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COMPUTER SIMULATION OF CHEMICAL COAGULATION AND SEDIMENTATION OF SUSPENDED SOLIDS

SYMULACJA KOMPUTEROWA KOAGULACJI I SEDYMENTACJI ZAWIESINY

Abstract: The computer program ZB2 was used to study simulated coagulation rate for the system containing spherical sol particles and spherical coagulant particles. The system performance was verified to the particle--cluster model of a fast and perikinetic coagulation process that fulfils Smoluchowski and/or Muller equations. The rate of the coagulation process satisfied both the kinetic equation of a first-order reaction and a second-order reaction. However, chosen concepts and models in the theory of bidispersive sol coagulation have been negatively verified. Also, attempts have been made to modify the Muller integral equation for selected boundary conditions.

Keywords: aggregation, coagulation rate, simulation

Introduction

Coagulation is one of the most important processes in chemical wastewater treatment. It is a composite process and many factors affect its rate and efficiency. The kinetics of coagulation, and the mechanism of this process requires regular monitoring from both a fundamental [1-5] and a utilitarian [6, 7] perspective. As part of the latter approach, the rate and efficiency of new inorganic coagulants and organic flocculants parameters are examined in a wastewater treatment plant [8, 9]. Studies of coagulation, flocculation and sedimentation processes are usually carried out in natural systems, such as wastewater [10], model systems like silica suspensions [1, 11, 12], as well as computer-simulated systems [13-16]. The results of computer simulations support the development of fundamental databases, and the resulting conclusions render them an important supplement to applied research.

This study reports a computer-simulated investigation of the coagulation rate for the system comprising simulated spherical sol and simulated coagulant particles. The quantitative proportions of both particle types satisfied the computer-simulated "coagulation threshold", which remained similar to that observed in natural systems, such as that in wastewater treatment plants. The results of kinetic measurements have been tested

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in view of first-order and second-order reactions, as well as in the light of classical Smoluchowski [17] and Muller [18] equations. Such-conducted verifications paved the way to successive measurements within a broad and controlled range. The results obtained for this group of tests supported the some negative verification of selected methods and concepts in the theory of bidispersive sol coagulation. Additional attempts were made to modify the Muller equation for selected boundary conditions.

Materials and methods

The simulation system ZB2 used in this paper is based on a semi-empirical concept, inspired by observations of coagulation-flocculation-sedimentation of wastewaters carried out in both natural and model systems

The simulation system ZB2 is a stochastic dynamic model that relies on random variables, and the system's state changes over simulation time. The program's core is a module solving the equation of motion for a given number of particles in a closed vessel. The program simulates rapid perikinetic coagulation where every collision of a coagulant particle and a sol particle produces an unbreakable combination, particles of the same type do not aggregate. The initial particle location values are randomly generated based on homogeneous distribution in the vessel. The direction of particle movement and their initial location are randomly drawn using the RANDOM command. The angle at which a particle bounces off the vessel wall is always equal to the angle of incidence.

The following input data were used in simulation tests:

N_c - number of coagulant particles, $N_{c\,max}$ = 100; in this study: from 50 to 100.

N_s - number of sol particles, $N_{s\,max}$ = 1200; in this study: from 700 to 1200.

V_c [cm/s] - initial speed of a coagulant particle expressed as the quotient of simulated distance and simulated time. Each particle has a randomly attributed initial speed, and if V_c = 50 cm/s, all particles have a velocity attributed in the range of 1-50 cm/s. The program prevents any particle from having an initial velocity equal to zero. In this study, V_c = 50, 5, 1 cm/s.

V_s [cm/s] - initial speed of a sol particle. The same conditions as for V_c were set. In this study, V_s = 50, 25, 10 cm/s.

E - coagulation threshold. The parameter denotes the number of sol particles which initiate the sedimentation of a cluster/floc, where a given number of sol particles correspond to one coagulant particle. The sedimentation rate grows with an increase in the number of sol particles in the cluster. In this study, E = 7 in most measurements, while E = 3, 10, 15 and 20 were applied in individual cases.

