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ORIGINAL CONTRIBUTION

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Flocculation by very high molecular weight polymers

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Abstract Polymer-induced flocculation in which the size of polymer molecules is much greater than that of colloidal particles is investigated. A dynamic analysis is conducted which takes the transient behaviors of the adsorption of particles to a polymer molecule and the particle-particle interactions into account. We show that the number of particles adsorbed to a polymer molecule follows approximately a binomial distribution. An approximate expression for the degree of flocculation of the system under consideration is presented.

Key words Bridging flocculation – polymer adsorption – very high molecular weight polymers – degree of flocculation

Introduction

The introduction of polymer to a suspension of colloidal particles to initiate flocculation is one of the basic operations in wastewater treatment. Here, the interactions between the dispersed entities are profound; both the adsorption of polymer molecules to the surfaces of colloidal particles and the collisions between particles need to be considered simultaneously. By referring to Fig. 1, depending on the relative magnitudes of the sizes of polymer molecules and colloidal particles, three cases can be identified [1, 2]. If the size of the former is much smaller than that of the latter, molecules adsorb to the surfaces of particles, and the collision effect of the adsorbed molecules leads to flocculation [3]. On the other hand, if the size of molecules is much greater than that of particles, the latter adsorb to the former and a molecule-particle aggregate is formed [2, 4, 5]. If the sizes of molecules and particles are comparable, the above two cases should be considered at the same time.

Assuming that a system is at equilibrium, Molski and Nowicki [4] studied the polymer-induced flocculation in which the size of polymer molecules is much greater than that of colloidal particles. Several interesting questions were raised. These include: a) the distribution of the number of adsorbed particles to a molecule, b) the interaction between particles, and c) the rate of sedimentation of molecules carrying adsorbed particles. In the present study attempts are made to answer the first two questions on the basis of a non-equilibrium analysis, which takes the transient behaviors of the adsorption of particles to a molecule and particle-particle interactions into account.

Theory

Let N and X_0 be, respectively, the number of polymer molecules and that of colloidal particles in the system. Suppose that the linear size of a polymer molecule is much greater than that of a colloidal particle. Denote S as the maximal number of colloidal particles that can be adsorbed by a polymer molecule. Let X be the number of free colloidal particles and n_i be the number of polymer molecules with i colloidal particles attached. These variables are functions of time t. Suppose that the adsorption of colloidal particles to a polymer molecule is reversible. The

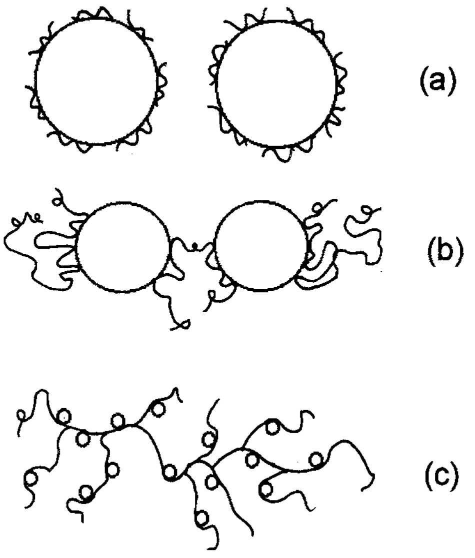


Fig. 1 Relative sizes of polymer molecule and particle. a) Polymer molecule is much smaller than particle, b) polymer molecule is comparable to particle, c) polymer molecule is much greater than particle

temporal variation of n_i is described by

$$\frac{dn_i}{dt} = b_{i-1}n_{i-1} - (b_i + c_i)n_i + c_{i+1}n_{i+1}, \quad i = 0, 1, 2, \ldots, S\,, \tag{1}$$

where b_i represents the rate of attachment of colloidal particles per polymer molecule, and c_i denotes the rate of detachment of colloidal particles per polymer molecule.

