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A Solution to Smoluchowski's Coagulation Equation Based on Experimental Data and a Model to Describe the Frequency of Particle Collisions

Svetlana B. Zueva[1,2], Alexander N. Ostrikov[2], Victor I. Ryazhskikh[3] & Francesco Vegliò[1]

[1] Department of Industrial and Information Engineering and Economics, University of l'Aquila, L'Aquila, Italy

[2] Department of Ecology and Chemical Technology, Voronezh State University of Engineering, Voronezh, Russian Federation

[3] Department of Higher Mathematics, Physical and Mathematical Modeling, Voronezh State Technical University, Voronezh, Russian Federation

Correspondence: Svetlana B. Zueva, Department of Ecology and Chemical Technology, Voronezh State University of Engineering, Revolution avenue 19, Voronezh, 394036, Russian Federation. Tel: 7-393-462-104-194. E-mail: sveta@zz.vrn.ru

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Abstract

Use of coagulants in treatment of wastewater from food industry is one of the most promising techniques to establish environment-friendly industries. To date, however, the coagulation process is not yet fully described in a manner which is conducive to practical applications and results. In fact, the coagulation process theoretical basis, i.e. the classical Smoluchowski's equation published in 1916, is so complex to solve that virtually no practical application exists in the field of applied chemistry.

This article illustrates the Authors' endeavor to overcome this impasse. This has been achieved by constructing a mathematical model of the guiding force in the phenomenon, i.e. the frequency of particles collisions, and then utilizing this model to define, starting from Smoluchowski's equation, a function which describes both the coagulation and sedimentation processes depending on space (vertical coordinate z) and the concentration of coagulant.

This study can be considered as the first step of a methodology of practical application of the Smoluchowski's equation to process and equipment design.

Keywords: dispersed systems, coagulation, frequency collisions, process design, sedimentation, Smoluchowski's equation

1. Introduction

Wastewater from food industry can be considered as a dispersed system (suspension), i.e. a heterogeneous system in which particles are dispersed in a continuous phase. Agglomeration of particles occurs during purification with coagulants, resulting in both coagulation and sedimentation.

The classic equation by Smoluchowski (Smoluchowski, 1916) spells the theoretical basis of the coagulation process. Its practical application, however, is limited because of the complexity of its solution. In particular, the lack of a mathematical model for the collisions in the dispersed phase, which is the guiding force in the phenomenon, has been so far a real bottleneck. To date researchers do not agree on how to overcome this difficulty. The authors of this paper are of the opinion that the definition of a model for the collisions is crucial in order to make significant progress.

Indeed, most research conducted so far has consisted in the effort of finding numerical solutions to the equation by means of theoretical approaches (Filbet and Laurencot, 2004; Qamar and Warnecke, 2007) using the homotopy perturbation method (Yəldərəm and Kocak, 2011) or stochastic particle method (Kolodko et. al, 1999). Some other study deals with the Smoluchowski equation with constant (Kostoglou, 2005) or time-varying kernel (Moseley, 2007). A popular method for the study of aggregation dynamics, is Brownian Dynamics Simulations (BDS) (Sauer et. al, 1996: Kelkar et. al., 2013; Struckmeier, 2005).

The authors' approach, as documented in this paper, consisted in using the experimental data obtained in previous research (Zueva et. all., 2013) to construct a mathematical model.

2. Construction of Mathematical Model

2.1 The Frequency of Collisions Function

The following assumptions were made:

1. That in volume L^3, at the time t=0, be N particles characterized by volume v_i.

2. That distance between particles is much grander than particles' size.

3. That characteristic time between collisions of particles with each other be τ .

4. That collisions of pairs of particles be much more numerous than collisions among grander number of particles (three or more), so that consideration shall be given only to collisions of pairs.

5. That the time of interaction of particles t_{in} (i.e. the time from the initial interaction to the time when a new particle with new properties comes into existence) is much shorter than τ .

6. That system concentration is low, so that particles are distributed randomly. This assumption justifies considering a stochastic (Marc) process of collision.