F - sedimentation coefficient accounting for a 30% decrease in floc speed after the floc bounces off the bottom of the vessel. To simulate the friction between the particle and the fluid, floc velocity in the direction of the surface decreases by 0.1% per unit of displacement. In this study, F = 0.2 in most measurements, while F = 0.01 was applied in individual cases.

R_c [nm] - diameter of a coagulant particle. Changes in R_c are not visible on the screen, but they are manifested by an increase in the distance between particles in a newly formed floc. In this study, R_c = 1 or 2 nm for most measurements, while R_c = 5 nm was set for several cases.

R_s [nm] - diameter of a sol particle. The same conditions as for R_c were set. In this study, R_s = 1 or 2 nm, while R_s = 0.1, 0.25 and 0.5 nm values were applied in individual cases.

I - simulated ratio of the mass of the coagulant particle to the mass of the sol particle determined by R_c and R_s parameters. A wide range of the above ratios was investigated. Ratios resulted directly from geometry, e.g. at R_c : R_s = 2, the ratio of the mass of the coagulant particle to the mass of the sol particle 2^3:1 = 8, at identical particle density. When variations in the density of coagulant and sol particles were taken into account, I = 0.01 to 320, while in individual cases I parameter was applied to 625, 1000 or 8000.

The program was equipped with the STOP function measuring the time of the simulated process, as well as a section counting the number of "coagulated" particles in the sediment, because the program counts particles with the speed of V_c = 0.

All the units are the simulated ones and constant in the all work. Therefore, a time unit is the simulated second. Time t was measured in seven replications. Two maximum and two minimum values were discarded to compute the arithmetic mean based on three measurements. Standard deviation values are shown in respective diagrams. Correlations between the coagulation rate and the number of particles remaining in the system were specified. The number of sol particles and coagulant particles remaining in the system after simulated time t was correlated with the number of particles calculated from the Smoluchowski equation and the Muller equation [17, 18].

Results and discussion

Examples of simulation measurements are illustrated in Figure 1. The diagrams present linear relationships $t = f(\ln 1/c)$ (Figs. 1a and 1b) and $t = f(1/c)$ (Figs. 1c and 1d) for coagulation systems comprising a number of coagulated particles at N_s = 800 (Figs. 1a and 1c) and a number of coagulated particles at N_s = 1100 (Figs. 1b and 1d), respectively. The demonstrated correlations were found at minimum values of I = 0.01 (Figs. 1a and 1c) and maximum values of I = 320 (Figs. 1b and 1d). The coefficients of determination R^2 for the four linear regressions present here were in the high-value range from 0.96 to 0.97. However, for comparable pairs of general dependencies $t = f(\ln 1/N_s)$ and $t = f(1/N_s)$, respectively, they did not show unequivocally a more favourable kinetic equation describing the coagulation rate of the simulated sol.

Classical mathematical relations based on the Smoluchowski [17] and the Muller [18] theories have been used to process and verify simulated measurement data in next parts of this study.

The Smoluchowski equation for calculating the number of particles n_t in the monodisperse system after time t of fast and perikinetic coagulation has the following form:

$$n_t = \frac{n_0}{1 + \frac{t}{t_{1/2}}} \tag{1}$$

where n_0 is initial number of particles and $t_{1/2}$ is half-time of n_0.

