc i.e. drag force in Eq. (2) and the difference of gravitational force and buoyancy force in Eq. (1) will result in Eq. (7):

\[ \frac{1}{2} \frac{24\mu}{\rho_w d_v s} (1 + 0.15Re^{0.687}) A_f \rho_w v_s^2 = V_p (\rho_p - \rho_w) \left( \frac{d}{d_f} \right)^{D_f} \]  

(7)

Assuming \( A_f \sim \pi d^2/4 \) and \( V_p \sim \pi d^2/6 \) and correcting for floc non-sphericity by using coefficients \( a \) and \( \beta \) as, Winterwerp (1998) derived the following formula for the terminal settling velocity of river mud flocs:

\[ v_m = \frac{16g \rho_p - \rho_w d_{50}^{a-b \gamma} - d_{50}^{D_f-1}}{1 + 0.15Re^{0.687}} \]  

Note that, in Eq. (8) primary particles are assumed to be perfect spheres, not fractals. Also, it is assumed that the floc cross-sectional area in the drag force (\( A_f \)) is proportional to \( d^2 \) which contradicts the fact that flocs are fractal. Recently, Maggi (2013) showed that the inclusion of fractal scaling into the cross-sectional area of flocs (\( A_f \)) in the drag force significantly improved the model of terminal settling velocity of flocs.

In our previous papers (Vahedi and Gorczyca, 2011, 2012), we modified the Eq. (8) by applying a fractal dimension (\( D_f \)) that varied with the floc size. However, even with that modification we were unable to predict the settling rate of a single floc, but rather an array of settling velocities possible for a floc of size \( d \). Khelifa and Hill (2006) made a similar observation and suggested that this may be due to the effect of variability of the primary particle sizes. Khelifa and Hill modified Eq. (8) by adding a coefficient \( \phi = m_3/m_2^{D_f} \) that represents the effect size distribution of the primary particles in the floc where \( m_3 = (\sum N_i d_i^3)/N \) and \( m_2 = (\sum N_i d_i^2)/N \). However, in their paper, Khelifa and Hill never actually considered the effects of various primary particle sizes as they always assumed a mono-sized primary particle for one floc (\( \phi = 1 \)):

\[ v_m = \frac{16g \rho_p - \rho_w d_{50}^{a-b \gamma}}{1 + 0.15Re^{0.687}} \]  

(9)

where \( d_{50} \) is the median size of the component particles within the floc and \( \theta = a/\beta \).

In summary, we have demonstrated that there are many erroneous and sometimes conflicting assumptions used in the development of models describing the settling of flocs formed in water treatment processes. Most importantly, all of the developed equations ignore the multilevel structure of flocs and the fact that different levels of aggregation may be constructed by different mechanisms, therefore, characterized by fractal scaling relationships different than Eq. (5).

3. Multifractal analysis of lime softening flocs

In a three dimensional space, the fractal floc volume scales with the fractal dimension as \( V \sim d^{D_f} \). Since the floc volume fractal dimension \( D_f < 3 \), therefore the total floc volume

![Fig. 1](image-url) - The variation of box-counting fractal dimension with size and two-stage relationship.
increases more slowly with the floc size than for an Euclidean objects, where \( V \sim d^3 \). All of the floc settling models developed so far use the volume fractal dimension, \( D_V \), to describe the morphology of aggregates. This volume fractal dimension that appears in Eq. (5) is often estimated by using box-counting method that is by summing up all the pixels filling the floc’s image. When box-counting method is used, the relationship between the floc’s volume and the characteristic size of the floc is found to have a single exponent \( D_V \).

Yet, Stanley and Meakin (1988) demonstrated that diffusion-limited aggregates require an infinite number of fractal relationships (ie. exponents \( D_q \)) to describe the relationship between the aggregate’s volume and its characteristic size. Such aggregates are classified as multifractals and can be characterized by a continuous spectrum of scaling exponents.

It is important to note that in derivation of settling equations, the volume fractal dimension was assumed to be equal to the mass fractal dimension, \( D_V \) in Eq. (5). Though, the volume fractal dimension calculated by using the box counting method, provides no information about the mass distribution inside the floc (Kinsner, 2005). Multifractal analysis of flocs may provide more information about the structure and flocculation mechanisms of these aggregates.

