

REGINA WARDZYŃSKA (ORCID: 0000-0002-6110-3412)¹

THE INFLUENCE OF COAGULANT/FLOCCULANT PARTICLE SIZE AND MASS ON THE KINETICS OF COAGULATION PROCESS. COMPUTER SIMULATION. THE APPLICABILITY OF THE SMOLUCHOWSKI–MÜLLER THEORY

Chemical coagulation is a crucial process in water treatment, hence the need for research on its optimization and increasing efficiency. This study explores coagulant/flocculant particle size, mass, and density's impact on coagulation kinetics. The study employed a computer program that simulates the perikinetic coagulation processes. The simulation's reliability was confirmed based on the classical Smoluchowski–Müller equations. Destabilization kinetics of the simulated sol revealed linear relationships. The coagulation rate adhered to both first-order ($R^2 = 0.97$) and second-order kinetics ($R^2 = 0.98$). Coagulant/flocculant particle size, mass, and density significantly influenced coagulation kinetics and efficiency. A tenfold increase in coagulant radius led to a fourfold rate increase.

1. INTRODUCTION

Contemporary challenges related to the protection and optimal utilization of water resources are driving researchers to seek effective methods for water and wastewater treatment [1–3]. Chemical coagulation is a process that plays a pivotal role in water and wastewater treatment by removing suspended and dissolved pollutants such as solid particles, colloids, organic substances, and heavy metals. This process is widely employed in both municipal wastewater treatment plants and the treatment of drinking, industrial, and recreational water [4, 5]. Chemical coagulation is a complex process – immediately after the addition of a coagulant, chemical and physical reactions occur, that lead to the destabilization of the system. The destabilization is caused by the ions and colloidal hydroxides – hydrolysis products of the coagulants. The coagulant ions

¹University of Warmia and Mazury in Olsztyn, Department of Chemistry, Plac Łódzki 4, 10-957 Olsztyn, Poland, email address: hannawar@uwm.edu.pl

neutralize the surface charge and promote the compression of the double layer of colloidal particles. In turn, colloidal hydroxides destabilize the system by either attaching to colloids of opposite charge or by adsorbing pollutants onto their surface [6]. The second phase of the coagulation process is flocculation, in which destabilized particles come together to form larger aggregates. The flocculation process can occur through one of two mechanisms: rapid, perikinetic flocculation, or orthokinetic flocculation. In perikinetic flocculation, the collisions of destabilized particles are primarily induced by Brownian motion, while in orthokinetic flocculation, particle collisions are influenced by external factors. Coagulation is a kinetic process that can occur at varying rates. The overall efficiency of the coagulation process and the structure of the resulting post-coagulation floc aggregates depend largely on the speed at which aggregation, flocculation, and sedimentation take place. The kinetics of the coagulation process is influenced by numerous chemical and physical factors such as the concentration and type of pollutants present in the water or wastewater being treated, pH, temperature, the type, and dosage of the coagulant/flocculant used, as well as the mixing time and speed, among many others. These parameters are interconnected, and their impact on coagulation kinetics can be complex. Therefore, achieving high efficiency in the coagulation process requires considering and optimizing many of these factors [7, 8].

Several theories attempt to explain the kinetics of the coagulation process. One of them is the theory developed by Smoluchowski [9] and Müller [10] in the early 20th century, which pertains to fast coagulation. Smoluchowski [10] assumes that colloidal particles are spherical, and their movement is governed by Brownian motion, where each collision leads to aggregation. Aggregates of two, three, four, and n particles are formed in the aggregation process. Aggregates with a sufficiently large number of particles undergo sedimentation. The probability of particle collision depends on the initial sol concentration, the diffusion coefficient, and the initial velocity of the particle, measured by the so-called ‘displacement in Brownian motion. Smoluchowski’s mathematical model describes the rate of change in the number of particles, and in simple cases, these reactions can be described by differential equations. Smoluchowski’s theory describes the simplest colloidal systems with spherical particles of the same size. In most cases, however, we deal with more complex colloidal systems composed of particles of different sizes. Müller extended Smoluchowski’s theory to polydisperse systems, claiming that large particles influence small ones and that small particles tend to settle on larger ones, acting as condensation centers.

