Chemical Engineering Journal 152 (2009) 146–150

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Computer simulation of the flocculation of suspended solids

L. Smoczyński [a], P. Mróz [b], R. Wardzynska [a,*], B. Załęska-Chróst [a], K. Dłużyńska [a]

[a] University of Warmia and Mazury Olsztyn, pl. Lodzki 4, 10-727 Olsztyn, Poland
[b] Environmental Protection Studies, Masurian Academy in Olecko, 19-400 Olecko, Pl. Zamkowy 3, Poland

ARTICLE INFO

Article history:
Received 25 September 2007
Received in revised form 27 March 2009
Accepted 8 April 2009

Keywords:
Flocculation
Sedimentation
Simulation
Wastewater

ABSTRACT

The paper presents the results of a study carried out using the computer program ZB1 simulating the flocculation of suspended solids. A description of the program is followed by an analysis of the effect of colloidal particle size and settling rate on sol destabilization. It was demonstrated that the tested program is consistent with the classical theories of particle motion and destabilization of colloidal systems. It was also found that the value of the diffusion coefficient increased along with an increase in the particle diameter *S*, regardless of the settling rate *Q*. An increase in the particle diameter caused an increase in the diffusion coefficient and allowed to shorten the duration of the destabilization process.

1. Introduction

Although the technologies of chemical and biological–chemical wastewater treatment are constantly improved, coagulation remains the most popular and widely applied method. Coagulation is a process in which colloidal particles form bigger agglomerates of sparingly soluble sludge. Sludge sedimentation is preceded by flocculation, i.e. the formation of flocs. This stage very often determines the overall efficiency of coagulation, flocculation and sedimentation.

Coagulation–flocculation may proceed in accordance with one of the two patterns. In orthokinetic coagulation–flocculation collisions of particles take place under the influence of external factors. The rate of flocculation may be increased if the particles are made to move, e.g. by stirring. This increases the probability of collisions between single colloidal particles and agglomerates. The final effect of orthokinetic flocculation–coagulation depends on the quantity of mechanical energy dispersed in a unit volume, since too much energy prevents colloid flocculation [1]. Gravity force may hinder the gelation of suspended solids [2]. During perikinetic flocculation–coagulation a decrease in the degree of system dispersion results from collisions of destabilized colloidal particles, caused primarily by Brownian motion. This kind of flocculation occurs, for instance, in pre-sedimentation and septic tanks at wastewater treatment plants. Colloidal particles suspended in wastewater have low kinetic energy, so destabilization and colloid precipitation occur at a slow rate.

Due to its complexity, flocculation still arouses interest among researchers and constitutes the object of both fundamental studies, e.g. on the mechanism and kinetics of particle flocculation [3–6], and utilitarian investigations [7]. Investigations into coagulation, aggregation, flocculation and sedimentation are usually carried out under natural conditions [8–13], or under model conditions, e.g. on silica suspension [14,15].

Computer simulation may be a viable alternative to laboratory tests. It guarantees unlimited reproducibility of experimental conditions and a high number of repetitions, thus enabling, for instance, to develop a model of collisions between particles [3], to describe the mechanisms of latent and slow (perikinetic) as well as visible and rapid coagulation [7,16] and aggregation [5,17,18] and to determine the kinetic parameters and conditions of these processes [5,6,19]. Today the model of computer simulation used most frequently is the so-called "Monte Carlo" simulation [20,21]. This method, based on the theory of probability and statistical mechanics, has a wide range of applications. It is employed, among others, to determine the fractal size [3,22] and structure [17] of post-coagulation sludge aggregates as well as to analyze the mechanism of coagulation, aggregation, flocculation and sedimentation [17,23–25]. The first computer-simulated model of particle–cluster aggregation, developed by Witten and Sander [24], was followed by the cluster–cluster model proposed by Meakin and Kolbe [17]. According to the particle–cluster model of Witten and Sander, single particles undergoing a random walk stick one after another to an immobile, growing cluster. The process is irreversible, and the cluster grows by the addition of single particles. The spherical particle–cluster aggregates are arranged around the center. According to the cluster–cluster model of Meakin and Kolbe, identical particles are evenly distributed in space within a constrained vol-

* Corresponding author. Tel.: +48 89 5233 37 38; fax: +48 89 523 48 01.
E-mail address: hannawar@uwm.edu.pl (R. Wardzynska).

