A simple model to study the flocculation of suspensions over time

Chassagne, C.

DOI
10.1016/j.ched.2021.06.006

Publication date
2021

Document Version
Final published version

Published in
Chemical Engineering Research and Design

Citation (APA)

Important note
To cite this publication, please use the final published version (if applicable). Please check the document version above.

Copyright
Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy
Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.
A simple model to study the flocculation of suspensions over time

C. Chassagne

Environmental Fluid Mechanics, Faculty of Civil Engineering and Geosciences, Delft University of Technology, 2600 GA Delft, The Netherlands

A R T I C L E   I N F O

Article history:
Received 30 January 2021
Received in revised form 2 June 2021
Accepted 7 June 2021
Available online 24 June 2021

Keywords:
Flocculation
Colloid
Clay
Logistic growth
Population balance

A B S T R A C T

The model based on logistic growth theory, that was introduced in Chassagne, Claire, and Zeinab Safar. “Modelling flocculation: Towards an integration in large-scale sediment transport models.” Marine Geology 430 (2020): 106361, can be used to model the time evolution of either the particle (floc) size or the concentration of particles of a given size. In the present article, we show how this model can easily be linked to the many studies performed over the years about the flocculation kinetics at the onset of flocculation experiments. Flocculation experiments done on kaolinite suspensions destabilized by addition of salt are used as examples. Both perikinetic and orthokinetic flocculation are considered. By fitting the experimental data over the whole experiment period, it is shown that the floc size \(L(t)\) time evolution follows the relation

\[
\frac{dL}{dt} = \frac{L}{t_0} - \frac{L^2}{L_{\infty} t_0}
\]

where \(t_0\) is a characteristic time and \(L_{\infty}\) a characteristic size, which are obtained from the fits.

© 2021 The Author(s). Published by Elsevier B.V. on behalf of Institution of Chemical Engineers. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Aggregation (flocculation) of particles in suspensions is a topic that has been widely studied over several decades (Elimelech et al., 2013; Chassagne, 2020; Russel et al., 1991). Quite some work (still ongoing today) has been performed on the study of stability ratios, defined as the ratio \(W = (dL/dt)_{t=0,\text{fast}}/(dL/dt)_{t=0,\text{slow}}\) where \(dL/dt\) represents the rate of increase of hydrodynamic diameter with time. The subscript fast refers to the reference experiment in a series, for which the rate is the fastest (the stability ratio is therefore in general always larger or equal to one). The stability ratio is particularly interesting to study as its theoretical value can be calculated, based on DLVO theory. Modelling \(W\) as function of ionic strength for example enables to test the DLVO theory and associated boundary conditions (constant potential, constant charge or intermediate regulation). In other applications, such as the study of the flocculation of clay in estuarine conditions which is our topic of interest, it is important to obtain information about the flocculation dynamics not only at short but also at long times, owing to the residence time of the particles in the water column.

The flocculation behavior as function of time can be modelled using Population Balance Equations (PBE) which give the time evolution of classes of colloidal particles, a class \(i\) being defined as a collection of particles with concentration \(n_i\), all particles in a same class having the same size (diameter) \(L_i\). The concentrations \(n_i\) can either be given in number, mass or volume of particles per unit of volume. A classical PBE is the one introduced by Smoluchowski in 1917 (Smoluchowski, 1917; Elimelech et al., 2013; Chassagne, 2020), and many studies have since then proposed aggregation and break-up parameters to be implemented in PBE’s (Elimelech et al., 2013; Russel et al., 1991; Barthelemes et al., 2003; Spicer and Pratsinis, 1996; Kusters, 1991; Flesch et al., 1999). PBE’s have also been modified to account for the role of adsorbed layers onto particles (Somasundaran and Runkana, 2005).

In a recent article (Chassagne and Safar, 2020), it was shown that the variations of \(n_i\) with time could be modelled by a set of uncoupled equations for \(n_i\) based on logistic growth theory. It was shown that the same type of equations can be used to fit the time evolution of particle sizes during the flocculation process. These equations have the great advantage that

E-mail address: c.chassagne@tudelft.nl

https://doi.org/10.1016/j.ched.2021.06.006

0263-8762/© 2021 The Author(s). Published by Elsevier B.V. on behalf of Institution of Chemical Engineers. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).
they do not require a significant computational effort and can therefore be implemented in numerical sediment transport models.

In the present article, we connect the theory developed in (Chassagne and Safar, 2020) to the aggregation and break-up parameters found by other authors in PBE models. We show that literature flocculation data can be modelled using equations based on logistic growth theory for the whole range of experimental time. The influence of several parameters, such as ionic strength, initial particle concentration and shear rate on the flocculation rate is discussed.