Research on the kinetics of chemical coagulation according to Smoluchowski–Müller theory leads to an understanding of essential aspects of the coagulation process, such as the influence of particle concentration and size on the rate of coagulation. The kinetics of chemical coagulation form the foundation for understanding intermolecular reactions and aggregation processes in colloidal systems. This theory provides tools for analyzing and predicting the rate of changes in suspended particle systems, which is of significant importance in the context of water purification processes and the field of

colloid physical chemistry. Modern mathematical and numerical tools allow modeling and simulating coagulation processes in line with the Smoluchowski–Müller theory. These models enable the prediction of particle behavior in a solution and the forecasting of agglomerate formation rates depending on various process parameters. These simulations are crucial in the design and optimization of water treatment processes and in other applications where coagulation plays a key role. The results of computer simulations can contribute to the development of fundamental databases, and due to certain practical implications and conclusions, they can significantly aid or even serve as an alternative to experimental research [11–13]. In recent times, there has been a steady increase in interest in using computer simulations in wastewater treatment technology. In many countries, simulation programs have become standard tools for designers and employees of modern wastewater treatment plants, and the results of such research and measurements are becoming increasingly useful in practice [14–16].

The kinetics of the coagulation process, which is a crucial part of water and wastewater treatment processes, is closely related to the characteristics of the coagulants and flocculants used. The choice of the appropriate coagulant depends on its ability to destabilize the targeted pollutants and ensure the formation of durable, stable, and poorly soluble flocs that are prone to sedimentation. As previously mentioned, the destabilizing role of coagulants/flocculants involves reducing the electrokinetic potential of colloids (suspensions) and facilitating particle aggregation, whether through bridging, crosslinking, or acting as a weight to the forming flocs, where their mass and size play a significant role. Research on the modification of existing coagulants or the search for new, often natural coagulants/flocculants is ongoing [17–22]. Therefore, this work aimed to determine the influence of the particle size, mass, and density of coagulant/flocculant on the kinetics of the coagulation process. Understanding this influence is crucial for optimizing purification processes and advancing technologies related to water and wastewater treatment.

2. METHODS

2.1. DESCRIPTION OF THE SIMULATION MODEL

The computer program ZB2 was used for the research, simulating the coagulation process following the Smoluchowski–Müller theory. This program has been developed based on extensive research conducted on coagulation and electrocoagulation processes in both natural and model wastewaters. The ZB2 simulation program is a stochastic-dynamic model, operating with random variables, and the system's state changes over simulated time. At its core, the program includes a module that solves the motion equations for a specified number of material points (particles) within a closed container. The initial positions of particles are generated randomly, following a uniform distribution

within the tank's area. There are two types of spherical particles present, which can represent coagulant/flocculant particles and sol particles. These particles can vary in size, mass, density, and initial velocity. The particles move through Brownian motion, a random motion resulting from collisions with solvent molecules. The program calculates the trajectory for each particle independently, with their movement direction determined by a RANDOM function. The angle of reflection of a particle from the vessel's wall is always equal to the angle of incidence. The program simulates fast perikinetic coagulation, where each collision between a coagulant/flocculant particle and a sol particle results in an irreversible aggregation. In the event of two particles colliding with different velocities, they merge, and the direction and velocity of the resulting cluster are calculated vectorially. The sedimentation rate increases with the growing number of sol particles within the cluster. To simulate friction between the particles and the fluid, the velocity of the floc is reduced by 0.1% per unit of displacement towards the surface.

The initial model parameters are as follows²:

- N_s – number of sol particles (1000)
- N_c – number of coagulant/flocculant particles (100)
- r_s – sol particle radius (2 nm)
- r_c – coagulant particle radius (1–10 nm)
- V_s – initial velocity of A sol particle (100 cm/s)
- V_c – initial velocity of A coagulant particle, (100 cm/s); each particle is given an initial velocity V randomly, and $V_s = 100$ cm/s means that all particles have velocities within the range of 1–100 cm/s
- F – sedimentation coefficient (0.2); it is a systemic parameter specifying the range of settling values assumed by a cluster
- E – coagulation threshold (10) when a floc/aggregate composed of a specified number of sol particles reaches a certain size, defined as the coagulation threshold E , it undergoes sedimentation and exits the system. $E = 10$ means that a floc undergoing sedimentation is composed of 1 coagulant/flocculant particle and 10 sol particles
- m_c/m_s – the ratio of the mass of a coagulant particle to the mass of a sol particle (0.125, 1, 2, 3, 3.4, 4, 8, 15.6, 27, 42.9, 64, 91, 125; ($m_c/m_s =$ depends on the size and density of the coagulant and sol particles

The mass of the particle is calculated as $m = dV_{\text{vol}}$, where: d is density, g/cm³, V – volume of a sphere, cm³. Both coagulant and sol particles have a spherical shape, thus $V = (4/3)\pi r^3$, hence

²Assumed values of constant parameters are given in parantheses.

$$\frac{m_c}{m_s} = \frac{\frac{4}{3}\pi r_c^3 d_c}{\frac{4}{3}\pi r_s^3 d_s} = \frac{r_c^3 d_c}{r_s^3 d_s} \quad (1)$$

where: d_c = density of the coagulant (g/cm^3), d_s = density of the sol (g/cm^3), r_c = coagulant radius (nm) r_s = sol radius (nm).

