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Historical perspective

Population balance modelling of particle flocculation with attention to aggregate restructuring and permeability

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ABSTRACT

A population balance model based on a detailed literature review is used to describe coagulation and flocculation kinetics as well as the time evolution of aggregate size distribution in a turbulent shear flow simultaneously with the breakage and restructuring of aggregates. The fractal nature and permeability of the aggregates and their evolution with time are also part of the model. Restructuring is absent in coagulation with soluble salts, but is present in flocculation caused by large polyelectrolyte molecules; in the latter, aggregates never reach a steady-state size, but a size that decreases gradually through particle and polymer rearrangement. The model is tested against available experimental data for monodisperse polystyrene particles coagulated with hydrated aluminium sulphate at different shear rates, and precipitated calcium carbonate flocculated with a cationic polyelectrolyte of very high molecular weight at different flocculant dosages. The numerical solution of the model requires adjusting three parameters, i.e, maximum collision efficiency (α_{max}), critical force needed for the breakage of the aggregates (B) and rate of aggregate restructuring (γ), which are obtained from minimising the difference between experimental data and model predictions. The model studied for the two very different systems shows excellent agreement with experimental flocculation kinetics and a reasonably good fit for aggregate size distributions. The model is most sensitive to the fragmentation rate through parameter B, somewhat less to the collision efficiency through parameter α_{max} and little to γ. When the aggregates undergo restructuring, properties such as permeability, breakage rate and collision rate change considerably over time. When the aggregates are permeable, the collision frequency is significantly smaller than when they are impervious.

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1. Introduction

The separation of small particles from a liquid medium can be very complex and difficult to control; the issue is of great importance, because it is a fundamental stage in many industrial applications, for instance, in

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mining, extracting oil, cellulose and paper production, water purification, wastewater treatment and industrial food preparation. Particularly in mining, the shortage of water strongly encourages recovering and recycling water from large thickeners. In recent times, this separation operation is as central as flotation, as thickeners cannot cope against increasing volumes of material, increasing amounts of fines in the feed ore to the plants and more saline waters; in some cases, the direct processing of seawater is involved. Sometimes, limitations in the thickeners force the drastic decision to stop plants from operating. For efficient separation, it is necessary to promote the aggregation of particles to form larger structures that can settle by gravitational effects [see for instance Refs. 1–6]. This can be stimulated in different ways, either by adding salts and small destabilising particles or by manipulating the pH of the medium; although, the more traditional method and usually the more effective one is to add a flocculant, that is, large macromolecules capable of adhering to suspended particles in order to form aggregates or flocs very quickly. Indeed, the characteristics of these aggregates and their size, structure and resistance to breakage directly determine the efficiency of the separation, including sedimentation speed, quality of the water recovered and rheological and mechanical properties of the resulting sediment [7]. For this reason, in recent years, the emphasis has been on directly studying flocculation by examining the characteristics of the aggregates with light-scattering techniques as a function of molecular weight, charge density and distribution of the flocculant, pH and temperature, flocculant dosage, shear velocity and so forth. [8–15]. At the same time, there have been several attempts to predict the behaviour of the aggregates through analytical models, particularly for automatic control and for reducing the experimental burden. These models usually make use of the classical equation of von Smoluchowski [16], which is based on population balance equations (PBEs) that describe the rate of irreversible aggregation. This equation is useful to describe aggregates that are dense and which density is preserved as in coagulation but not to describe aggregates that are irregular and loose as in the case of flocculation. Thus several authors have proposed modifications achieving considerable progress in the modelling of particle flocculation through heuristic methods with adjustable parameters that are ultimately responsible for reconciling experimental data with model [see for instance Ref. 17]. More recently, such physics of the aggregation problem has also been enriched. The irregular structure of the aggregates has been included through the fractal dimension, which is crucial, according to Thomas et al. [18], if the model is to represent a real system. Thus, some authors began to include the fractal dimension in the PBE [19–21]. However, most assume a fixed fractal dimension, meaning that the structure of the flocs is preserved throughout the process, which is not generally the case. In many cases, the measured flocculation kinetics show that particles are added to structures that increase in size until they reach a maximum, and then they decrease until they reach a stable size [4,5, 22–24]. According to Heath et al. [4], the reduction in floc size is caused by polymer degradation and consequent floc break up. However, experimental studies have indicated that it is also because of changes in structure, owing to the rearrangement of aggregates, particles and flocculant; therefore, considering a unique fractal dimension prevents the model from being representative of such behaviour. Selomulya et al. [25] successfully incorporated the restructuring in the PB by considering that the fractal dimension changes during flocculation. The introduction of more than one fractal dimension implies changes in the porosity of the aggregates. More recently, Antunes et al. [26] and Sang and Englezos [27] correctly modelled flocculation kinetics curves by changing the fractal dimension, but failed to take into consideration the permeable nature of the aggregates. Although their results fit the experimental data well, the adjustable parameters are of limited value to other systems. Somasundaran and Runkana [28] have demonstrated that permeability affects the movement of the aggregates and thus the collision rate. According to these results, a permeability law in terms of the changing porosity of the aggregates, seems necessary. Ahmad et al. [29] considered the aggregates as a permeable structure, but use the fractal dimension with a constant value, thus ignoring the restructuring. Here, we develop a PBE-based model that takes into account both aggregate permeability and restructuring.