2. Logistic growth function for flocculation

In this section, we recall the logistic growth expression proposed in Chassagne and Safar (2020). We consider one class of particles and hence will define \( n \) as the number of particles inside this class. The time-dependence of \( n \) (which could also be expressed as a mass or volume of particles per unit of volume) is given by

\[
\frac{dn}{dt} = [b(t) - d(t)] n
\]

whereby the (positive) functions for birth \( b(t) \) and decay \( d(t) \) are given by:

\[
b(t) = \frac{a_b}{\tau_b} \frac{\exp(-t/\tau_b)}{1 + a_b \exp(-t/\tau_b)}
\]

\[
d(t) = \frac{a_d}{\tau_d} \frac{\exp(-t/\tau_d)}{1 + a_d \exp(-t/\tau_d)}
\]

The coefficients \( a_b, \tau_b, a_d, \tau_d \) are to be parameterized. The characteristic times for birth and decay are given by \( \tau_b \) and \( \tau_d \) and \( a_b/\tau_b \) and \( a_d/\tau_d \) are characteristic rates for birth and decay. We note a typological error in Chassagne and Safar (2020) where a\( n^2 \) appears at the right-hand-side of the equation corresponding to Eq. (1). The names “birth” and “decay” are solely chosen because they appear with a plus and minus sign in the balance equation Eq. hyperlinkbalance((1)). Setting \( d(t) = 0 \) it is easy to verify that the growth of \( n \) will nonetheless be limited in time (as if a decay process is limiting the growth) and \( n \) will reach a steady-state value \( n_\infty \) at long time. The analytical solution of Eq. (1) is given by

\[
n(t) = n_\infty \frac{1 + a_d \exp(-t/\tau_d)}{1 + a_b \exp(-t/\tau_b)}
\]

Note that we have here changed the notations compared to (Chassagne and Safar, 2020), to better follow what other authors do. The variable \( N(t) \) in (Chassagne and Safar, 2020) is now defined as \( n(t) \). The variable \( N(t) \) in the present article represents the number of primary particles inside a floc of size \( L(t) \).

The advantage of Eq. (4), which makes it possible to model each class independently of another, is that it enables to chose the definition of a class of particles. It is for instance possible to define a class as a collection of particles with time-dependent size \( L(t) \). The PBE models do not allow for this, as the transfer of particles from one class to another is based on parameters that explicitly depends on the size of particles within a class, see Eq. (20). In this article, we will show that the growth of floc’s sizes can also be modelled using an equation similar to Eq. (4). For sediment transport models as well as for other numerical models based on flocculation, it is nonetheless important to obey mass conservation. In the appendix, a small discussion about mass conservation in the context of sediment transport in the marine environment is given. It is shown how this mass conservation can be linked to the logistic growth model presented above. The values used for the fits presented in the article are given in Tables 1–6.

3. General PBE theory

In this section, we recall the main features of the Population Balance Equation (PBE) used to describe the flocculation of colloidal particles in natural systems (Chassagne, 2020; Chassagne and Safar, 2020; Maggi, 2009; Mietta et al., 2011; Shen et al., 2018; Lai et al., 2018). The PBE is a set of equations describing the time evolution of the concentration of particles in a size class, where a size class is defined as the ensemble of particles of a given size and density. A PBE equation for a size class \( i \) (there are as many PBE’s as there are size classes) is given by the time derivative of the mass, volume or number concentration of particles in the size class. This derivative is function of the sum of four terms, representing the gain by aggregation (particles of smaller sizes aggregating to form a particle of size \( i \)), the gain by break-up (particles of higher classes breaking to form particles of size \( i \)), the loss by aggregation (particles of size \( i \) aggregating and therefore leaving class \( i \) ) and loss by break-up (particles of size \( i \) breaking and therefore leaving class \( i \)). These terms depend in particular on four parameters: the collision efficiency, the collision frequency, the break-up rate and the break-up distribution function. In principle, each of these parameters is class-dependent.

The equation representing the population evolution in time then can be reduced to the sum of two terms (given in square brackets), the first one being representing the changes in population due to aggregation and the second one the changes due to break-up:

\[
\frac{dn_i}{dt} = \left[ \frac{1}{2} \sum_{j=1}^{i-1} a_{ij} \beta_{ij} n_{i-j} n_j - N_i \sum_{j=1}^{n-1} a_{ij} \beta_{ij} n_j \right] + \sum_{k=i+1}^{n} \gamma_{ik} s_{i} n_i - s_{i} n_i
\]

where \( n_i \) represents the number of particles in a class \( i \). The functions \( a_{ij}, \beta_{ij}, \gamma_{ij} \) and \( s_{i} \) are discussed in the following subsections. From a simple dimension analysis, it follows that the characteristic aggregation (birth) and break-up (decay) rates are proportional to

\[
k_b \sim a_{ij} \beta_{ij}
\]

\[
k_d \sim s_{i}
\]

3.1. Break-up rate and distribution

The break-up rate is given by \( s_{i} \) and break-up distribution function by \( \gamma_{ij} \). The break-up rate is related to the property of a single particle to be able – or not – to break and is taken to be independent of the other classes, as it is usually assumed that it is a function of shear and particle size only. A simple expres-
sion for \( s_i \) is of the form (Spicer and Pratsinis, 1996; Barthelmes et al., 2003):

\[
s_i = s_b \left( \frac{\rho G}{\tau} \right)^{1/4} L_i^p
\]  