In most cases, the simulated initial parameters correspond to conditions in wastewater treatment plants or typical laboratory jar-test experiments. The simulations were repeated five times, and the highest and lowest values were discarded. The arithmetic mean value was calculated from the remaining three values. Standard deviations were typically plotted on the corresponding plots.

2.2. VERIFICATION OF THE COMPUTER PROGRAM SIMULATING COAGULATION PROCESSES

The verification of the simulation program was carried out over a wide range of output parameters. To verify the database of measurement data, classical, fundamental mathematical relationships derived from the Smoluchowski and Müller theories were applied, including empirical equations. For the verification of the simulation program, the Smoluchowski equation was used, allowing the calculation of the number of particles n_t in the system after a time t :

$$n_t = \frac{n_0}{1 + \frac{t}{t_{1/2}}} \quad (2)$$

where n_0 is the initial number of particles, $t_{1/2}$ – half-life of particles.

Considering that the simulated coagulation system used in this study involves particles of various sizes, the program's performance was also verified using Müller's equation [10], which extends the Smoluchowski theory [9] to polydisperse systems

$$N_t + n_t = \frac{N_0}{1 + \frac{t}{T_{N_0}}} \left(1 + \frac{\lambda}{(\lambda N_n + 1) \left(1 + \frac{t}{T_{N_0}} \right)^{\lambda-1}} \right) \quad (3)$$

where N_0 is the initial number of large particles, n_0 – the initial number of small particles, N_t and n_t – the corresponding number of particles after time t , T_{N_0} – the half-life time of large particles, where

$$\lambda = \frac{V_r^2 + 1}{2V_r}, \quad V_r = \frac{R_p}{r_p}$$

R_p is the radius of large particles, r_p – radius of small particles, and $V_n = N_0/n_0$.

Table 1

Actual number of particles in a simulated system compared to the number of particles calculated based on the Smoluchowski and Müller equations [9, 10]

Actual number of particles	Smoluchowski equation			Müller equation		
	n_t	Δ [%]	Δ_{av} [%]	N_t	Δ [%]	Δ_{av} [%]
$N_c = 100, N_s = 1000, F = 0.2, m_c/m_s = 1, E = 10, r_c = 1, r_s = 2$						
990	982	0.8	2.6	968	2.2	3.4
880	860	2.3		850	3.4	
770	720	6.4		735	4.5	
660	640	3.0		625	5.3	
550	548	0.4		524	4.7	
440	430	2.7		440	0	
$N_c = 50, N_s = 1000, F = 0.2, m_c/m_s = 1, E = 10, r_c = 10, r_s = 2$						
990	968	2.2	3.1	980	1.0	1.5
880	860	3.4		870	1.1	
770	752	2.3		765	0.6	
660	650	1.5		652	1.2	
550	530	3.6		535	2.7	
440	416	5.5		430	2.3	
$N_c = 100, N_s = 1000, F = 0.2, m_c/m_s = 0.125, E = 10, r_c = 2, r_s = 2$						
990	974	1.6	2.3	964	2.6	2.6
880	868	1.4		870	1.1	
770	740	3.9		735	4.5	
660	650	1.5		645	2.3	
550	545	0.9		540	1.8	
440	420	4.5		425	3.4	
$N_c = 100, N_s = 1000, F = 0.2, m_c/m_s = 125, E = 10, r_c = 10, r_s = 2$						
990	955	3.5	4.2	960	3.0	3.4
880	842	4.3		850	3.4	
770	725	5.8		738	4.2	
660	629	4.7		635	3.8	
550	530	3.6		535	2.7	
440	425	3.4		427	3.0	

n_t – number of particles, Δ – deviation parameter, Δ_{av} – average deviation parameter.

In Table 1, the number of particles in the system at time t was calculated using the Smoluchowski and Müller equations and compared with the actual number of particles

remaining in the simulated system at time t . In each case, the theoretically calculated number of particles from the Smoluchowski and Müller equations differed from the number of particles in the simulation system at time t , typically with a deviation of a few percent. The table shows only sample results. In general, deviations Δ between theoretically calculated numbers and real values (for a wide range of output parameters) were in the range of 0–8.4%. This could indicate the correctness of the functioning of the tested simulation program.