2. Model description

The PBE used here is that of Hounslow et al. [17] with particle grouping, as suggested by Spicer and Pratsinis [30], divided into sizes based on a geometric progression. The discrete form of the resulting balance, based on doubling the particle or aggregate volume (V_i) after each interval ($V_{i+1} = 2V_i$) describing the rate of change for number concentration, is:

$$\begin{aligned}\frac{dN_i}{dt} = & \sum_{j=1}^{i-2} 2^{j-i+1}\alpha_{i-1,j}\beta_{i-1,j}N_{i-1}N_j + \frac{1}{2}\alpha_{i-1,j}\beta_{i-1,j}N_{i-1}^2 \\ & - N_i\sum_{j=1}^{i-1} 2^{j-1}\alpha_{i-1,j}\beta_{i-1,j}N_j - N_i\sum_{j=1}^{\max 1}\alpha_{i-1,j}\beta_{i-1,j}N_j - S_iN_i \\ & + \sum_{j=1}^{\max 2}\Gamma_{i,j}S_jN_j\end{aligned} \quad (1)$$

where N_i is the number of aggregates or flocs containing 2^{i-1} particles, whereas N_1, for the size interval $i = 1$, is the number concentration of primary particles, t is the aggregation–breakage–restructuring time. The first two terms from the right-hand side of Eq. (1) account for the formation or growth of aggregates in the i-th size interval from the collisions of aggregates of smaller size ranges. The third and fourth terms represent the loss of aggregates in the i-th size interval by the aggregation of flocs from size interval i with those from other size intervals. The fifth term accounts for the loss of aggregates in the i-th size interval through fragmentation, whereas the sixth term denotes the gain of aggregates in the i-th size interval by fragmentation of larger flocs. The super indexes, max 1 and max 2, respectively, represent limiting size intervals to which the fourth and sixth terms of Eq. (1) are to be evaluated. The expression by Hounslow et al. and Spicer and Pratsinis involves four functions that represent particulate systems; the functions are (i) collision efficiency (α_{ij}), (ii) collision frequency (β_{ij}), (iii) fragmentation rate of flocs in the i-th interval (S_{ij}) and (iv) breakage distribution function for the break up of aggregates in the j-th interval, which generates fragments of sizes that fall in the i-th interval (Γ_{ij}). Detailed description and analysis of these functions are given by Elimeleh and Gregory [31]. More recently, Selomulya et al. [25] and Bonanomi et al. [32] introduced a new function to account for the change in floc structure as flocculation progresses, which can be quantified through the variation in the fractal dimension of the flocs with time. All of the five functions come from heuristic rules, and the parameters involved are determined by solving Eq. (1) against experimental data. These parameters determine the predictive power of the model in Eq. (1). Details for discretising the PB and the "lumping" of size intervals can be found in previously published reports (see for instance Ref. [20]). Next, these functions are described for general permeable particles or flocs that are fractal in nature and for which the fractal dimension evolves with time. Spherical aggregates, impermeable aggregates and fractal aggregates with constant fractal dimensions are particular cases.

2.1. Collision frequency

The overall collision frequency between two particles in the i-th and j-th intervals, which is due to the Brownian motion of the particles and aggregates, the shear rate applied to the system, and the sedimentation by gravity, can be written as

$$\beta_{i,j} = \beta_{i,j}^{Br} + \beta_{i,j}^{Sh} + \beta_{i,j}^{g} \quad (2)$$

where $\beta_{i,j}^{Br}$ is the collision frequency for perikinetic aggregation of aggregates belonging to intervals i and j, $\beta_{i,j}^{Sh}$ is the collision frequency for orthokinetic aggregation of flocs belonging to intervals i and j when