(7)

where \( s_b \) is a parameter to be fitted, \( \rho \) is the viscosity of the suspension, \( G \) is the shear rate and \( L_i \) is the diameter of a particle of class \( i \). Furthermore, \( \tau^* \) is a characteristic shear stress which is a measure for the aggregate strength: the larger \( \tau^* \) the less the particles are susceptible for breakage. The product \( \rho G \) is the shear stress in shear flows: the higher the stress, the more flocs are susceptible to break. The simplest models assume that \( s_i \) scales with the size of particles \( p = 1 \). However, in the case of fractal flocs as the ones formed by salt-induced aggregation of hard spheres, the smaller the fractal dimension, the less particle bonds per aggregate volume, the smaller the floc strength. Therefore the breakage rate should increase with decreasing fractal dimension \( D \), which Barthelmes (Barthelmes et al., 2003) accounts for by introducing the term

\[
v_1^{1/3} \left( \frac{L_i}{v_1} \right)^{3/D}
\]  

(8)

in Eq. (7) to yield

\[
s_i = s_b \left( \frac{\rho G}{\tau} \right)^{1/4} v_1^{1/3} \left( \frac{L_i}{v_1} \right)^{3/D}
\]  

(9)

where \( L_1 \) is the size of a primary particle (Class 1) and \( v_1 \) its volume. Note that this implies that \( p = 3/D \)

\[
\rho = 3/D
\]  

(10)

One then finds that \( 3 \geq p \geq 1 \). In the case of solid particle (\( D = 3 \)) one recovers \( p = 1 \).

Other expressions for the break-up of fractal flocs have been proposed, see (Kusters, 1991; Flesch et al., 1999) where the break-up rate is given by

\[
s_i \sim \Delta u \exp \left( -\Delta u_2^2 / \Delta u^2 \right)
\]  

(11)

where \( \Delta u \) is the root mean square velocity difference across the distance \( L_i \) and \( \Delta u_2 \) the critical velocity difference at which break-up occurs – which is a function of the aggregate size. For the eddy frequency in the inertial subrange (the range of eddies intermediate in size between large-scale eddies and Kolmogorov microscale), one obtains

\[
\frac{\Delta u}{L_i} \sim \varepsilon^{1/3} L_i^{-2/3}
\]  

(12)

where \( \varepsilon \) is the dissipation rate per unit of mass. This is the range primarily affecting polymer-induced flocs, as salt-induced flocs are limited in growth by the Kolmogorov length scale. For the viscous subrange (where dissipation of turbulent energy by viscous effects increases as the size of eddies decrease), one gets

\[
\frac{\Delta u}{L_i} \sim (\varepsilon / \nu)^{1/2}
\]  

(13)

which is the range affecting salt-induced flocs. The variable \( \nu \) represents the kinematic viscosity. If \( \Delta u^2 \gg \Delta u_2^2 \) we get

\[
s_i \sim (\varepsilon / \nu)^{1/2}
\]  

(14)

Note that \( (\varepsilon / \nu)^{1/2} \) is the inverse of the Kolmogorov time scale, which is usually taken to be a measure for characteristic shear rate

\[
G \approx (\varepsilon / \nu)^{1/2}
\]  

(15)

If \( \Delta u^2 \gg \Delta u_2^2 \) one therefore gets for the viscous subrange

\[
s_i \sim G
\]  

(16)

The corresponding fragmentation exponent \( q \) is in this case equal to 1. The fragmentation exponent \( q \) is usually experimentally found to be \( 1.5 < q < 6.5 \) (Barthelmes et al., 2003). Several types of break-up distribution function \( \gamma_{ij} \) have been proposed in literature. Binary break-up is for instance expressed as

\[
\gamma_{ij} = \frac{v_j}{v_i}
\]  

(17)

where \( v_i \) is the volume of a Class \( i \) particle. Expressions for ternary breakage and normally distributed fragments are given in (Spicer and Pratsinis, 1996).

3.2. Collision efficiency and collision frequency

The term corresponding to aggregation depends on the product of the number of particles in two classes, as it depends on the interaction between two particles. The collision efficiency \( a_{ij} \) is either taken to be constant, \( a_{ij} = a \) (Mietta et al., 2011), class-dependent (Kusters, 1991) or shear dependent (Soos et al., 2008). The collision efficiency is related to the stability ratio \( W \) by \( W = 1/a \) whereby \( a \) is then the average collision efficiency of the suspension (Kretzschmar et al., 1998). In (Kretzschmar et al., 1998), it has been shown experimentally that the coagulation (aggregation by salt) rate constant \( k_b \) is linked to the initial particle size and initial particle concentration \( c \) by

\[
\left( \frac{dl}{dt} \right)_{t=0} = A_b k_b c
\]  

(18)

where \( A_b \) is an optical factor that is a function of particle size, scattering angle and wavelength of light in the medium. The average collision efficiency, for a given concentration \( c \) can be estimated by

\[
a = \frac{\left( dl/dt \right)_{t=0}}{\left( dl/dt \right)_{t=0, \text{fast}}}
\]  

(19)

where \( (dl/dt)_{t=0, \text{fast}} \) is the growth rate in the absence of repulsion between particles, for instance at high salinity in most coagulation experiments.