Based on the above assumptions the experimental data allowed defining an initial calculation of number of particles in the sample, as follows:

$$n_0 = \frac{C_0}{\rho_0 v_0}\text{, m}^{-3} \tag{1}$$

$$\text{where } v_0 = \frac{1}{6}\pi l_0^3\text{, m}^3 \tag{2}$$

in which C_0 ($1480 \cdot 10^{-3}$ mg/L) is average content of solid residue, ρ_0 ($2.7 \cdot 10^3$ g/cm^3) is average density, l_0 (3.54 μm) is average size of suspended particles (Zueva et. al., 2013).

$$n_0 = \frac{6C_0}{\pi \rho_0 l_0^3} = \frac{6 \cdot 1480 \cdot 10^{-3}}{3.14 \cdot 2.7 \cdot 10^3 \left(3.54 \cdot 10^{-6}\right)^3} = 2.359 \cdot 10^{13}$$

To analyze experimental data (Table 1) the Smoluchowski coagulation equation was applied (Smoluchowski, 1916):

$$\frac{\partial \phi(\mathrm{v},t)}{\partial t} = \frac{1}{2}\int_0^v \beta(v-v_1,v_1)\phi(v-v_1,t)\phi(v_1,t)dv_1 - \phi(v,t)\int_0^\infty \beta(v,v_1)\phi(v_1,t)dv_1 \tag{3}$$

where t is the current time; v is particle volume; $\phi(v,t)$ is density function of particles distribution depending on particle volume; β is the coagulation kernel, which governs the time rate at which particles aggregate.

After integration according to v within the interval from 0 to ∞, (1) takes the following form:

$$\frac{\partial n(t)}{\partial t} = -\frac{1}{2}\int_0^\infty \int_0^\infty \beta(v,v_1)\phi(v_1,t)\phi(v,t)dv\,dv_1 . \tag{4}$$

Introducing the dimensionless variables $\mathrm{x} = v/v_0$, $\tau = [n_0 - n(t)]/n_0$, where $v_0 = \frac{1}{n_0}\int_0^\infty v\,\phi\,(v,0)dv$ is an average particle volume in the initial time, τ age of spectrum $\left(0 \le \tau \le 1\right)$.

Assuming that $\beta_0 = \beta = const$ is a function of particle frequency collision.

Assuming that the number of particles N at time t is equal to:

$$N\left(t\right) = \int_0^\infty v\phi\left(v,t\right)dv \tag{5}$$

Table 1. Kinetics of coagulation process in wastewater of dairy plant with different doses of aluminum sulfate

t, s	10 µl/L		30 µl/L		50 µl/L	
	l, µm	l^3, µm^3	l, µm	l^3, µm^3	l, µm	l^3, µm^3
0	$3.54\cdot10^{-6}$	$4.44\cdot10^{-17}$	$3.54\cdot10^{-6}$	$4.44\cdot10^{-17}$	$3.54\cdot10^{-6}$	$4.44\cdot10^{-17}$
12	$3.54\cdot10^{-6}$	$4.44\cdot10^{-17}$	$3.60\cdot10^{-6}$	$4.66\cdot10^{-17}$	$3.54\cdot10^{-6}$	$4.44\cdot10^{-17}$
24	$3.54\cdot10^{-6}$	$4.44\cdot10^{-17}$	$3.60\cdot10^{-6}$	$4.66\cdot10^{-17}$	$3.60\cdot10^{-6}$	$4.66\cdot10^{-17}$
36	$1.00\cdot10^{-5}$	$1.00\cdot10^{-17}$	$3.40\cdot10^{-5}$	$3.93\cdot10^{-14}$	$3.70\cdot10^{-5}$	$5.06\cdot10^{-14}$
48	$2.80\cdot10^{-5}$	$2.19\cdot10^{-14}$	$3.00\cdot10^{-4}$	$2.70\cdot10^{-11}$	$1.06\cdot10^{-4}$	$1.19\cdot10^{-12}$
60	$1.19\cdot10^{-4}$	$1.68\cdot10^{-12}$	$8.31\cdot10^{-4}$	$5.74\cdot10^{-10}$	$3.30\cdot10^{-4}$	$3.59\cdot10^{-11}$
72	$2.50\cdot10^{-4}$	$1.56\cdot10^{-12}$	$1.31\cdot10^{-3}$	$2.25\cdot10^{-9}$	$5.10\cdot10^{-4}$	$1.33\cdot10^{-10}$
84	$4.12\cdot10^{-4}$	$6.99\cdot10^{-11}$	$1.57\cdot10^{-3}$	$3.87\cdot10^{-9}$	$7.42\cdot10^{-4}$	$4.08\cdot10^{-10}$
96	$4.66\cdot10^{-4}$	$1.01\cdot10^{-10}$	$1.64\cdot10^{-3}$	$4.41\cdot10^{-9}$	$8.50\cdot10^{-4}$	$6.14\cdot10^{-10}$
108	$4.80\cdot10^{-4}$	$1.10\cdot10^{-10}$	$1.65\cdot10^{-3}$	$4.49\cdot10^{-9}$	$8.80\cdot10^{-4}$	$6.81\cdot10^{-10}$
120	$4.80\cdot10^{-4}$	$1.10\cdot10^{-10}$	$1.65\cdot10^{-3}$	$4.49\cdot10^{-9}$	$8.90\cdot10^{-4}$	$7.05\cdot10^{-10}$