We assume

$$b_i = K_a(S - i)X \tag{2a}$$

$$c_i = K_d i\,, \tag{2b}$$

where $n_{-1} = n_{S+1} = 0$, and $b_{-1} = b_S = c_{S+1} = 0$, K_a and K_d are, respectively, the adsorption rate constant and the desorption rate constant. Substituting these expressions into Eq. (1) yields

$$\frac{dn_i}{dt} = K_a(S - i + 1)Xn_{i-1} - [K_a(S - i)X + K_d i]n_i + K_d(i + 1)n_{i+1}, \quad i = 0, 1, \ldots, S\,. \tag{3}$$

Let X_c be the number of colloidal particles aggregated due to the interaction of polymer-free particles. Then

$$X = X_0 - \sum_{i=0}^{S} i n_i - X_c\,. \tag{4}$$

Differentiating this expression with respect to t yields

$$\begin{aligned}\frac{dX}{dt} &= -\sum_{i=0}^{S} i\frac{dn_i}{dt} - \frac{dX_c}{dt}\\ &= -K_a X[SN - X_0 + X + X_c]\\ &\quad + K_d[X_0 - X - X_c] - \frac{dX_c}{dt}\,.\end{aligned} \tag{5}$$

To solve this equation, the value of dX_c/dt needs to be determined. Let Y_i be the number of aggregates which contains i polymer-free colloidal particles. Then

$$\frac{1}{K_c}\frac{dY_2}{dt} = \frac{X^2}{2} - Y_2\left(X + \sum_{i=2}^{R} Y_i\right) \tag{6a}$$

$$\frac{1}{K_c}\frac{dY_3}{dt} = XY_2 - Y_3\left(X + \sum_{i=2}^{R} Y_i\right) \tag{6b}$$

$$\cdots\cdot$$

$$\frac{1}{K_c}\frac{dY_R}{dt} = \frac{XY_{R-1}}{2} + \frac{1}{2}\sum_{\substack{i=2\\ j=R-i}}^{R-1} Y_iY_j - Y_R\left(X + \sum_{i=2}^{R} Y_i\right), \tag{6c}$$

where K_c denotes the rate constant for particle-particle collision, and R is the maximum size of an aggregate. We have

$$X_c = \sum_{i=2}^{R} iY_i\,. \tag{7}$$

Therefore, Eqs. (5), (6a)–(6c), and (7) need to be solved simultaneously.

The number of particles captured by polymer molecules, N_c, is

$$N_c = \sum_{i=0}^{S} in_i\,. \tag{8}$$

Suppose that sedimentation of polymer-particle aggregates occurs only to those polymer molecules with n_f particles attached. Then the number of particles removed from liquid phase due to the introduction of polymer molecules, N_f, is

$$N_f = \sum_{i=n_f}^{S} in_i\,. \tag{9}$$

Define the degree of flocculation, F, by [4]

$$F = 1 - (N_a/N_b)\,, \tag{10}$$

where N_a and N_b are, respectively, the number of particles left in the system with polymer and that without polymer.

The distribution of aggregate size in a polymer-free suspension can be derived by following a similar procedure as that employed for the derivation of Eqs. (6a)–(6c). If we denote the number of aggregates which contain

i colloidal particles as N_i, then

$$\frac{1}{K_c}\frac{dN_1}{dt} = -N_1 \sum_{i=1}^{R_c} N_i \tag{11a}$$

$$\frac{1}{K_c}\frac{dN_2}{dt} = (N_1^2/2) - N_2 \sum_{i=1}^{R_c} N_i \tag{11b}$$

$$\frac{1}{K_c}\frac{dN_3}{dt} = N_1 N_2 - N_3 \sum_{i=1}^{R_c} N_i \tag{11c}$$

$$\cdots\cdot$$

$$\frac{1}{K_c}\frac{dN_K}{dt} = \frac{1}{2} \sum_{\substack{i=1 \\ j=K-i}}^{K-1} N_i N_j - N_K \sum_{i=1}^{R_c} N_i \,, \tag{11d}$$

where R_c is the maximum size of an aggregate.