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.04.020

ume. All particles move randomly. When two particles come into contact, they start to move together maintaining their orientation. A dimer may bind to another dimer or to a single particle. The aggregates are usually elongated or ellipsoidal, with matter arranged along the preferred axis.

This paper presents the results of the application of the computer program ZB1 simulating the flocculation of suspended solids. The effect of colloidal particle size and settling rate on sol destabilization were determined. Neither pH values nor pH changes in the analyzed system are considered in the ZB1 model, which means that the model simulates coagulation–flocculation at a constant (continuously adjusted) pH. This is often the case at wastewater treatment plants. Such factors as GT and T are reflected in the value of V_0, i.e. the initial velocity of sol particles, controlled in ZB1. V_0 = const. = 50 was adopted in the study. Further tests with ZB1 will include the determination of the effect of V_0 on the course of simulated processes of coagulation, flocculation and sedimentation. It was also tested whether the developed database can be applied in practice under conditions of the optimum dosage of inorganic coagulants.

2. Methods

The simulation model applied in our study, ZB1, is a stochastic-dynamic one [26], based on random variables. The state of the system changes due to the passage of simulation time. The kernel of the operating system is a module solving equations of motion for a given number of units of matter (particles) in a closed vessel. The program simulates the process of destabilization of spherical particles of a homodisperse sol. ZB1 was developed based on our observations of coagulation/flocculation of (a) model and natural pulp-and-paper wastewater [27], (b) municipal wastewater [28], and (c) model wastewater [13,15], carried out with the use of PAC, PIX and $Al_2(SO_4)_3$. The initial values of particle positions are generated randomly in uniform distribution within the vessel. The particles move according to Brownian motion. The program computes the trajectories of individual particles, and the direction of motion is selected randomly (RANDOM function). The angle at which the particle bounces off the vessel wall is equal to the incident angle. A collision of two particles which have different velocities results in the formation of a cluster (e.g. a dimer) whose direction and velocity are resultants calculated and then converted into vectors. In this way aggregates composed of three, four and more particles are formed. During the process of aggregation the number of single particles decreases gradually, and the original homodisperse sol turns into a polydisperse system. Having reached an adequate size, the aggregates undergo sedimentation and are eliminated from the system. The program was written in Pascal, using an easily available tool, i.e. "Turbo Pascal" Version 6.0 (Borland Inc.). The following input variables were used:

N_0—number of particles,
V_0 [u/s]—initial velocity of a particle (u—simulated measure of length, s—simulated time),
D [u]—size of sedimenting flocs determined by the number of particles forming an agglomerate,
Q—settling rate, i.e. a systemic parameter specifying the range of "settling values" assumed by a cluster,
S [u]–particle diameter.

The values of N_0, V_0, Q, D and S can be changed within a wide range, i.e. N_0 from 1 to 2000, V_0 from 1 to 9999, Q from 0.01 to 9999.00, D from 1 to 2000, S from 0.01 to 9999.00. During the test the ranges of all parameters are set each time so as to assure compliance between visual observations of the colloidal systems and observations of model or natural wastewater, coagulated chemically under laboratory conditions or at a sewage treatment plant. In our study, sol particle size was S_1 = 1.5, S_2 = 5 and S_3 = 11, while Q was equal to 0.01, 0.05 and 0.11. Constant parameters were N_0 = 1000, V_0 = 50, D = 20. Variable parameters were settling rate Q and particle diameter S. All measurements were performed in three replications. The graphs were plotted for mean values, showing standard deviations.

3. Results and discussion

At the beginning of the experiment 1000 spherical particles of a homodisperse sol were put in perikinetic motion. According to Smoluchowski [29], the probability of collisions of particles depends on the initial concentration of sol (in the present study: N_0 = 1000 = const.), diffusion coefficient, D_f, and the initial velocity, V_0, of a particle, whose measure is the so-called displacement in Brownian motion. The number of stable particles, remaining in colloidal state after time t, is determined by the Smoluchowski equation [30]:

$$\sum N_t = \frac{N_0}{1 + \beta t} \tag{1}$$

where $\beta = 4\pi D_f R N_0$ and is a measure of the diffusion coefficient, and R denotes a radius of the sphere shown in Fig. 1, where irreversible aggregation of two particles takes place.