The collision frequency due to shear (orthokinetic aggregation) can be estimated by (Russel et al., 1991)

\[
\beta_{ij} = \frac{G}{6} (L_i + L_j)^3
\]  

(20)

Other expressions for \( \beta_{ij} \) are available. For Brownian motion-induced (\( \kappa \) perkinetic) flocculation (Elimelech et al., 2013; Russel et al., 1991) one gets

\[
\beta_{ij} = \frac{2kT}{3\eta} \left( \frac{L_i + L_j}{L_i} \right)^2
\]  

(21)
3.3. A simplified PBE

At the early stage of aggregation, primary particles (Class 1 particles) will aggregate to form doublets (Class 2 particles). Doublets are thus flocs made of a pair of primary particles. Note that this is true for salt-induced flocculation but not necessarily true for polymer-induced flocculation as the radius of gyration of a polymer can be such that in a small time step a polymer can “catch” multiple primary particles. At the early stage of doublet formation, the PBE reduces to:

\[
\frac{dn_1}{dt} = -\alpha_{1,1} \beta_{1,1} n_1^2 + \gamma_{1,2} n_2 n_1 \\
\frac{dn_2}{dt} = \frac{1}{2} \alpha_{1,1} \beta_{1,1} n_1^2 - \gamma_{1,2} n_2 n_1
\]

(22)

In the equations, the variable \( n_1 \) is the number of primary particles (Class 1) per unit of volume and \( n_2 \) is the number of doublet per unit of volume (a Class 2 floc is made out of 2 Class 1 particles). The doublets can only break in two (there is no other possibility), hence \( \gamma_{1,2} = 2 \). Assuming a constant collision efficiency and orthokinetic aggregation, one gets

\[
\beta_{1,1} = \frac{G}{6}(2L_1)^3
\]

\[
\alpha_{1,1} = \alpha
\]

(23)

The break-up rate \( s_2 \) is here assumed to be zero (only aggregation is occurring).

Adding and comparing the two equations for \( n_1 \) and \( n_2 \) in eqs. (22) one gets, by defining \( n = n_1 + n_2 \):

\[
\frac{dn}{dt} = \frac{1}{2} \alpha_{1,1} \beta_{1,1} n_1^2
\]

(24)

In Eq. (24), which represents the very early stage of aggregation, the characteristic lengthscale is the size of primary particles, i.e. \( L_1 \). Eq. (24) can however be generalized to represent the rate of change of the total particle concentration (total number of particles per unit of volume) \( n = \sum n_i \) provided that the rate constants \( \alpha_{ij} \beta_{ij} \) are assumed to be equal for all classes (see (Elimelech et al., 2013), p.162). One then obtains, defining \( \alpha_{ij} \beta_{ij} = \alpha \beta \):

\[
\frac{dn}{dt} = \frac{1}{2} \alpha \beta n^2
\]

(25)

For particles not too different in size, one finds that for perikinetetic flocculation Eq. (21) reduces to

\[
\beta_{ij} = \beta \approx \frac{8kT}{3\eta} = 1.2 \times 10^{-17} \text{ m}^3/\text{s}
\]

(26)

which implies that \( \alpha_{ij} \beta_{ij} \) is indeed independent of class i and j provided that \( \alpha_{ij} = \alpha \). However, for orthokinetic flocculation (which is the flocculation required to model clay flocculation in estuarine conditions), one finds that, assuming that all flocs have the same size

\[
\beta_{ij} = \beta_i \approx 4GL_i^3
\]

(27)

which implies that \( \beta_{ij} \) will increase while \( L_i \) is increasing.

4. Aggregation over time

In this section, we show how the analytical formulation for particle size growth given below can be used to study the early stages of floc growth as well as the flocculation process over a longer period of time. Based on the work presented in (Chassagne and Safar, 2020) the change in floc size as function of time can be modelled with an equation similar to Eq. (4):

\[
L(t) = L_{eq} + \frac{1}{1 + a_b} \exp \left(-t/t_d \right)
\]

(28)

where \( a_d, a_b, t_d, t_b \) are adjustable parameters. At times such as \( t \ll t_b, t_d \) Eq. (28) reduces to

\[
L(t) \approx \frac{1}{1 + a_d} L_{eq} + \frac{\left( \frac{dt}{dt} \right)_{t\ll t_b, t_d}}{t/t_b}
\]

(29)

where the flocculation rate \( (dt/dt)_{t\ll t_b, t_d} \) is defined by

\[
\left( \frac{dt}{dt} \right)_{t\ll t_b, t_d} = \frac{a_d/a_b}{(1 + a_d) - a_d/t_d} \frac{L_{eq}}{1 + a_b^2}
\]

(30)

If one defines \( n_0 = n(t=0) \) to be the number of primary mineral sediment particles per unit of volume in a closed volume (as for example in a jar test experiment) it follows that \( n_0 \) is a constant as function of time, whereas the size of particles in suspension will be time-dependent as flocs are growing. The total number of primary particles per unit of volume is given by

\[
n_0 = \sum_i n_i n_i
\]

(31)

where \( n_i \) is the number of particles of size \( L_i \) per unit of volume and \( N_i \) the number of primary particles in a particle of size \( L_i \). Note that \( N_1 = 1 \) with \( L_1 = L_p \) (\( L_p \) is the size of primary particles) and that at \( t = 0 \), \( n_0 = n_1 \).