Suppose that sedimentation occurs to those polymer-free aggregates having n_c or more particles. Then Eq. (10) can be written as

$$F = 1 - \frac{(N_c - N_f) + \sum_{i=2}^{n_c-1} iY_i + X}{\sum_{i=1}^{n_c-1} iN_i}$$
$$= 1 - \frac{\sum_{i=0}^{n_f-1}(in_i/X_0) + \sum_{i=2}^{n_c-1}(iY_i/X_0) + (X/X_0)}{\sum_{i=1}^{n_c-1}(iN_i/X_0)} \,. \tag{12}$$

Since solving Eqs. (5), (6a)–(6c), and (7) is almost impossible, an approximate analysis is conducted. We assume that the rate of decrease in the number of particles due to particle-particle interaction is proportional to the rate of collision between particles, i.e.,

$$dX_c/dt = K_c X^2 \tag{13}$$

Substituting this expression into Eq. (5) yields

$$dX^*/dt^* = -X^*(r - 1 + X^* + X_c^*)$$
$$+ K_1(1 - X^* - X_c^*) - K_2 X^{*2} \tag{14}$$

where $X^* = X/X_0$, $t^* = K_a X_0 t$, $K_1 = K_d/K_a X_0$, $K_2 = K_c/K_a$, $r = SN/X_0$, and $X_c^* = X_c/X_0$. Also, Eq. (13) can be rewritten as

$$dX_c^*/dt^* = K_2 X^{*2} \,. \tag{15}$$

Let p_i be the fraction of the sites on a polymer occupied by i colloidal particles, and p be its mean value. Then it can be shown that [6]

$$p = \sum_{i=0}^{S} in_i/SN = (1 - X^* - X_c^*)/r \tag{16a}$$

$$p_i = n_i/N = C_i^S p^i (1-p)^{S-i} \,, \tag{16b}$$

where the combinatorial symbol C_i^S is defined by

$$C_i^S = S!/(S-i)!i! \tag{16c}$$

These expressions reveal that the distribution of the number of particles adsorbing to a polymer molecule follows a binomial distribution.

Since obtaining an explicit expression for X_p based on Eqs. (11a)–(11d) and (12) is almost impossible, an approximate treatment is performed. We assume that the decrease in the number of colloidal particles is due to the collision of primary particles, i.e.,

$$dX_p/dt = -K_c X_p^2 \tag{17a}$$

or

$$dX_p^*/dt^* = -K_2 X_p^{*2} \,, \tag{17b}$$

where X_p denotes the number of colloidal (primary) particles in a polymer-free suspension, and $X_p^* = X_p/X_0$. The solution to Eq. (17b) subject to the initial condition $X_p^* = 1$ at $t^* = 0$ is

$$X_p^* = 1/(1 + K_2 t^*) \,. \tag{18}$$

In this case Eq. (12) is rewritten as

$$F = 1 - \frac{(N_c - N_f) + R_1 X_c + X}{R_2(X_0 - X_p) + X_p}$$
$$= 1 - \frac{(r/s)\sum_{i=0}^{n_f-1} ip_i + R_1 X_c^* + X^*}{R_2(1 - X_p^*) + X_p^*} \,. \tag{19}$$

Here, R_1 is the fraction of primary particles contained in polymer-free aggregates which are left in the suspension for a system with polymer, and R_2 is the fraction of primary particles contained in aggregates which are left in the suspension for a system without polymer. Apparently, R_1 is a function of the distribution of the size of polymer-particle aggregates, and R_2 is a function of the distribution of the size of polymer-free aggregates. As pointed by Molski and Nowicki [4], determining these functions analytically is nontrivial, a realistic treatment in practice is to consider them as adjustable parameters.

Results and discussions

Figure 2 shows the simulated distribution of the number of colloidal particles adsorbed to a polymer molecule p_i at $t^* = 1200$ for various values of r. Both the results for irreversible adsorption ($K_1 = 0$) and reversible adsorption are illustrated. Figure 2(a) shows that, for an irreversible adsorption, p_i is symmetric and shifts to the left as r is increased. Also, the maximum of the distribution decreases with r, passes a minimum, and then increases with a further increase in r. Since the area under each curve is unity, the greater the maximum, the narrower the distribution. According to the definition of r ($=SN/X_0$), a small r implies that the number of particles is greater than the