### 3.1. Materials and methods

The studied lime softening flocs were collected in 2010 from the circular solid blanket clarifiers of Portage la Prairie (Manitoba, Canada) water treatment plant. The flocs were mainly composed of calcium carbonate (85%), and compounds of Mg (9%), Fe (5%) and Al (1%). The equivalent circular diameter (ECD) of the studied flocs ranged from 2 \( \mu m \) to 250 \( \mu m \) with the arithmetic mean of 49 \( \mu m \) and standard deviation of 36 \( \mu m \). There are a few very large flocs (>250 \( \mu m \)) in the sample.

#### 3.1.1. Imaging

A CCD camera and an optical microscope equipped with a motorized stage (Zeiss AxioImager Z1) were used for acquisition of section images of flocs. The microscope had inverted bright field. The motorized stage of the microscope also allowed for 3D imaging. The maximum image resolution of the microscope was 1.4. The magnifications of lenses used in this study were 10X, 20X and 40X. Axio Vision 4.5 Software was used for deconvolution of the images. More information on the experimental methods can be found elsewhere (Vahedi and Gorczyca, 2011, 2012).

#### 3.1.2. The probability-based approach for multifractal analysis

Let us define \( p_{i,j} \) as the probability that the floc area is captured in \( j \)th the covering element (pixel) of size \( r \):

\[
P_{i,j} = \lim_{N_{r} \to \infty} \frac{n_{i,j}}{N_{r}}
\]

\[
N_{r} = \sum_{i=1}^{N_{r}} n_{i,j}
\]

where, \( n_{i,j} \) is the number of floc area measurement points inside the pixel of size \( r \), and \( N_{r} \) the total number of floc area measurement points.

For a multifractal object that is covered by \( N_r \) elements of size \( r \), the general fractal dimension (Rényi fractal dimensions) can be defined by using the following power-law relationship:

\[
D_q = \lim_{r \to 0} \frac{1}{q-1} \frac{\log \sum_{j=1}^{N_r} (p_{i,j})^q}{\log(r)} - \infty \leq q \leq +\infty
\]

To achieve a bounded spectrum for different fractal dimensions the following transformation is used (Kinsner, 2005):

\[
a_q = \frac{d}{dq} [(q-1)D_q]
\]

\[
f_q = qa_q - (q-1)D_q
\]

The parameters \( a_q \) and \( f_q \) are called singularity strength and singularity spectrum respectively. Each point on the singularity spectrum represents a specific fractal dimension. By rearranging Eq. (14), the fractal dimension associated to a given point on the singularity spectrum can be derived:

\[
D_q = \frac{f_q - qa_q}{1-q}
\]

Only for \( q = 0 \), the Rényi dimension is equivalent to the self-similarity or box-counting dimension \( D_0 \) that we used in the settling model in our earlier papers (Vahedi and Gorczyca, 2011, 2012). Note that the Rényi dimension becomes singular for \( q = 1 \), however it can be shown that for \( q = 1 \), it is equivalent to information dimension \( D_0 \) (Atmanspacher et al., 1988):

\[
D_0 = \lim_{r \to 0} \frac{1}{q-1} \frac{\log \sum_{j=1}^{N_r} p_{i,j} \log p_{i,j}}{-\log(r)}
\]
A number of researchers have used the above approach to determine the Rényi dimensions of multifractal aggregates formed in rivers and biological wastewater treatment processes (Perrier et al., 2006; Maggi et al., 2006; Yang et al., 2008).

In this study, the singularity spectrum and Rényi dimensions were determined for 21 lime softening flocs with different sizes ($10^{230}$ mm). The results of two representative flocs with different sizes are presented in the next section as the multifractal spectra for analyzed flocs were very similar.

### 3.2. Results of multifractal analysis and discussion

Results of multifractal analysis of two individual lime softening flocs are presented in Fig. 2 and Fig. 3. These figures show a relationship between singularity spectrum and singularity strength for different values of $q$ that is typical for a multifractal object. Therefore, the lime softening flocs are multifractal and one fractal dimension may not be sufficient to describe the characteristics of these flocs.