If it is assumed that, at any moment in time, a suspension is well represented by a characteristic size and concentration, one may write

\[
0 = \frac{dn}{dt} + n \frac{dN}{dt}
\]

(32)

It is here implicitly assumed that all flocs of same size \( L \) contains the same number of primary particles \( N \). The relation between number of primary particles in a floc and floc size is given by Kranenburg (1994)

\[
N(t) = \left( \frac{L(t)}{L_p} \right)^D
\]

(33)

where D is usually termed “fractal dimension”, in reference to the case of monodisperse primary particles, where the concept of self-similarity can be used. Experiments have been conducted to assess the fractal dimension for diffusion-limited and reaction-limited aggregates (Russel et al., 1991), where the initial growth of flocs is also investigated. For a given number of primary particles per floc \( N \) (and hence the same floc size \( L \)) the number of flocs in suspension \( n \) is linearly proportional to the concentration \( c \) (which is a linear function of \( n_0 \)).
Combining Eqs. (32), (33) gives

\[
\frac{1}{n} \frac{dn}{dt} = \frac{1}{N} \frac{dN}{dt} = -D \frac{dL}{t} \frac{L}{\tau}
\]  

This expression is to be compared to Eq. (25) from which we deduce that

\[
dL \frac{dt}{t} = n \alpha^B L
\]

We recall that this equivalence holds only if \(\alpha^B\) is the same for all classes – an hypothesis that is not necessarily satisfied. This implies in the present case that \(\alpha^B\) is a-priori not depending on time. It can be deduced that the growth rate of \(L\) is depending on the concentration of clay \(c\) (g/L), since the number of flocs per unit volume \(n\) is directly proportional to \(c\) for a given floc size \(L\) and \(n_0 L_0^{3+2} \sim c\). It is not certain however whether the growth rate of \(L\) is proportional to \(n\) or a power thereof, as the dependence of \(L\) on \(n\) is at this stage unknown.

If we assume that flocs are only growing, but that their growth is limited by, for instance, the fact that their size is reaching the Kolmogorov lengthscale, the evolution of their mean particle size is described by setting \(\alpha^d = 0\) in Eq. (28), which then reduces to

\[
L(t) = L_{eq} \left( \frac{1}{1 + \alpha_0 \exp(-t/t_b)} \right)
\]

with

\[
\frac{dL}{dt} = \left( \frac{1}{L(t)} - \frac{1}{L_{eq}} \right) \frac{1}{t_b} L^2
\]

In contrast to Eq. (35), the dependence of the growth rate \(dL/dt\) on \(L\) in Eq. (37) is explicit and can therefore be tested, which is done in the next subsection.

4.1. Dependence on initial particle concentration

The dependence of the floc growth rate is investigated as function of initial clay concentration, using literature data taken from Kretzschmar et al., 1998, see Fig. (1). The values found from fitting the data are given in Table 1. Kaolinite suspensions with size fraction \(<1\mu m\) were used in the experiments. The flocculation was triggered by the addition of 0.01 M of NaClO4 at pH = 4. The data could be fitted using Eq. (36), implying that we set \(\alpha^d = 0\). From Fig. (1), it can be seen that the initial flocculation rate, estimated using Eq. (38) is proportional to particle concentration. This dependence seems to be more quadratic (see the dashed curve, right panel of Fig. (1)) than linear (see full lines) for the fits at small times. This seems to suggest, following Eq. (35), that at short times the particle size is linearly proportional to concentration. The dependence of the initial flocculation rate on concentration is however linear when the dataset is fitted over the whole time period.

The dependence of the flocculation rate on particle size and time is shown in Fig. (2). The dashed line plotted on the 25 mg/L data corresponds to the fit found by considering only the first 10 min of the experiment, and illustrates the fact that the flocculation kinetics at the onset of the experiment might be different from the kinetics at longer times. The flocculation rate dependence on particle size follows the dependence given by Eq. (37), as being of the form \(L + bL^a\) where \(a\) and \(b\) are constants. The flocculation rate is decaying exponentially as function of time, also as expected.

4.2. Dependence on ionic strength

The dependence on ionic strength has been studied using data taken from Aurell and Wistrom (2000), see Fig. (3). The values
Fig. 2 – (Left panel): normalized flocculation rate \( (dL/dt)/L \) as function of particle size \( L \) for different clay concentrations, indicated in the legend. The full lines correspond to the fits of the data between 0 and 30 min using Eq. (28); the dashed line corresponds to a fit for the first 10 min (Right panel): normalized flocculation rate as function of time. The data is taken from Kretzschmar et al. (1998).