Transformation of Eq. (1) at N_0 = 1000 leads to the following relationship:

$$\frac{1}{\sum N_t} = 0.001 + 0.001\beta t \tag{2}$$

By reading the number of stable particles at moment t of the destabilization process from the counter of the ZB program, we obtain a linear functional relationship in the form of Eq. (2).

Fig. 2 presents the curves of relationship (2), i.e. the inverse of the number of stable particles during sol destabilization. The measurements were performed for simulated values of particle diameter S = 1.5, 5, 11 and for simulated values of settling rate Q = 0.01 (Fig. 2a), Q = 0.05 (Fig. 2b) and Q = 0.11 (Fig. 2c).

A measure of good matching of the simulated database to the converted Smoluchowski equation are high values of the determination coefficient $R^2 > 0.9$. In laboratory studies regarding the coagulation and electrocoagulation of pulp-and-paper wastewater [27], the mean standard deviation (SD) was approximately 5%, while the value of SD in simulation studies was much lower and often did not exceed 0.25%. A comparison of SD determined in laboratory and simulation tests points to higher precision and repeatability and

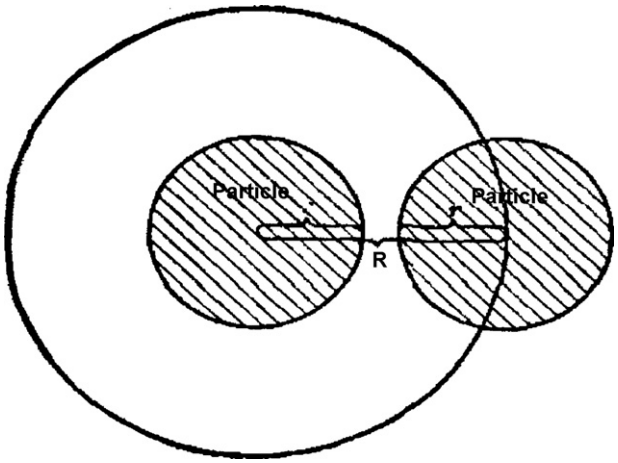

Fig. 1. Range of coagulation efficiency [30].