3. DISCUSSION AND RESULTS

3.1. THE ORDER OF THE SIMULATED COAGULATION PROCESS IN A POLYDISPERSE SOL

To determine the order of the simulated coagulation process in a polydisperse sol, a graphical method was used by converting the classical kinetic equations for first-order reactions $\ln c = f(t)$ and second-order reactions $1/c = f(t)$ into the respective forms $t = f(\ln(1/N_s))$ and $t = f(1/N_s)$.

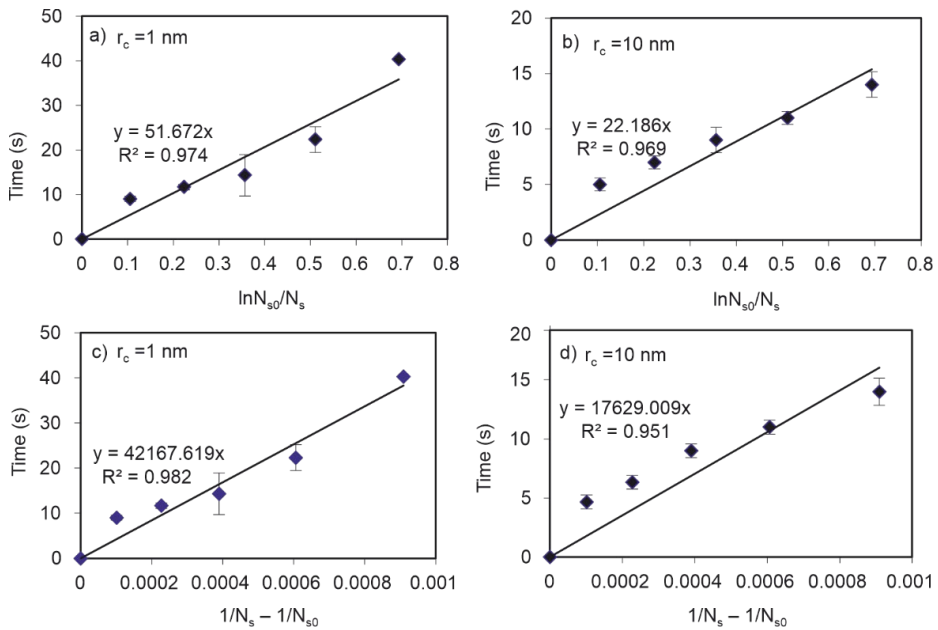


Fig. 1. Dependences $t = f(\ln(1/N_s))$ (a, b) and $t = f(1/N_s)$ (c, d) for the simulated coagulation process with coagulant sizes r_c of 1 nm and 10 nm

In Figure 1, linear relationships are shown for $t = f(1/N_s)$ and $t = f(\ln(1/N_s))$ for simulated systems in which the coagulant/flocculant particle radii change, specifically,

$r_c = 1$ nm (Figs. 1a, b) and $r_c = 10$ nm (Figs. 1c, d). As the coagulant particle radius increases, its mass also increases, and the density of the coagulant approaches the sol density, $d_c = d_s$. Other parameters of the simulation system are constant and equal to sol particle radius $r_s = 2$ nm sol particle number $N_s = 1000$, coagulant/flocculant particle number $N_c = 100$. The initial velocity of the sol and coagulant particles are equal, $V_s = V_k = 100$ cm/s. The coefficients of determination R^2 for eight linear regressions (Figs. 1, 2) ranged in the high values regime of 0.951–0.982.

Table 2

R^2 values for $t = f(\ln(1/N_s))$ and $t = f(1/N_s)$ in simulation systems at increasing size and mass of coagulants/flocculants

r_c	m_c/m_s	R^2 for $\ln(1/N_s)$	R^2 for $1/N_s$
		R^2	R^2
1	0.125	0.983	0.990
2	1	0.963	0.973
3	3.4	0.958	0.989
4	8	0.959	0.977
5	15.6	0.977	0.982
6	27	0.982	0.990
7	42.9	0.989	0.992
8	64	0.989	0.993
9	91.1	0.984	0.982
10	125	0.980	0.987
		Mean $R^2 = 0.976$	Mean $R^2 = 0.986$

In Tables 2 and 3, all values of the coefficients of determination for the compared pairs of general relationships $t = f(\ln(1/N_s))$ and $t = f(1/N_s)$ are presented. The calculated coefficients of determination (R^2) relate to various simulated coagulation systems. Table 2 shows R^2 values for systems in which the coagulant/flocculant particle sizes were increased from 1 to 10 nm, assuming a constant density of coagulant particles. As the coagulant particle sizes increased, their masses also increased, increasing the mass ratio of coagulant to sol particles (m_c/m_s) from 0.125 to 125.