Fig. 3 – (Left panel): Hydrodynamic diameter \( L \) as function of time for different ionic strength, indicated in the legend. The full lines correspond to the fit of the data between 0 and 60 min using Eq. (28); the dotted lines correspond to the fit of the data below 5 min, using Eq. (28); the dashed lines correspond to linear fits at origin (Right panel): flocculation rate \( (dL/dt) \), estimated using Eq. (29) and the slope of the linear fit. The values are obtained from the fits of the data on the left panel. The data is taken from Aurell and Wistrom (2000).

<table>
<thead>
<tr>
<th>100 mM</th>
<th>200 mM</th>
<th>300 mM</th>
<th>500 mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L_0 ) (nm) fit&lt;5 min</td>
<td>140</td>
<td>331</td>
<td>685</td>
</tr>
<tr>
<td>( L_0 ) (nm) fit 60 min</td>
<td>140</td>
<td>411</td>
<td>1433</td>
</tr>
<tr>
<td>( a_1 ) fit&lt;5 min</td>
<td>0</td>
<td>1.6</td>
<td>2.7</td>
</tr>
<tr>
<td>( a_1 ) fit 60 min</td>
<td>0</td>
<td>1.1</td>
<td>4.7</td>
</tr>
<tr>
<td>( t_f ) (min) fit&lt;5 min</td>
<td>26.5</td>
<td>5.0</td>
<td>1.4</td>
</tr>
<tr>
<td>( t_f ) (min) fit 60 min</td>
<td>32</td>
<td>12</td>
<td>6.5</td>
</tr>
<tr>
<td>( (dL/dt) ) fit 60 min</td>
<td>3</td>
<td>17</td>
<td>50</td>
</tr>
<tr>
<td>( (dL/dt) ) fit&lt;5 min</td>
<td>3</td>
<td>27</td>
<td>138</td>
</tr>
<tr>
<td>( (dL/dt) ) lin fit&lt;5 min</td>
<td>3</td>
<td>28</td>
<td>260</td>
</tr>
</tbody>
</table>

Table 2 – values used to generate Fig. (3). \( (dL/dt) \) is given in nm/min.

found from fitting the data are given in Table 2. The experiments were performed by adding known amounts of NaCl electrolyte to kaolinite suspensions. These particles were prepared in a carbonate rich groundwater at pH in the range 7–8. The average clay concentration in each experiment was about \( n_0 = 1.6 \times 10^9 \) particles per mL, and the average particle diameter was 160 nm (with a thickness between 8 and 17 nm). The dataset has been fitted for the whole 60 min period (full lines) and for the data in the range [0–5 min] (dotted lines). The dataset has also been fitted using a linear fit at origin (dashed lines). Using Eq. (28), the flocculation rates are estimated using the values found for the whole 60 min fit (fit 60 min) and for the data below 5 min fit (fit<5 min). The remaining flocculation rate (lin fit) is the slope of the linear fit at origin.

One can observe that there is a shift in flocculation dynamics with increasing ionic strength. For ionic strengths below 300 mM the flocculation can be modelled with almost the same parameters for the fits below 5 min and for the whole 60 min, which is reflected by the fact that the full and dotted curves overlap for the whole time range. For and above 300 mM, a deviation appears: the parameters used for the fitting curves are different. As the distance between flocs increases, the flocculation rate decreases. This implies that the estimated flocculation rate found by fitting the data over the whole 60 min is smaller than the estimated flocculation rate found by fitting the data between 0 and 5 min (right panel of Fig. (3)). The flocculation is a perikinetic flocculation process, implying that the initial flocculation rate can be estimated by, assuming \( \alpha = 1 \),

\[
\frac{dL}{dt} = \frac{n_0}{2D} \frac{8kT}{\eta} L
\]  

Using a fractal dimension \( D = 3 \) and \( L = 160 \) nm, one obtains

\[
\frac{dL}{dt} = \frac{1.6 \times 10^9}{6 \times 10^{-6}} \times 1.2 \times 10^{-17} \times 160 \times 60 = 30 \text{ nm/min}
\]
which is the initial flocculation rate at 300 mM. The initial flocculation rate at 500 mM is even larger and about 130–200 nm/min, but is difficult to estimate. Fitting the data for the data points below 10 min, one finds a flocculation rate of about 50 nm/min, therefore in range of the one found for 300 mM. This is also what Aurell and Wistrom have used, who have analyzed their data in terms of stability ratio using DLVO theory. The average collision efficiency, for the early stage of aggregation can be estimated using Eq. (19), and hence it is found that the average collision efficiency is of the order of \( \alpha = 0.1 \) for 200 mM NaCl.