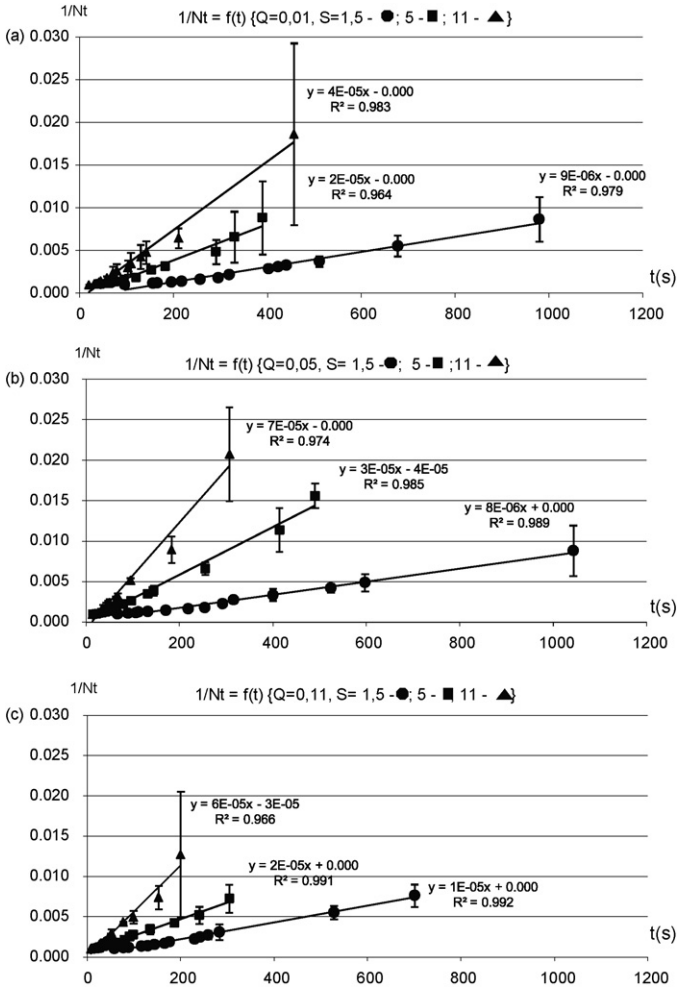

Fig. 2. Number of stable particles during sol destabilization at particle diameter $S = 1.5$, 5, 11 and settling rate $Q = 0.01$ (a), $Q = 0.05$ (b), $Q = 0.11$ (c).

smaller measurements errors in the latter. Small standard deviations of the results of simulation measurements indicate both "laboratory precision" and conditions close to the natural behavior of a sol. Therefore, the colloidal system examined in the study, similarly as, e.g. suspended solids, is characterized by certain variation and diversity, contributing to its naturalness.

The coefficient β was calculated on the basis of the slopes of respective straight lines. The calculated values of coefficients β, being a measure of the diffusion coefficient D_f, are presented in Table 1.

The data in Table 1 show that the value of the coefficient β increased along with an increase in the simulated diameter S of a single particle, regardless of the simulated settling rate Q. Simultaneously, an increase in the settling rate from 0.01 to 0.05 caused an increase in β for higher values (5 and 11) of particle diameter.

Table 1
Values of the coefficient β characterizing the simulated destabilization of a sol.

Settling rate, Q	Particle diameter, S		
	1.5	5	11
	Coefficient β		
0.01	0.009	0.02	0.04
0.05	0.008	0.03	0.07
0.11	0.01	0.02	0.06

The simulated settling rate Q is a measure of viscosity resistance of a dispersion medium, described by the equation:

$$T = 6\pi\eta SV \tag{3}$$

where T—resistance force of a dispersion medium, V—velocity of a particle = const., η—viscosity of a dispersion medium = const., so it increases along with an increase in the particle diameter S. Small differences in β for $S = 1.5$ and a slight decrease in β when the settling rate increased from 0.05 to 0.11 may be a result of an increase in the Reynolds number changing the character of aggregate displacement in a sol whose degree of dispersion is increasing. The Reynolds number, Re, i.e. the ratio between inertia forces and viscosity forces, is defined as follows [31]:

$$Re = \frac{SV\rho}{\eta} \tag{4}$$

Therefore, at V, ρ and η = const. Re increases along with an increase in the particle diameter S. According to Subramanian and Balasubramaniam [31], the settling rate of spherical particles is always dependent on both the so-called coefficient of "dragging" and the Reynolds number. An increase in the number of dimers, trimers and bigger clusters in the suspension must affect the motion of particles, which may change from laminar to partially turbulent, or vice versa. Based on the obtained results, a hypothesis may be proposed that $Q = 0.05$ is a boundary value between the Re range for laminar flow and the Re range for turbulent flow. The simulated settling rate Q should be a measure of three combined functions:

(a) viscosity resistance of a dispersion medium,
(b) range of the Reynolds number determining particle motion,
(c) coefficient of particle dragging in a dispersion medium.

Fig. 3(a–c) illustrates the effect of the simulated diameter of a particle on the time needed for the formation of the first sedimenting floc (Fig. 3a), destabilization of 50% of the system, i.e. sedimentation of 500 particles of the analyzed dispersoid in the form of flocs (Fig. 3b), and removal of 900 particles, i.e. 90% of the system (Fig. 3c). The measurements were performed for $Q = 0.05$, i.e. for an intermediate value among those tested before.