Than the average volume of particles at the time t is:

$$v(t)=\frac{N(t)}{n(t)}\,. \tag{6}$$

As the total volume of particles does not change (we can assume in first approximation) we can divide it by n_0 :

$$v(t)=\frac{N(t)/n_0}{n(t)/n_0}=\frac{v(t)}{1-\tau}=\frac{v_0}{1-\tau} \tag{7}$$

We can therefore conclude that the following formula gives the average volume of particles in function of time (t):

$$\bar{v}(t)=v_0\left(1+\frac{1}{2}n_0\beta_0 t\right)=v_0+v_0\frac{1}{2}n_0\beta_0 t\,, \tag{8}$$

Plotting experimental data as shown in Figure 1, i.e. considering a cubed dimension on the y axis, the data show a linear dependence ($y=a\cdot x+b$), that is, regressive equations which can be calculated using the method of least squares. The task is significantly simplified if to take into account the slope coefficient only, the reciprocal value of which will be $\frac{1}{2}n_0\beta_0$ ($\frac{1}{a}=\frac{1}{2}n_0\beta_0$):

$$\beta_0=\frac{2}{n_0\,a} \tag{9}$$

Which we shall call the **Frequency of Collision Function**

We need to define the coefficient a in Eq. (9). We will do this as follows. We have a linear equations and we have to find coefficients a and b with the condition

$$\varepsilon(a,b)=\sum_{i=1}^{n}\left(y_{\text{э}1}-y_{Ti}\right)^2\rightarrow\min \tag{10}$$

i.e.

$$\varepsilon(a,b)=\sum_{i=1}^{n}\left[y_{\text{э}i}-\left(a\cdot x_i+b\right)\right]^2\rightarrow\min\,. \tag{11}$$

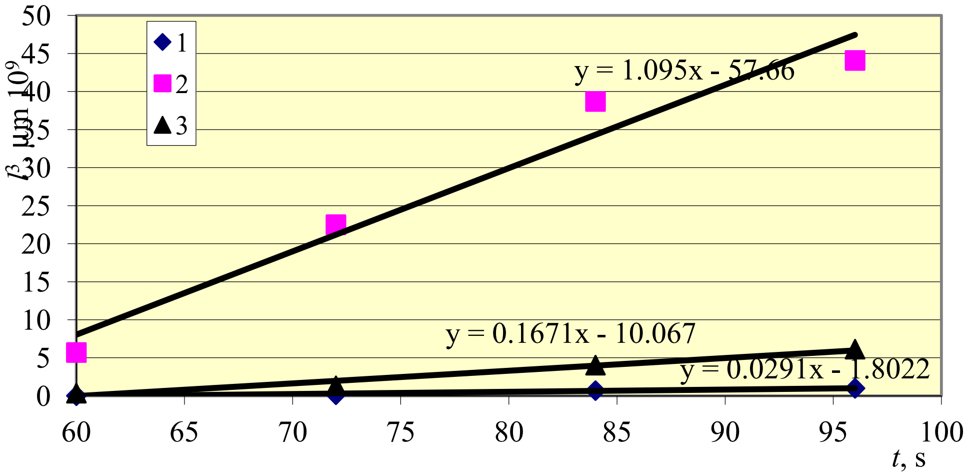

Figure 1. Kinetics of the coagulation process in the form of inverse relationship. Aluminum sulfate dosage: 1 – 10 μl/L; 2 – 30 μl/L; 3 – 50 μl/L