### 4.3. Influence of shear

It has been shown that the mean floc size evolution as function of time can be fitted by Eq. (28). An empirical expression for the stable floc size is given by (Chassagne, 2020),

\[
L_{eq} = CG^{-\gamma}
\]

where \( C \) and \( \gamma \) are fitted coefficients. For salt-induced flocs, it has been shown that the stable floc size follows in good approximation the Kolmogorov microscale (Mietta, 2010),

\[
L_{eq} \sim \left( \frac{G}{\nu} \right)^{-1/2} = \left( \frac{C}{\gamma} \right)^{-1/4}
\]

where \( \nu \) is the kinematic viscosity, which is of the order of \( 10^{-6} \text{m}^2/\text{s} \) for water at 20°C. We have here used \( G \sim (\nu/\nu)^{1/2} \) as an estimation of the shear rate. This implies that in that case

\[
\gamma = 1/2
\]

\[
C = \nu^{1/2} = 10^{-3} \text{m/s}^{1/2}
\]

For a shear rate of about 50–100 s\(^{-1}\), this gives \( (G/\nu)^{-1/2} = 140–100 \mu\text{m} \). This is of the right order of magnitude for \( L_{eq} \) for salt-induced aggregation (Mietta, 2010). It has however been shown that \( L_{eq} \) also depends on the type and amount of salt used to flocculate the suspension, as well as the pH of the suspension.

Values found for \( C \) and \( \gamma \) are in the range [10\(^{-3}\) – 10\(^{-2}\)] m/s\(^{1/2}\) for \( C \) and [0.29–0.81] for \( \gamma \) (Jarvis et al., 2005).

From Eqs. (6), (7), (27), one can estimate that

\[
k_0 \sim a_0/t_0 \sim \alpha q \sim \alpha G L^3
\]

\[
k_4 \sim a_4/t_4 \sim (\frac{G}{\nu})^4
\]

where it is usually found that \( q \) is close to 1.5 and \( p = 1 \) (Barthelmes et al., 2003). This implies that birth rate should scale with \( G \) whereas decay rate should scale with \( G^{3/2} \).

The dependence of the flocc growth rate on shear is investigated as function of particle size, using literature data taken from Wang et al. (2018), see Fig. (4). The values found from fitting the data are given in Tables 3–5. The samples consisted of kaolinite particles of size 3.6 \( \mu\text{m} \) dispersed in a polyaluminium solution with concentration 0.1% w/w. The suspension was stirred in an home-made tank with an agitator (R1342-type IKA, Germany). The conversion between rpm and shear rates is given in Table 1 of Wang et al. (2018). From the fitted data the flocculation rate \( k \) (% number of particles/s) was evaluated by linearizing Eq. (4), which gives, similarly to Eq. (30)

\[
k = \frac{a_k/a_0}{(1 + a_k) - a_0/a_0 (1 + a_k)^{n_\infty}}
\]

This flocculation rate \( k \) (which represents the flocculation rate at origin) is plotted in Fig. (5). The values found from fitting the data are given in Table 6. The cumulative % number of particles in the four size classes is also given in the same figure.

From the dependence of \( k \) on shear, one can see that the size class [2–3 \( \mu\text{m} \)] has, at start, a positive flocculation rate,
implying that this class is populated by flocculated particles from lower classes. At low shear (11 s$^{-1}$) the [3–15 μm] size class has the same flocculation rate as the [2–3 μm] class, however, at higher shears, the flocculation rate of the [3–15 μm] size class is much larger. The number of particles in the class [3–15 μm] is hence increasing more rapidly as function of shear. The flocculation rates of the three classes [3–15 μm], [15–50 μm] and (>50 μm) are increasing with shear rate almost linearly, which is in line with the expectation that the birth rate should scale as G. For each shear the flocculation rate is decreasing with particle size, as obviously the largest particle size classes are the last ones to be populated.

5. Conclusion

In this article, we showed that the logistic growth model proposed in Chassagne and Safar (2020) can be applied to fit a large range of flocculation data, for the whole duration of the experiment. The datasets were all for (different) kaolinite suspensions, in the presence of salt, for different kaolinite concentrations and shear rates. Perikinet as well as orthokinetic flocculation was studied. By fitting the data at the onset of the experiments, one can evaluate flocculation rates that are in line with the traditional linear fits used to study stability ratios. When the data is fitted over the whole experimental period, the flocculation rates are lower than when the onset of experiments are fitted, indicating that the flocculation dynamics are slowing down over time. For the dataset used as an example, it would seem that the dependence of the flocculation rate dL/dt on kaolinite concentration is quadratic instead of linear when the onset of flocculation is studied.

The experimental flocculation rate, for the whole experimental period, has a particle size dependence which matches the one given by Eq. (37), and is of the form $dL/dt = k/n - L^2/(L_0g/3)$ where $t_b$ is a characteristic time and $L_0$ a characteristic size, which are obtained from the fits. This is the case because the data could be fitted using only the birth function $b(t)$, the only required function to model the growth of flocs at constant shear, for suspensions destabilized by ionic strength.

The number of particles as function of time for a given shear can be fitted using both a birth $b(t)$ and a decay function $d(t)$ as each class of particle size is first populated by the aggregation of smaller particles, and then emptied when the particles within the considered class are aggregating themselves. Flocculation rates can in that case also be evaluated, which give quantitative estimations of the kinetics of the different particle size classes.

Funding

This work has been performed in the frame of the grant NW0869.15.011, entitled “Flocs and fluff in the Delta” and the MUDNET academic network (https://www.tudelft.nl/mudnet).

Conflict of interest

The authors declare no conflict of interest.