At this stage of the study the optimum matching ($R^2 > 0.95$) was obtained for a power dependence of the $y = ax^b$ type. Respective equations and R^2 are given in the upper right corner of each graph. Attention should be paid to the extremely low values of SD, confirming a high precision of ZB1. An increase in the particle diameter S reduces the time needed for system destabilization. The most significant effect of S was observed at 90% destabilization, where the value of the constant $a \approx 1200$ was about fourfold greater than in the equation representing 50% destabilization ($a \approx 300$). The constant "a" was considered "responsible" for different courses of the curves shown in Fig. 3 due to a certain regularity. Namely, it was found that the values of the constant "b" in respective equations "$y = ax^{b''}$ remained within a relatively narrow range, i.e. –0.84 to–0.72, which may indicate that this constant is independent of (a) the degree of system destabilization and (b) the diameter of a particle in the analyzed dispersoid.

According to Smoluchowski [29], the probability that one particle meets another is directly proportional to a displacement in a unit of time, resulting from Brownian motion. In practice, the displacement defined in this way must be directly related to the diameter of a particle in the simulation program ZB1. The courses of the curves in Fig. 3 show that the effect of S on the time needed to initiate destabilization is insignificant, which may suggest that the diameter of a particle has an inconsiderable influence on the rate of slow and latent coagulation, which agrees with the coagulation theory formulated by Smoluchowski. After the stage of rapid coagulation and agglomeration–flocculation, a big "discharged" cluster

(20 particles) settles gravitationally (orthokinetically), falling down through "swarms" of smaller aggregates and single particles, carrying them away at the stage of the so-called sweep coagulation within the cluster's sheath.

An increase in the diameter of a particle *S* increases the contribution of sweep coagulation in the process of coagulation–flocculation. In ZB1 this is reflected in a shorter period of time needed for the elimination from the system of (a) the first particle (Fig. 3a), (b) 50% of particles (Fig. 3b) and (c) 90% of particles (Fig. 3c).

Under practical conditions, at wastewater treatments plants, a similar effect may be observed in consequence of inorganic coagulant "overdosing". Such a phenomenon is usually accompanied by a partial change in the surface charge (partial micelle overcharging), manifested in a higher contribution of sweep coagulation to the process of coagulation–flocculation. It can be easily calculated that big particles have a smaller specific surface area than small particles. Therefore, particle size reduction leads to an increase in the total surface charge determining the efficiency of slow and latent coagulation. Research results and observations carried out at many wastewater treatment plants show that the maximal chemical efficiency of coagulation can be obtained at the maximal contribution of slow and latent coagulation to sol destabilization, because these processes use to the maximum the surface charge of the destabilized system.