To define a and b we write the following equations system:

$$\begin{cases} \dfrac{\partial(a,b)}{\partial a} = 0; \\ \dfrac{\partial \varepsilon(a,b)}{\partial b} = 0, \end{cases} \tag{12}$$

This is equal to a minimization condition. Expanding this system:

$$\begin{aligned} &\frac{\partial \varepsilon(a,b)}{\partial a} = \frac{\partial}{\partial a}\sum_{i=1}^{n}\left[y_{\text{эi}} - (a x_i + b)\right]^2 = \sum_{i=1}^{n}\frac{\partial}{\partial a}\left[y_{\text{эi}} - (a x_i + b)\right]^2 = \\ &= \sum_{i=1}^{n} 2\left[y_{\text{эi}} - (a x_i + b)\right](-x_i) = -2\sum_{i=1}^{n}\left(y_{\text{эi}} x_i - a x_i^2 - b x_i\right) = 0; \end{aligned} \tag{13}$$

thus,

$$\begin{cases} \left(\sum_{i=1}^{n} x_i^2\right) a + \left(\sum_{i=1}^{n} x_i^2\right) b = \sum_{i=1}^{n} y_{\text{эi}} x_i; \\ \left(\sum_{i=1}^{n} x_i\right) a + n b = \sum_{i=1}^{n} y_{\text{эi}}. \end{cases} \tag{14}$$

$$\Delta = n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2$$

$$\Delta a = n\sum_{i=1}^{n} y_{\text{эi}}\, x_i - \left(\sum_{i=1}^{n} y_{\text{эi}}\right)\left(\sum_{i=1}^{n} x_i\right) \tag{15}$$

$$\Delta b = \left(\sum_{i=1}^{n} x_i^2\right)\left(\sum_{i=1}^{n} y_{\text{эi}}\right) - \left(\sum_{i=1}^{n} x_i\right)\left(\sum_{i=1}^{n} y_{\text{эi}}\, x_i\right). \tag{16}$$

Consequently $a = \dfrac{\Delta a}{\Delta}$; $b = \dfrac{\Delta b}{\Delta}$.

We will conduct a calculation according to the condition that $y \to t$, $x \to l^3$. Since the order t and l^3 is different, we will apply a system of dimensions of minutes (t/60) and 0.1 mm. Results of calculations are presented in Table 2.

2.2 The Coagulation and Sedimentation Function

Information on the value of the frequency of collision enables us to describe the simultaneous processes of coagulation and sedimentation. In order to do this we shall examine a one-dimensional case (z coordinate). The left hand side of Smoluchowski's equation (1) in this case shall contain a divergent operator, as follows:

$$\frac{\partial\phi(\mathrm{z,v,t})}{\partial \mathrm{t}}-\frac{\partial}{\partial z}\left[u\phi(z,v,t)\right]=$$
$$=\frac{1}{2}\int_0^v\beta(v-v_1,v_1)\phi(z,v-v_1,t)\phi(z,v_1,t)\,dv_1-\phi(z,v,t)\int_0^\infty\beta(v,v_1)\phi(z,v_1,t)\,dv_1 \tag{17}$$

in which u is the speed of sedimentation.

