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A population balance model for flocculation of colloidal suspensions by polymer bridging

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Abstract

A detailed population balance model for flocculation of colloidal suspensions by polymer bridging under quiescent flow conditions is presented. The collision efficiency factor is estimated as a function of interaction forces between polymer coated particles. The total interaction energy is computed as a sum of van der Waals attraction, electrical double layer repulsion and bridging attraction or steric repulsion due to adsorbed polymer. The scaling theory is used to compute the forces due to adsorbed polymer and the van der Waals attraction is modified to account for presence of polymer layer around a particle. The irregular structure of flocs is taken into account by incorporating the mass fractal dimension of flocs. When tested with experimental floc size distribution data published in the literature, the model predicts the experimental behavior adequately. This is the first attempt towards incorporating theories of polymer-induced surface forces into a flocculation model, and as such the model presented here is more general than those proposed previously.

Keywords: Population balance; Flocculation; Colloids; Surface forces; Fractals; Polymers

1. Introduction

Flocculation of colloidal suspensions is an important unit operation in many industries such as pulp and papermaking (Pelton, 1999), mineral processing (Somasundaran et al., 1996) and water treatment (Thomas et al., 1999). Polymers and polyelectrolytes, inorganic salts and surfactants are routinely used to either flocculate or disperse a suspension. Flocculation by polymers is a complex phenomenon, which involves several steps or sub-processes occurring sequentially or concurrently. These include (Gregory, 1988): (i) mixing of particles and polymers in solution, (ii) adsorption of polymer chains on particle surface, (iii) reconformation of adsorbed chains on the surface, (iv) formation of aggregates, (v) restructuring of flocs, and (vi) subsidence, or sedimentation of flocs. Polymers and polyelectrolytes are common additives for controlling stability as well as rate of sedimentation of flocculating suspensions. These changes are brought about by altering polymer adsorption and conformation at the solid-solution interface by manipulating a number of variables such as pH, ionic strength, polymer concentration and temperature.

The key variable in flocculation is floc size distribution (FSD) as it influences rate of floc sedimentation and suspension turbidity. It is a complex function of several process variables including initial or feed particle size distribution, solution pH, electrolyte concentration, temperature, polymer concentration and its molecular weight distribution. Population balances have been applied extensively for modeling flocculation and for predicting the evolution of FSD with time. The two important parameters in the flocculation model are collision frequency factor and collision efficiency factor. Depending on the process operating conditions and material properties, aggregation takes place by one or more of the following mechanisms: perikinetic aggregation,

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orthokinetic aggregation and differential sedimentation. Appropriate equations or kernels are included in the flocculation model to capture the mode and frequency of particle and/or aggregate encounters. Collision efficiency, on the other hand, has been mostly employed as a fitting parameter, even though it is actually a function of the interaction forces between particles which, in turn, depend critically on the type of flocculant used. Because collision efficiency factor is treated as a fitting parameter, the population balance models are restricted in their applicability to specific processes.

Flocculation in presence of polymers can occur by any one or more of the four well-known mechanisms: simple charge neutralization, charge patch neutralization, polymer bridging and polymer depletion (Napper, 1983; Levine and Friesen, 1987). The first three mechanisms take place due to polymer adsorption while depletion occurs in the presence of nonadsorbing polymers. In an earlier paper, we presented a discretized population balance model for flocculation of colloidal suspensions by simple charge neutralization in presence of inorganic electrolytes or polymers (Runkana et al., 2004). Here we extend the treatment for bridging flocculation under quiescent flow conditions by incorporating a collision efficiency model, which takes into account bridging attraction or steric repulsion, van der Waals attraction and electrical double layer repulsion between particles. The objective is to predict the evolution of FSD preferably or at the minimum, mean floc diameter with time as a function of important flocculation process variables. It is of course recognized that mean diameter may not furnish a definitive validation of the model and FSD data are required for a more authentic validation.

2. Bridging flocculation model

2.1. Population balance equation

The starting point of our model is the discretized and geometrically sectioned population balance equation (PBE) proposed by Hounslow et al. (1988) for modeling aggregation. The rate of change of particle or floc concentration due to aggregation alone is given by Hounslow et al. (1988)

$$\begin{aligned}\frac{\mathrm{d}N_i}{\mathrm{d}t} &= N_{i-1}\sum_{j=1}^{i-2} 2^{j-i+1}\alpha_{i-1,j}\,\beta_{i-1,j}N_j \\ &\quad + \frac{1}{2}\,\alpha_{i-1,i-1}\beta_{i-1,i-1}N_{i-1}^2 \\ &\quad - N_i\sum_{j=1}^{i-1} 2^{j-i}\alpha_{i,j}\beta_{i,j}N_j \\ &\quad - N_i\sum_{j=i}^{\max}\alpha_{i,j}\beta_{i,j}N_j, \qquad (1)\end{aligned}$$

where N_i is number concentration of particles or flocs in section i, t is flocculation time β is collision frequency factor and α is collision efficiency factor. The first term on the right-hand side accounts for growth of aggregates in section i due to aggregation of clusters that belong to sections smaller than i, except the immediately adjacent smaller section. The second term represents growth due to aggregation of clusters belonging to the immediately adjacent smaller section. The third term describes loss of aggregates in section i due to their interaction with entities belonging to smaller sections and the fourth term represents loss of aggregates due to aggregation of clusters in section i and their interactions with aggregates belonging to sections larger than i. The smallest section corresponds to primary particles and the section designated max contains aggregates of largest characteristic volume. Details of discretizing the PBE and lumping of size classes are available elsewhere (Spicer and Pratsinis, 1996; Runkana et al., 2004).

2.2. Collision frequency

Aggregation occurs by particle–particle, particle–cluster and cluster–cluster collisions followed by the formation of flocs, which are highly irregular in shape and structure. The irregular structure of flocs is taken into account by explicitly incorporating the mass fractal dimension of flocs into the expression for collision frequency factor. The rate of flocculation is primarily a function of collision frequency if the forces of attraction between particles dominate the forces of repulsion. The collision frequency depends strongly on particle (or aggregate) collision radius, which increases due to adsorption of polymer chains on the surface. Its magnitude depends on adsorbed layer thickness, which is determined by polymer adsorption density and conformation at the solid–liquid interface.

Adsorption of polymers at the solid–liquid interface is a complex phenomenon and depends on various factors such as polymer concentration in solution and at the interface, polymer molecular weight and charge density distribution, nature of solvent, surface charge density distribution, pH, temperature and type and concentration of electrolyte species present in solution (Fleer et al., 1993). Polymer adsorption on particles occurs by collisions between particles and polymer chains. In absence of any applied shear, these collisions also take place under Brownian motion. The process essentially involves three steps: diffusion of polymer chains from bulk solution to the interface, attachment of polymer segments to surface sites and relaxation or reorientation of polymer chains at the interface (Cohen Stuart and Fleer, 1996). Adsorption of polymers on oppositely charged surfaces is generally fast, strong and irreversible. Moreover, polymer relaxation times are of the order of few seconds (van de Ven, 1994). Hence, it is reasonable to assume that polymer attains its equilibrium conformation before particles undergo any meaningful number of collisions.

Depending on the affinity of the polymer to the surface, polymer chains can have one or a combination of three