As discussed earlier in this paper, Eq. (5) is based on the assumption of a single mechanism of flocculation and homogeneous mass distribution in the floc. The scaling factor ($D_f$) is assumed to be constant for all levels of aggregation, the fioccule, the microfloc and the fully grown floc. In our previous paper we reported at least two different flocculation mechanisms for lime softening flocs (Fig. 1). The multifractal analysis of lime softening flocs presented here, confirms that these aggregates may exhibit a range (spectrum) of fractal dimensions and therefore can be formed through multiple mechanisms resulting in nonhomogeneous mass distribution and extremely complex structures.

An important detail of the $D_q$ spectrum is the almost constant dimension when $q > 0$ particularly for large values of $q$. These points correspond to the regions inside the floc with high mass density (Atmanspacher et al., 1988). The high density region is the region where the probability of the pixel being filled with the floc material is high. In fact, the constant fractal dimension indicates the regions with probabilities of almost 1. This dimension is the lowest fractal dimension of the object.

For a mono fractal (a fractal that is formed by one scaling or aggregation mechanism) with equal probabilities (typically 1), $D_q$ does not vary with $q$ (Theiler, 1990). Therefore, the variation of $D_q$ with $q$ quantifies the heterogeneity of the fractal. Comparing the two presented flocs in Figs. 2 and 3, it is evident that the $D_{:0} - D_{:+}$ is larger for the larger floc which is consistent with the results of our previous study (Vahedi and Gorczyca, 2011) that suggested more heterogeneous structure for larger flocs. Similar trend was more or less observed for all analyzed flocs.

Note that the spectrum of fractal dimensions described by Eq. (12) is obtained for a single floc, and it is completely different from various fractal dimensions for a population of differently sized flocs presented in our earlier paper (Fig. 1). In...
the earlier paper, we argued that two flocs with the same size can have different volume fractal dimensions. Here, we argue that two flocs with the same size and same volume fractal dimension may have been formed by different mechanisms of aggregation and consequently have different arrangement of primary particles and hence, different mass distributions. As a result, two flocs of the same size may have different masses or different mass distributions. Estimation of the floc mass is critical for the development of the floc settling equation.

The lime softening flocs in this study were somewhat similar to activated sludge flocs (Yang et al., 2008) and river mud flocs (Maggi et al., 2006; Yang et al., 2008), which also exhibited a singularity spectrum and a range of various fractal dimensions (Rényi dimension). However, the relationships between the various fractal dimensions (the points on singularity spectrum) and the physical properties of the flocs are still not clear. Therefore, we are still unable to predict the settling velocity for an individual floc. This is because these flocs are formed by a variety of different mechanisms. Different aggregation mechanisms produce flocs with different sizes, different configuration of the primary particles inside them and consequently, different densities and mass distributions. So far, we have been able to incorporate the variable floc sizes and the morphology-based fractal dimension (volume fractal dimension, $D_v$) into the floc settling equation. More research is required to investigate how to utilize the information obtained from the multifractal spectra to incorporate the variable floc density and nonhomogeneous mass distribution of flocs into the floc settling models. At this point, we may only conclude that the flocs in water treatment processes have very complex structures that cannot be adequately described by fractal dimensions that are only based on the morphology alone. Multiple flocculation mechanisms and therefore multiple fractal relationships have to be incorporated into the floc settling models.

4. Conclusions

A number of different flocculation mechanisms are involved in the formation of flocs in the water treatment processes. Therefore, the resulting flocs have very complex structures and cannot be adequately described by their morphology alone. We have reviewed assumptions typically used in the development of floc settling equations and we have made the following conclusions:

1. A single and constant fractal relationship between the floc size and floc volume has always been assumed in development of floc settling models. This incorrectly suggests a single mechanism of flocculation for the floc and its levels of aggregation. Different mechanisms of flocculation result in different scaling relationships between the floc size and its volume.
2. Two flocs of the same size may be formed through a variety of different mechanisms and by different primary particles. Therefore, flocs of the same size may have different primary particles and different arrangements of primary particles inside them and consequently different densities and mass distributions. Although the correct estimation of the floc mass is critical for the development of the floc
settling model, none of the models incorporate the information on mass distribution and variable density of flocs. 3. The advanced analysis of images of lime softening flocs demonstrated that these aggregates are multifractal; the multifractal spectra indicate the existence of fractal dimensions other than the ones describing the floc morphology typically introduced into the Stokes’ Law. These other fractal dimensions may provide information on the distribution of mass inside the floc.

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