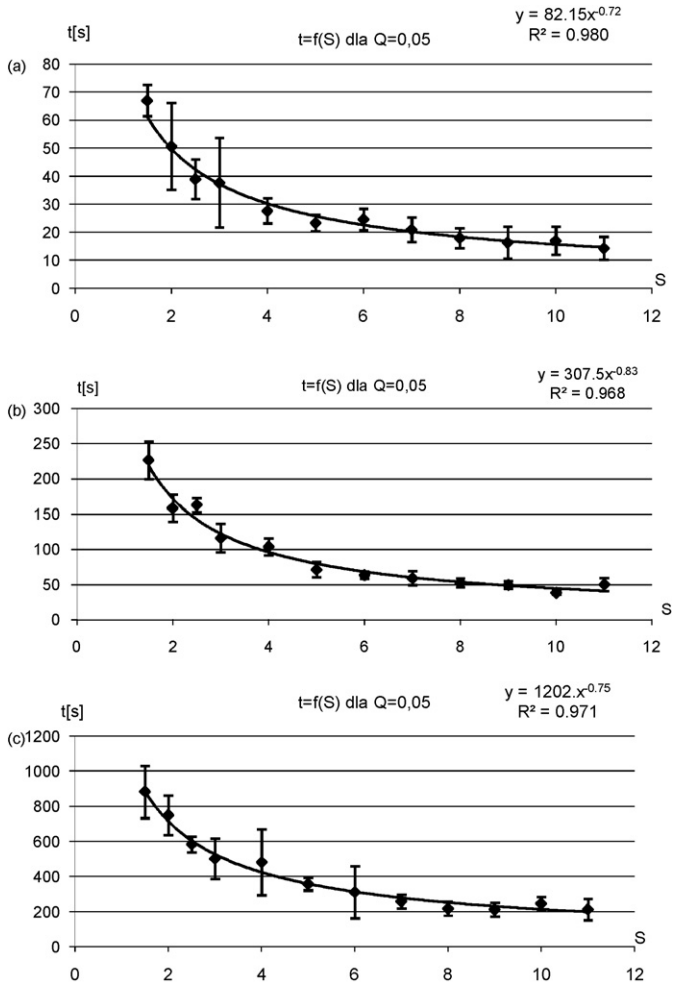

Fig. 3. Time needed for the sedimentation of: (a) the first floc, (b) 500 particles (50%), (c) 900 particles (90%) of the system, as dependent on the particle diameter *S*.

4. Summary and conclusions

The study on the destabilization kinetics of a simulated sol showed that the dependence $1/N_t = f(t)$ was linear and characterized by a very high value of the determination coefficient R^2, reaching 0.99. This indicated good matching of the simulated database to the Smoluchowski equation. It was also found that the value of the diffusion coefficient increased along with an increase in the particle diameter *S*, regardless of the settling rate *Q*. An increase in particle diameter caused an increase in the diffusion coefficient and allowed to shorten the duration of the destabilization process.

The effect of the particle diameter *S* on sol destabilization indicated that the simulated increase in *S* increased the contribution of the undesirable coagulation stage, i.e. sweep coagulation, to the process of coagulation–flocculation. It was demonstrated that the effect of the particle diameter *S* on the time needed to initiate destabilization was insignificant, and the same relationships for the destabilization of 50% and 90% of suspended solids can be described by a power function.

The results of the present study enabled to formulate the following conclusions:

1. The computer program ZB1 tested in the study allows to determine the effects of numerous parameters on coagulation, aggregation, flocculation and sedimentation of the simulated suspended solids.
2. The majority of the results of measurements obtained using ZB1 are consistent with the classical theories of particle motion and destabilization of colloidal systems.
3. The database developed in simulation tests is burdened with a low experimental error similar to that recorded in laboratory analyses, which confirms a high precision of the program.
4. An increase in the particle diameter *S*, simulated in ZB1, increases the diffusion coefficient and shortens the time needed for the destabilization of the first particle, 50% of particles and 90% of particles of the tested simulated suspension.
5. The effect of the particle diameter *S* on the time needed to initiate destabilization is insignificant.
6. The method of computer simulation may find many practical applications as a supplemental tool to laboratory tests.

References

[1] A.L. Kowal, M. Świderska–Bróż, Oczyszczanie wody, PWN, Warszawa–Wrocław, 1998.
[2] C. Allain, M. Cloitre, M. Wafra, Aggregation and sedimentation in colloidal suspensions, Phys. Rev. Lett. 74 (1995) 1478–1481.
[3] X.Y. Li, J.J. Zhang, Numerical simulation and experimental verification of particle coagulation dynamics for a pulsed input, J. Colloid Interface Sci. 262 (2003) 149–161.
[4] D.G. Lee, J.S. Bonner, L.S. Garton, A.N.S. Ernest, R.L. Autenrieth, Modelling coagulation kinetics incorporating fractal theories: comparison with observed data, Water Res. 36 (2002) 1056–1066.
[5] J. Dzubiella, J.A. McCammon, Substrate concentration dependence of the diffusion-controlled steady-state rate constant, J. Chem. Phys. 122 (2005) 184902–184907.
[6] N. Kallay, S. Zalac, Introduction of the surface complexation model in the theory of colloid stability, Croat. Chem. Acta 74 (2001) 479–497.
[7] L.A. Chen, G.A. Serad, R.G. Carbonell, Effect of mixing conditions on flocculation kinetics of wastewaters containing proteins and other biological compounds using fibrous materials and polyelectrolytes, Braz. J. Chem. Eng. 15 (1998) 1–15.
[8] H. Ratnaweera, E. Gjessing, E. Oug, Influence of physical–chemical characteristics of natural organic matter (NOM) on coagulation properties: an analysis of eight Norwegian water sources, Water Sci. Technol. 40 (1999) 89–95.
[9] C.R. O'Melia, Coagulation and sedimentation in lakes, reservoirs and water treatment plants, Water Sci. Technol. 37 (1998) 129–135.
[10] J.K. Edzwald, Coagulation in drinking water treatment: particles, organics and coagulants, Water Sci. Technol. 27 (1993) 21–35.
[11] J. Fettig, H. Ratnaweera, H. Odegaard, Synthetic organic polymers as primary coagulants in wastewater treatment, Water Supply 8 (1990) 19–26.
[12] H.R. Maier, N. Morgan, C.W.K. Chow, Use of artificial neural networks for predicting optimal alum doses and treated water quality parameters, Environ. Model. Softw. 19 (2004) 485–494.