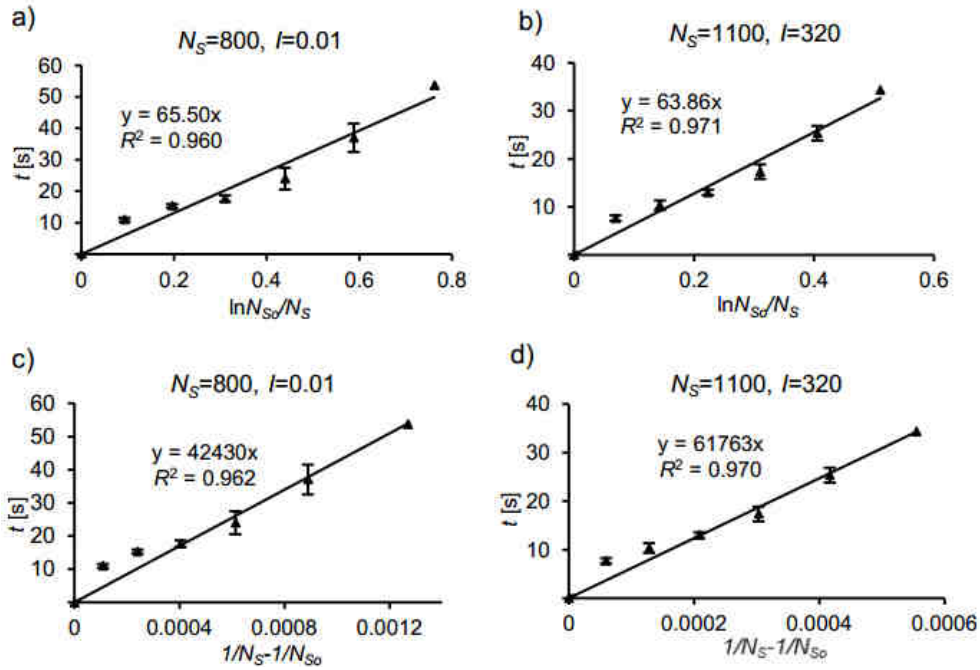

Fig. 1. Relationships a), b) $t = f(\ln 1/N_s)$ and c), d) $t = f(1/N_s)$ for extreme I and N_s values (mean values ± standard deviation)

Muller suggested that the probability of collision between two particles of various size was higher than the probability of collision between particles with identical radii, where their radii of attraction are equal to the sum of radii of the small and the large particle. According to Muller, in the simplest bidispersive system, deviations from the course of the coagulation process for a monodispersive system (Smoluchowski) appear only when the ratio of particle radii R_p/r_p is higher than 10:1. In this case, the Smoluchowski equation ceases to adequately describe the course of the coagulation process. The Muller equation for a bidispersive system has the following form:

$$N_t + n_t = \frac{N_0}{1+\frac{t}{T_{N_0}}}\left[1+\frac{\lambda}{(\lambda\cdot V_n+1)\cdot(1+\frac{t}{T_{N_0}})^{\lambda}-1}\right] \tag{2}$$

Part "X" part "Y"

where N_0 is initial number of large particles, n_0 is initial number of small particles, N_t and n_t are respective numbers of particles after time t, T_{N_0} is half-time of large particles and

$$\lambda = \frac{V_r^{\,2}+1}{2\cdot V_r} \tag{3}$$

where: $V_r = \frac{R_p}{r_p}$, and $V_n = \frac{N_0}{n_0}$.

The above clearly illustrates that when the "contents" of square brackets in the Muller equation "Y" = 1, the formula differs from the Smoluchowski equation only in respect of the value of n_0 (initial number of large particles), whereas in the Smoluchowski formula, n_0 simply denotes the initial number of particles.

Table 1

The actual number of particles in the system, where the number of particles has been calculated based on: a) the Smoluchowski equation [17], b) Muller equation [18]

Actual number of particles	**Number of particles calculated from Muller equation**	**Deviation parameter Δ [%]**	**Average deviation parameter Δ [%]**	**Number of particles calculated from Smoluchowski equation**	**Deviation parameter Δ [%]**	**Average deviation parameter Δ [%]**
N_c = 100, N_s = 1000, E = 3, F = 0.2, R_c = 2, R_s = 2, I = 1						
1060	949	10.5	12.2	961	9.3	10.3
1020	900	11.8		915	10.3	
980	885	12.8		873	10.9	
940	815	13.3		835	11.2	
900	775	12.8		806	10.4	
860	755	12.3		777	9.7	
N_c = 100, N_s = 1000, E = 10, F = 0.2, R_c = 2, R_s = 2, I = 1						
990	965	2.5	5.8	976	1.4	3.9
880	911	3.5		926	5.2	
770	825	7.1		844	9.6	
660	612	7.3		638	3.3	
550	524	4.7		550	0	
440	398	9.5		423	3.9	
N_c = 50, N_s = 1000, E = 15, F = 0.2, R_c = 2, R_s = 2, I = 1						
970	926	4.5	3.9	932	3.9	2.7
890	887	0.3		894	0.4	
810	799	1.2		809	0.1	
730	693	4.9		705	3.4	
650	609	6.2		622	4.3	
570	533	6.5		546	4.2	