If we assume that $u=u_0=const$ (value of u_0 taken from experimental data), then the equation (11) again admits integration according to *v* within the scale from 0 to ∞, which leads the equation in the form:

$$\frac{\partial n(\mathrm{z,t})}{\partial \mathrm{t}}-u_0\frac{\partial n(z,t)}{\partial z}=-\frac{1}{2}\int_0^\infty\int_0^\infty\beta(v,v_1)\phi(z,v_1,t)\phi(z,v,t)\,dv\,dv_1 \tag{18}$$

with a differential equation as a result:

$$\frac{\partial N(Z,\Theta)}{\partial\Theta}-\frac{\partial N(Z,\Theta)}{\partial Z}=-N^2(Z,\Theta) \tag{19}$$

in which:

$$Z=\frac{1}{2}n_0\beta_0 z/u_0 \tag{20}$$

$$\Theta=\frac{1}{2}n_0\beta_0 t \tag{21}$$

$N(Z,\Theta)=n(z,t)/n_0$ with the initial boundary condition

$$N(Z,0)=N(0,\Theta)=1 \tag{22}$$

Introducing the new variable M defined as follows:

$$M(Z,\Theta)=1/N(Z,\Theta) \tag{23}$$

then (19) and (22) take the form:

$$\frac{\partial M(Z,\Theta)}{\partial\Theta}-\frac{\partial M(Z,\Theta)}{\partial Z}=1 \tag{24}$$

$$M(Z,0)=M(0,\Theta)=1 \tag{25}$$

Applying Laplace's transformation to (23) and (24) according to Θ variable:

$$\frac{dM_L(Z,s)}{dZ}+sM_L(Z,s)=1+\frac{1}{s} \tag{26}$$

$$M_L(0,s)=\frac{1}{s} \tag{27}$$

in which s, M_L are Laplace's real numbers Θ and M.

Solving (26) and (27) by Cauchy:

$$M_L(Z,s)=\frac{1}{s}+\frac{1}{s^2}-\frac{1}{s^2}\exp(-sZ) \tag{28}$$

the original of which is:

$$\mathrm{M}(\mathrm{Z},\Theta)=1+\Theta-(\Theta-Z)\perp(\Theta-Z). \tag{29}$$

The above is the solution of Eq. (24) and Eq. (25), in which $\perp(\Theta - z)$ is the Heaviside step function.

Considering $M(Z,\Theta)$ and $N(Z,\Theta)$, recalling Eq. (23), the description of coagulation and sedimentation takes the following form:

$$N(Z,\Theta) = \frac{1}{1+\Theta-(\Theta-Z)\perp(\Theta-Z)} \quad . \tag{30}$$

Which we shall call the **Coagulation and Sedimentation Function (CSF)** (Figure 2).

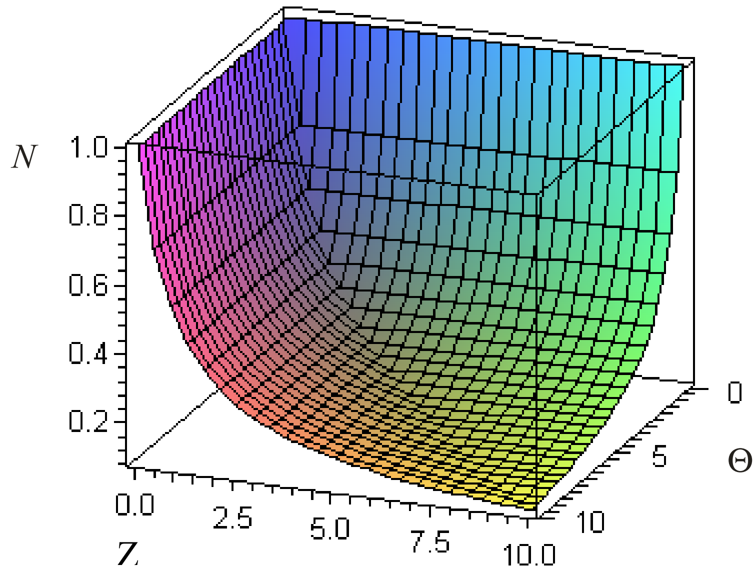

Figure 2. Graphic rendering of Coagulation and Sedimentation Function (obtained by using MAPLE)

Given h as the height of a coagulation and sedimentation zone (from experiment) then the dimensionless operator Z_h is known and the average concentration throughout the height can be calculated as follows:

$$\overline{N}(\Theta) = \frac{1}{Z_h}\int_0^{Z_h} N(Z,\Theta)dZ = \frac{1}{z_h}\left[\ln(1+\Theta) + \frac{Z_h - \Theta}{1+\Theta}\right], \tag{31}$$

where

$$Z_{\mathrm{h}} = \frac{1}{2} n_0 \beta_0 h / u_0 \, . \tag{32}$$

In our experiment, waste water was treated with dosage of coagulant 10 μl/l and h was equal to 0,15 m. Consequently, the value of Z_h was:

$$Z_{\mathrm{h}} = \frac{1}{2} 2.359\ 10^{13}\ 1.83\,10^{-13}\ 0.15/0.01 = 32.3$$

Results of calculations are presented in Table 2.