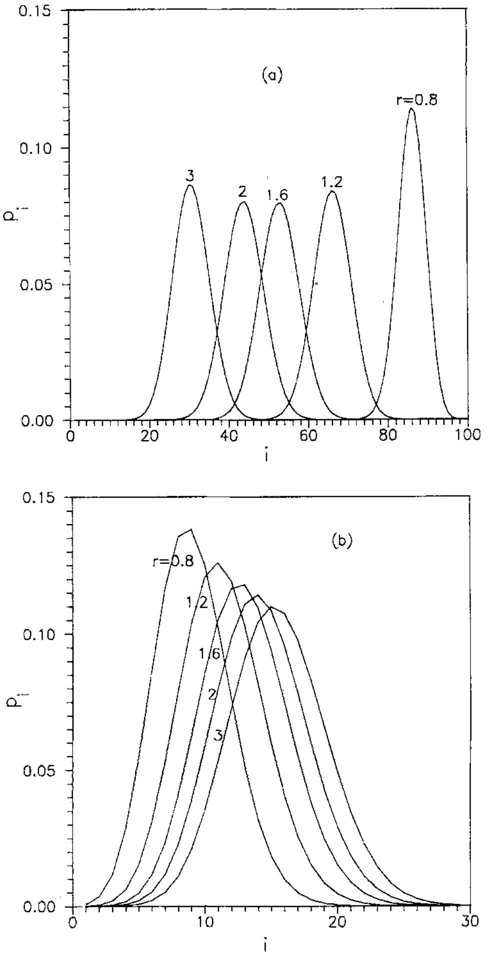


Fig. 2 Distribution of the number of colloidal particles adsorbed to a polymer molecule at equilibrium for various values of r at $t^* = 1200$ and $K_2 = 0.5$. a): $K_1 = 0$ (irreversible adsorption); b): $K_1 = 0.1$

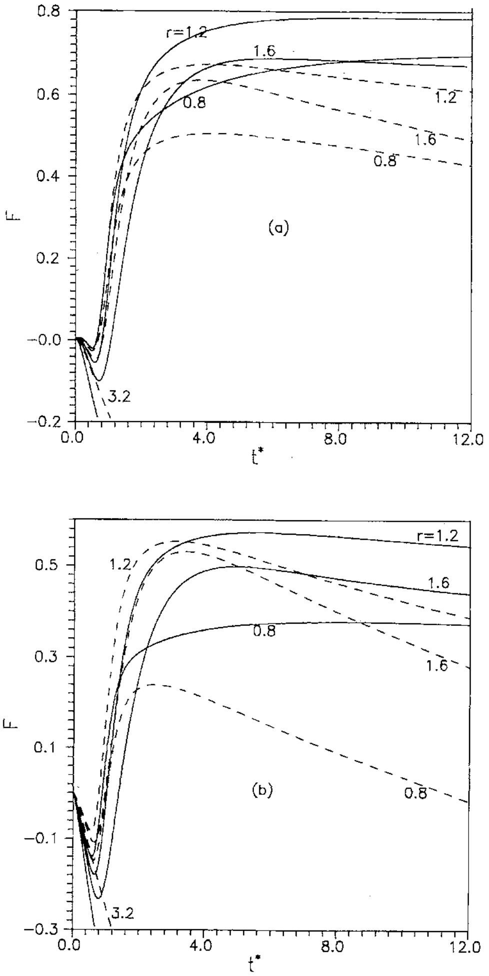


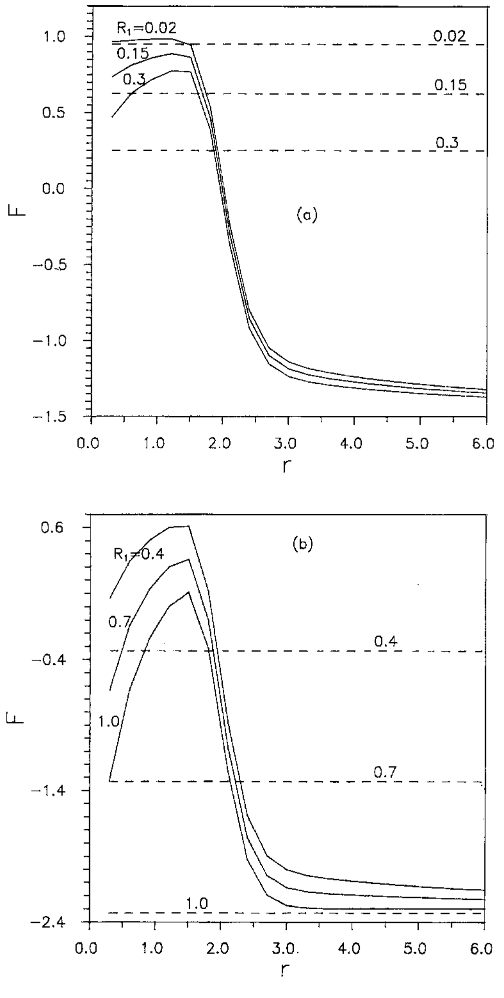
Fig. 3 Transient variation in the degree of flocculation F for various values of r. Parameters used are: $K_2 = 1$, $n_f = 41$, and $S = 100$. $R_1 = 0.3$ and $R_2 = 0.4$ in a); $R_1 = 0.5$ and $R_2 = 0.3$ in b). Solid lines: $K_1 = 0$ (irreversible adsorption); dashed line: $K_1 = 0.1$