Tables 1 and 2 demonstrate the number of particles in the system after time t (calculated based on the Smoluchowski and Muller equations) and the actual number of particles in the analyzed system. Table 1 lists constant values of n_0 (N_s = 1000) at R_p/r_p = 1 (R_c = 2, R_s = 2 and I = 1) for a varied coagulation threshold E = 3, 10 or 15. In general, deviations Δ between theoretically calculated numbers and real values were in the range of 0 to 13.3%. The lowest Δ = 0.1-6.5% was determined at E = 15, when the "average Smoluchowski deviation" reached 2.7%, and the "average Muller deviation" - 3.9%. For the minimum value of E = 3, the average Smoluchowski deviation was noted at 10.3%, and the average Muller deviation - at 12.2%. At E = 10, the average Smoluchowski deviation of Δ = 3.9% also proved to be significantly lower than that of the average Muller deviation parameter (Δ = 5.8%).

The values of the Δ parameter for different values of n_0 (N_s = 700-1200) and R_p/r_p (I = 0.01; 0.12 or 6) at constant E = 7 are presented in Table 2. Thus, at low values of N_s, the Smoluchowski Δ was lower than that of the Muller, while at N_s = 1100 and 1200, the

Muller Δ was lower than the Smoluchowski Δ. In general, the Δ parameter in both cases (Smoluchowski and Muller) changed with every increase in the value of *I*.

Table 2

Average deviation in the number of particles calculated based on: a) the Smoluchowski equation, b) the Muller equation in reference to the actual number of particles for $E = 7$

N_s	I	Δ Smoluchowski	Δ Muller
700	0.01	4.7%	5.3%
	0.12	2.9%	5.9%
	6	3.0%	4.7%
800	0.01	4.2%	6.9%
	0.12	4.9%	6.6%
	6	3.7%	4.9%
900	0.01	8.4%	8.7%
	0.12	6.6%	8.6%
	6	3.6%	4.4%
1000	0.01	7.3%	8.0%
	0.12	7.1%	7.5%
	6	5.8%	5.7%
1100	0.01	10.5%	8.5%
	0.12	11.3%	9.3%
	6	12.5%	9.9%
1200	0.01	9.5%	9.3%
	0.12	7.6%	7.6%
	6	11.4%	10.4%

At extreme values of I = 625-8000 (which resulted from the R_c/R_s ratio of 5 to 50), the Smoluchowski equation still allowed the calculation of the actual number of particles in the system with a low deviation of several percent in most cases, while the Muller equation was unfit for calculations of the type. However, it is theoretically recommended that the Muller equation be used when $R_c / R_s > 10$.

The problems with the application of the Muller equation lead to two situations:

a) the Muller equation yields correct results when the number of large particles significantly exceeds the number of small particles - in this study, when N_0 = 700-1200.
b) the Muller equation does not yield correct results when the number of small particles is significantly higher than the number of large particles - in this study, when V_n = 0.1-0.08.

In general, a given ratio between the number of differently sized particles has to be maintained to support the calculation of the number of small and large particles from the Muller equation after time *t*. In accordance with the Muller equation, particles exhibit mutual interactions. An increase in the radii of a given number of particles increases the probability of particle collision. The first part of the Muller equation (X) is similar to the complete form of the Smoluchowski equation. Muller simply replaced n_0 in the Smoluchowski equation with N_0 - the number of large particles, and half-time Tn_0 was replaced with the half-time of large particles T_{N0}. The authors of this work have proposed to replace Muller's N_0 with n_w, which indicates the number of *dominant* particles in the system, regardless of whether they are large or small ones. T_{N0} is replaced with Tn_w, i.e. the half-time of particles n_w, which changes the value of V_n (the ratio of large to small paricles)

to V_w (the ratio of more numerous particles to less numerous particles) in Y. This modification of the Muller equation takes on the following form:

$$N_t + n_t = \frac{n_w}{1+\frac{t}{T_{nw}}}\left[1+\frac{\lambda}{(\lambda \cdot V_w + 1)\cdot(1+\frac{t}{T_{N_0}})^{\lambda}-1}\right] \tag{4}$$