Table 2. The values of *l*, u_0, β_0 and Z_h calculated with the above formulas

Coagulant dosage, μl/L	*l*, μm	u_0, m/s	β_0, m^3/s	Z_h
10	454	0.01	1.83 10^{-13}	32.33
30	786	0.03	0.08 10^{-13}	0.45
50	642	0.02	0.71 10^{-13}	6.25

3. Conclusions

This research has defined two functions: the Frequency of Particle Collision β_0, Eq. (9) and the Coagulation and Sedimentation Function $N(Z,\Theta)$ Eq. (30).

In designing a treatment process, the value of β_0 can be calculated utilizing the expression Eq. (9) and filling in experimental data. Once β_0 is determined, filling it in the Coagulation and Sedimentation Function Eq. (30) results in a description of the coagulation and sedimentation processes which can be usefully applied to equipment design.

Reference

Filbet, F., & Laurenзot, P. (2004). Numerical simulation of the Smoluchowski coagulation equation. *SIAM J. Sci. Comput., 25*(6), 2004–2048. http://dx.doi.org/10.1016/j.nonrwa.2005.12.001

Kelkar, A. V., Dong, J., Franses, E. I., & Corti, D. S. (2013). New models and predictions for Brownian coagulation of non-interacting spheres. *J. Colloid Interface Sci., 389*, 188–198. http://dx.doi.org/10.1016/j.jcis.2012.08.037

Kolodko, A., Sabelfeld, K., & Wagnerb, W. (1999). A stochastic method for solving Smoluchowski's coagulation equation. *Math. Comput. Simul., 49*, 57–79. http://dx.doi.org/10.1016/S0378-4754(99)00008-7

Kostoglou, M. (2005). On the constant kernel Smoluchowski equation: fast algorithm for solution with arbitrary initial conditions. *Comput. Phys. Commun., 173*, 34–40. http://dx.doi.org/10.1016/j.cpc.2005.07.004

Moseley, J. L. (2007). The discrete agglomeration model with a time-varying kernel. *Nonlinear Anal. RWA 8*, 405–423. http://dx.doi.org/10.1016/j.nonrwa.2005.12.001

Qamar, S., & Warnecke, G. (2007). Solving population balance equations for two-component aggregation by a finite volume scheme. *Chem. Eng. Sci., 62*, 679–693. http://dx.doi.org/10.1016/j.ces.2006.10.001

Sauer, S., & Lowen, H. (1996). Theory of coagulation in charged colloidal suspensions. *J. Phys.: Condens. Matter, 8*, 803–808. http://dx.doi.org/10.1088/0953-8984/8/50/005

Smoluchowski, M. V. (1916). Versuch einer mathematischen Theorie der Koagulationskinetik kolloider Losungen. *Z. Phys. Chem., 92*, 129–168.

Struckmeier, J. (2005). A deterministic scheme for Smoluchowski's coagulation equation based on binary grid refinement. *Numer. Algor., 40*, 233–249. http://dx.doi.org/10.1007/s11075-005-4186-3

Yəldərəm, A., & Kocëak, H. (2011). Series solution of the Smoluchowski's coagulation equation. *J. King Saud Univ. Sci., 23*, 183–189. http://dx.doi.org/10.1016/j.jksus.2010.07.007

Zueva, S. B., Ostrikov, A. N., Ilyina, N. M., De Michelis, I., & Vegliò, F. (2013). Coagulation Processes for Treatment of Waste Water from Meat Industry. *Int. J. Waste Resources, 3*(2). http://dx.doi.org/10.4172/2252-5211.1000130

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