[13] L. Smoczyński, R. Wardzyńska, Study on macroscopic aggregation of silica suspensions and sewage, J. Colloid Interface Sci. 183 (1996) 309–314.
[14] B.S. Lartiges, J.Y. Bottero, L.S. Derrendinger, B. Humbert, P. Tekely, H. Suty, Flocculation of colloidal with hydrolyzed aluminum: An^{27} Al solid state NMR investigation, Langmuir 13 (1997) 147–152.
[15] L. Smoczyński, Aggregation of the silica suspension by Al-coagulants, Pol. J. Chem. 74 (2000) 1617–1624.
[16] L. Smoczyński, R. Wardzyńska, B. Załęska-Chróst, Z. Bukowski, Computer simulation of latent coagulation, Pol. J. Nat. Sci. 22 (2007) 73–82.
[17] P. Meakin, T. Kolb, Formation of fractal cluster and networks by irreversible diffusion-limited aggregation, Phys. Rev. Lett. 51 (1983) 1119–1122.
[18] G. Yang, P. Biswas, Computer simulation of the aggregation and sintering restructuring of fractal-like clusters containing limited numbers of primary particles, J. Colloid Interface Sci. 211 (1999) 142–150.
[19] H. Ratnaweera, L. Lei, O. Lindholm, Simulation program for wastewater coagulation, Water Sci. Technol. 46 (2002) 27–33.
[20] T. Pushkar, D.E. Rosner, Monte Carlo simulation of particle aggregation and simultaneous restructuring, J. Colloid Interface Sci. 213 (1999) 273–286.
[21] E. Kołodziński, Symulacyjne metody badania systemów, PWN, Warszawa, 2002.
[22] M. Lattuada, H. Wu, M. Morbidelli, A simple model for structure of fractal aggregates, J. Colloid Interface Sci. 268 (2003) 106–120.
[23] M. Nazzarro, F. Nieto, A.J. Ramirez-Pastor, Influence of surface heterogeneities on the formation of diffusion-limited aggregates, Surf. Sci. 497 (2002) 275–284.
[24] T.A. Witten, L.M. Sander, Diffusion-limited aggregation, a kinetic critical phenomenon, Phys. Rev. Lett. 47 (1981) 1400–1403.
[25] J. Quispe, F. Concha, P.G. Toledo, Discrete sedimentation model for ideal suspensions, Chem. Eng. J. 80 (2000) 135–140.
[26] P. Perkowski, Technika symulacji cyfrowej, WNT, Warszawa, 1980.
[27] L. Smoczyński, R. Wardzyńska, B. Załęska-Chróst, Electrocoagulation vs. chemical coagulation comparison of methods for treating sewage from pulp and paper industry, Acta Sci. Pol., Form. Circumiectus 3 (2) (2004) 3–14.
[28] L. Smoczyński, R. Wardzyńska, Removal of phosphates from wastewater by coagulation, Ochr. Śr. (Wroc.) 3 (1996) 41–43.
[29] M. Smoluchowski, Versuch einer mathematischen theorie der koagulationskinetic kolloider lsungen, Z. Phys. 92 (1917) 129.
[30] H.B. Weiser, A Textbook of Colloid Chemistry, John Wiley & Sons, NewYork, 1950.
[31] R.S. Subramanian, R. Balasubramaniam, The Motion of Bubbles and Drops in Reduced Gravity, Cambridge University Press, Cambridge, UK, 2001.