number of available sites on molecule, and therefore each site has a higher probability to be occupied by particle. This leads to a narrow distribution in the number of adsorbed particles. As can be seen from Fig. 2(b), for a reversible adsorption of particles to polymer, p_i is slightly skewed to the right, and shifts to the right as r increases. The maximum of p_i decreases with an increase in r.

The transient behavior of the degree of flocculation F for various values of r is illustrated in Fig. 3. According to the definition of F, Eq. (10), if $F > 0$, the polymer plays the role of flocculant. On the other hand, if $F < 0$, it behaves as a stabilizer. The value of F depends on the relative significance of the rate of aggregation due to polymer-induced aggregation and that due to polymer-free aggregation. For a small r, F decreases at the early stage, passes through a minimum, and then increases to an equilibrium value. This is because that in the early stage the number of particles adsorbed to polymer is less than n_f, and the competition of polymer-induced aggregation and polymer-free aggregation leads to a decrease in F. At the late stage, the number of polymer molecules which contain more than n_f particles increases, so does F. If r is too large, the number of particles adsorbed to a polymer molecule is less than n_f, and F decreases monotonically to an equilibrium value. If r is not large, the greater its value, the smaller the minimum value of F. This is because it requires a longer time for a polymer molecule to adsorb n_f particles. The equilibrium value of F increases with r, passes through a maximum, and then decreases with a further increase in r. If r is small, although it is easy for molecules to have their active sites occupied by particles, the number of particles removed by polymer is limited. On the other hand, if r is large, only a small portion of molecules has more than n_f particles attached. Therefore, there exists an optimum value for r at which the equilibrium F is at maximum. The qualitative behavior of F for a reversible adsorption is similar to that for an irreversible adsorption.

Figure 4 shows the variation in the degree of flocculation F as a function of r for various values of R_1 at equilibrium. The corresponding variations for various values of R_2 are presented in Fig. 5. Figure 4 suggests that, for an irreversible adsorption at fixed r, F decreases with the increase of R_1. Since R_1 is the fraction of particles in polymer-free aggregates that are not large enough to settle down, this is expected. Figure 5 shows that F increases with R_2 for obvious reason. For a reversible adsorption, F is independent of r at equilibrium, as suggested by Eq. (19). This is because that the desorbed particles will aggregate with each other and leave the suspension eventually. Therefore, p_i vanishes as time approaches infinity.

Fig. 4 Variation in the degree of flocculation F as a function of r for various values of R_1 at equilibrium. Parameters used are: $K_2 = 0.9$, $n_f = 41$, and $S = 100$. $R_2 = 0.4$ in a); $R_2 = 0.3$ in b). Solid lines: $K_1 = 0$ (irreversible adsorption); dashed line: $K_1 = 0.1$