Table 3

The actual number of particles in the system and the number of particles calculated from the modified Muller equation

Actual number of particles	Number of particles calculated from Muller equation	Deviation parameter Δ [%]	Average deviation parameter Δ [%]
N_c = 50, N_s = 1000, V_c = 5, V_s = 25, E = 20, F = 0.2, R_c = 5, R_s = 1, I = 625			
945	837	11.5	7.6
840	755	10.1	
735	675	8.2	
630	581	7.8	
525	504	4	
420	402	4.2	
N_c = 50, N_s = 1000, V_c = 50, V_s = 50, E = 20, F = 0.2, R_c = 5, R_s = 1, I = 625			
945	811	14.2	8.8
840	751	10.6	
735	634	13.8	
630	577	8.4	
525	505	3.9	
420	429	2.2	
N_c = 50, N_s = 1000, V_c = 50, V_s = 50, E = 20, F = 0.01, R_c = 5, R_s = 1, I = 625			
945	747	20.9	13.8
840	649	22.7	
735	599	18.4	
630	563	10.6	
525	504	3.9	
420	443	5.7	
N_c = 100, N_s = 1000, V_c = 1, V_s = 10, E = 10, F = 0.2, R_c = 5, R_s = 0.1, I = 1000			
990	990	7.8	6.8
880	880	6.9	
770	770	5.6	
660	660	4.6	
550	550	9.0	
N_c = 100, N_s = 1000, V_c = 1, V_s = 10, E = 10, F = 0.2, R_c = 5, R_s = 0.5, I = 1000			
990	927	6.4	8.7
880	801	9.0	
770	704	8.7	
660	588	11.0	
550	501	8.8	
N_c = 100, N_s = 1000, V_c = 1, V_s = 10, E = 10, F = 0.2, R_c = 5, R_s = 0.25, I = 8000			
990	949	4.1	4.5
880	825	6.3	
770	763	0.9	
660	674	2.2	
550	500	9.1	

The equation (4) has been tested for $T = 0$, producing a correct correlation $N_t + n_t = N_0 + n_0$. The modified equation yields correct results in simulated cases, where the number of large particles exceeds the number of small particles and for a reverse case, i.e. when the number of small particles exceeds the number of large particles.

The actual number of particles in the coagulation system and the number of particles calculated from the modified Muller equation are presented in Table 3. Average values of the deviation Δ parameter are low and satisfactory and are close to those obtained from the Smoluchowski equation.

The cases when the amount of large particles in the system is congruous to the number of small particles have not been included in this study. In case the above-discussed computer simulation is concerned (e.g. at $N_c = N_s$), small aggregates (e.g. $E = 5$) restrict the examination of the decay of coagulant particles to 20%. Nonertheless, as for as practice is concerned, it is difficult to imagine a situation wherein wastewater is treated with the use of a coagulant in quantities similar to the amount of waste being disposed.

Conclusions

1. The rate of the simulated coagulation process, within the range described in this paper, satisfies both the first-order kinetic equation and second-order kinetic equation.
2. Within the range described in this study, the simulated aggregation takes place according to the *particle-cluster* model as a fast and perikinetic coagulation process that fulfils the Smoluchowski equation.
3. When the ratio of large particle radii to small particle radii exceeds 10, the coagulation process does not satisfy the Muller equation, but it continues to satisfy the Smoluchowski equation.
4. A modification of the Muller equation proposed in this study supported the calculation of the number of particles in the system upon condition that the number of “large” and “small” particles is diversified accordingly.

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