Appendix A. Mass conservation using a logistic growth model

One of the main advantages of the Population Balance Equation model is that it by construction obeys mass conservation (that is: mineral sediment mass conservation) which is a necessary condition for sediment transport models. As already discussed in Chassagne and Safar (2020), it does not necessary obey mass conservation for the other floc components, organic matter in particular. This can have serious consequences in terms of the estimation of mineral sediment transport. Indeed, at present, most models are validated using in-situ measurements based on particle size measurements. In order to connect particle size to sediment content, it is usually assumed that the density of flocs is a decreasing power-law function of the particle size. In reality, there is a very large spread in particle density for a given particle size in the range [20–200 μm] which is due to the fact that in this size-range the ratio mineral sediment/organic matter can be very different within a sample. In Chassagne and Safar (2020), a very simple approach was proposed, as illustration to how mass conservation can be connected to the logistic growth model. Two classes were created: one containing mineral sediment (of known density, say $ρ_p = 2600$ kg/m$^3$), and one containing flocs.
where $m_p$ represents the mass of unflocculated mineral sediment per unit of volume and $m_{pf}$ represents the mass of mineral sediment inside flocs per unit of volume. The variation in mineral mass $m_p$ can very easily be connected to the volume of mineral sediment leaving the class mineral sediment using $m_p = \rho_p V_p$, where $V_p$ is the total volume of unflocculated mineral sediment per unit of volume. This mineral sediment can be represented by an average clay size $L_p$ (of the order of a few microns), and hence mass and size are connected. This approach has the following advantages:

1 – the mineral sediment class is fully characterized by a volume concentration (measurable in-situ through laser diffraction techniques, i.e. by recording the volume concentration corresponding to the clay-size fraction); this fraction is associated to a computable settling velocity $w_p$:

$$w_p = \frac{1}{16\eta} \left( \rho_p - \rho_w \right) g$$

(47)

where $\eta$ represents the water viscosity, $\rho_w$ the density of water and $g$ the gravitational acceleration. This settling velocity $w_p$, as well as $L_p$ is not expected to vary much for a given location. In regions where the sediment fraction is polydisperse (clay and silt fractions), two sub-classes can be created, one for each fraction. It remains to be seen if the result is worth the effort.

2 – the settling velocity of the floc class can be estimated. The floc class is associated with a mean floc size $L_f(t)$. It is here emphasized that the floc size is time-dependent, as flocs can continuously grow, coagulate and sometimes break under different hydrodynamic conditions, input of new organic matter or decay of organic matter within flocs. The link between floc growth and organic matter models still remains to be done. The mean floc size $L_f$ can be estimated from in-situ measurements and usually corresponds to the D50 of a particle size distribution. From the same measurement techniques, the density of flocs can be estimated. This density is given by, assuming that organic matter has a density very close to the one of water:

$$\rho_f(t) = \left( 1 - \frac{\rho_w}{\rho_p} \right) m_{pf} V_f$$

(48)

where $V_f$ is the volume occupied by the flocs per unit of volume. It is usually assumed that $V_f \gg V_p$ and hence $V_f = V_{no}$ where $V_{no}$ is the volume occupied by all particles per unit of volume. This assumption is in most cases valid, as mineral sediment particles occupy much less volume than flocs. It is also usually assumed that $m_{pf} = m_{no}$ where $m_{no}$ represents the total mass of mineral sediment per unit of volume. This assumption is questionable considering the large density difference between mineral sediment and flocs. Using Eq. (46), however, $m_{pf}$ and therefore $\rho_f$ can be estimated, from which the settling velocity associated to the floc class can be estimated:

$$w_f(t) = \frac{L_f(t)}{16\eta} \left( \rho_f(t) - \rho_w \right) g$$

(49)

Mathematically, assuming that aggregation only takes place, Eq. (46) can be written

$$\frac{\partial m_p}{\partial t} = - m_f d(t)$$

(50)

This equation implies that when no unflocculated sediment is present in the sample volume ($m_p = 0$), no transfer of mass transfer is occurring. The function $d(t)$ can be approximated by

$$d(t) = d_0 = \frac{a_d}{t_d} \left( \frac{0}{1 + a_d} \right) \quad \text{for} \quad t \ll t_d$$

(51)

For long times, no aggregation is occurring anymore ($d(t) = 0$). Note that this is not necessarily because of a depletion in mineral sediment particles. One could, for instance, have a depletion of organic matter, or the colliding frequency could tend to zero over time. At short times, $d(t) = d_0$ is a constant. In that case, which is of importance for numerical sediment transport models, one gets:

$$\frac{\partial m_p}{\partial t} = - d_0 m_p$$

(52)

The analytical solution yields:

$$m_p = m_{p,0} \exp (- d_0 t)$$

$$m_{pf} = m_{p,0} \left[ 1 - \exp (- d_0 t) \right]$$

(53)

Once can verify that at each time $t$, mass is conserved: $m_{p,0} = m_p + m_{pf}$. The mass of mineral sediment inside flocs $m_{pf}$, the volume occupied by flocs $V_f$ and the floc density $\rho_f$ are related by Eq. (48).

References