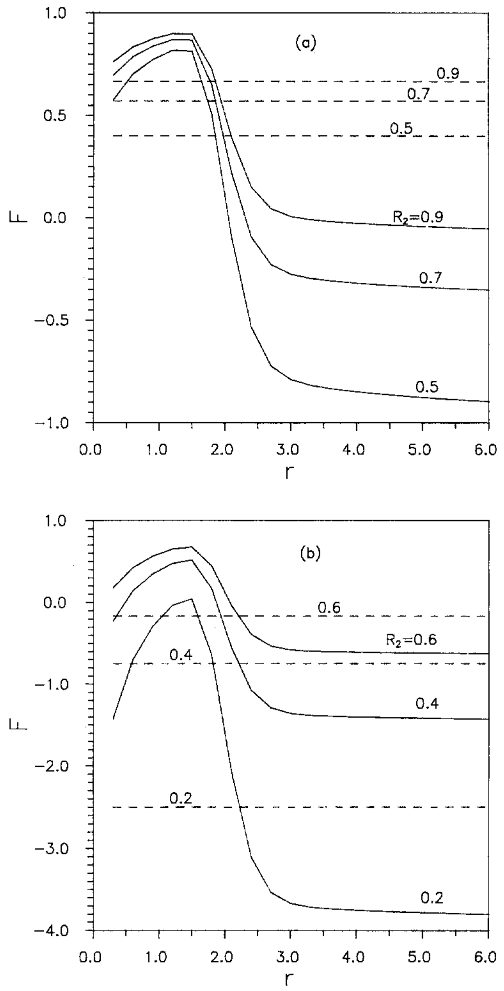


Fig. 5 Variation in the degree of flocculation F as a function of r for various values of R_2 at equilibrium. Parameters used are: $K_2 = 0.9$, $n_f = 41$, and $S = 100$. $R_1 = 0.3$ in a); $R_1 = 0.7$ in b). Solid lines: $K_1 = 0$ (irreversible adsorption); dashed line: $K_1 = 0.1$

The relative magnitude of R_1 and R_2 is not clear at the present stage. Apparently, the existence of polymer will affect the distribution of aggregate size through the reduction in the number of primary particles. Since the number of available primary particles for a system containing polymer is less than that for a polymer-free system, the size distribution of the former will be more concentrated about its mean than the latter. Therefore, the relative magnitude of R_1 and R_2 depends largely on the distribution of aggregate size. However, Figs. 3–5 reveal that the qualitative behavior of F is insensitive to the relative magnitude of R_1 and R_2.

The applicability of the present model is justified by analyzing the experimental data examined by Molski and Nowicki [4], where polyacrylamide-sol AgI was used as the model system. The experimental data for the case where the electrolyte concentration is 0.05 M are illustrated in Fig. 6. Also shown in this figure are the results calculated based on the model of [4] and on the present model. As can be seen from Fig. 6, the performance of the present model is satisfactory.

As suggested by Eqs. (13) and (17a), we only consider an irreversible collision between particles which leads to aggregation [7]. A more general treatment needs to take the interaction energy between particles into account. In this case, K_c plays the role of the rate constant for slow coagulation. By definition, $K_c = K_r/W$, K_r is the rate constant for the corresponding fast coagulation, and W is the stability ratio [8]. The latter is a function of the interaction energy between two particles, which is a complicated function of the condition of the system under consideration.

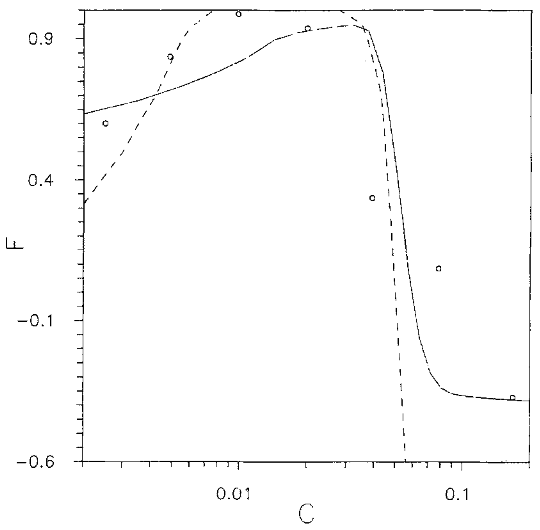


Fig. 6 Analysis of the experimental data of [4] (Fig. 4, with 0.05 M KNO_3). The estimated values of the adjustable parameters are $R_1 = 0.35$, $R_2 = 0.70$, $K_1 = 0$, $K_2 = 0.2$, and $n_f = 61$. The concentration of polymer, C, and r are related by $r = CN_AS/M_pX$, where N_A and M_p are, respectively, the Avogadro number and the molecular weight of polymer. Dashed line: the result predicted by Molski and Nowicki [4]; solid line: the result predicted by the present model

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