Table 3 lists the R^2 values obtained for simulated coagulation systems in which the mass ratio of coagulant particles to sol particles remained constant ($m_c/m_s = 1$). In these cases, as the coagulant size increased, its density decreased. The conducted studies on the kinetics of destabilization of the simulated suspension showed that the relationships $t = f(\ln(1/N_s))$ and $t = f(1/N_s)$ had a linear character with a high coefficient of determination. The average value of R^2 for $t = f(\ln(1/N_s))$ (for all tested simulation systems) was 0.97, which was slightly lower than the average R^2 for $t = f(1/N_s)$, which was 0.98. Therefore, the coagulation process rate in the range described in the simulated system satisfied both first-order kinetic equations and second-order kinetic equations, with a slight predominance for the second-order kinetic equation.

Table 3

R^2 values for $t = f(\ln 1/N_s)$ and $t = f(1/N_s)$
in simulation systems at increasing coagulant/flocculant particle size

R^2 for $\ln 1/N_s$		R^2 for $1/N_s$	
r_c	R^2	r_c	R^2
	$m_c/m_s = 1$		$m_c/m_s = 1$
1	0.974	1	0.982
2	0.963	2	0.973
3	0.952	3	0.971
4	0.966	4	0.979
5	0.976	5	0.988
6	0.962	6	0.977
7	0.968	7	0.971
8	0.977	8	0.960
9	0.982	9	0.965
10	0.969	10	0.941
Mean $R^2 = 0.969$		Mean $R^2 = 0.971$	

Similar results were obtained by Igwegbe et al. [23] who performed studies on the removal of total dissolved solids from aquaculture wastewater. In their paper, the coagulation-flocculation regression coefficients were determined to be $R^2 = 0.93$ for the first-order reaction and $R^2 = 0.98$ for second-order reaction. Mageshkumar et al. [24], while studying the kinetics of the coagulation process for removing turbidity from wastewater in the leather tanning industry, concluded that it proceeds according to second-order kinetics. Similarly, a study done by Iloamaeke et al. [25] on color removal through coagulation-flocculation by using bio-coagulants suggests a second-order kinematic process.

3.2. THE EFFECT OF SIZE, MASS, AND DENSITY OF COAGULANT/FLOCCULANT PARTICLES ON THE COAGULATION RATE

The reaction rate constants (k) shown in Fig. 2 were obtained in simulated coagulation systems in which the radius r_c of the coagulant/flocculant particle was varied from 1 to 10 nm, while the radius of the colloidal particles remained constant at $r_s = 2$ nm. The ratio of the mass of the coagulant particle to the mass of the colloidal particle was constant at $m_c/m_s = 1$, meaning that the density of the coagulant/flocculant particle decreased with increasing particle size ($d_c < d_s$).

With an increase in the radius of the coagulant/flocculant particle, the reaction rate (k) increased. However, for particles with a radius ranging from $r_c = 1$ nm to $r_c = 5$ nm, this effect was relatively small. A significant impact of the coagulant/flocculant particle size on the reaction rate constant was observed for particles with $r_c > 5$ nm, which means

a radius 2.5 times greater than that of the colloidal particle. A tenfold increase in the coagulant particle's radius from $r_c = 1$ nm to $r_c = 10$ nm resulted in an almost twofold increase in the rate constant, from $k = 2.37E-05$ s⁻¹ to $k = 5.63E-05$ s⁻¹.

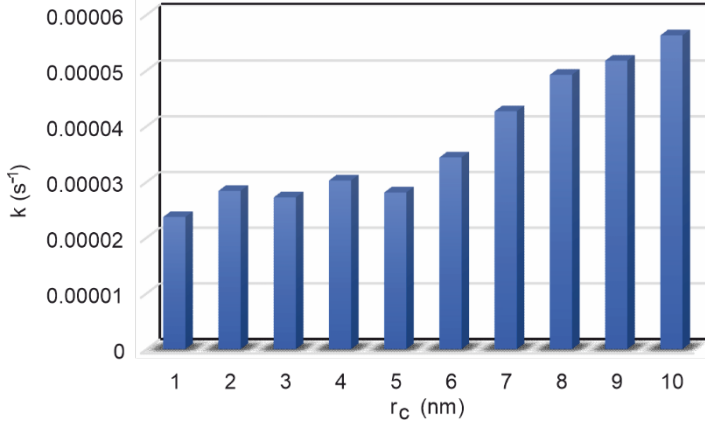


Fig. 2. The effect of coagulant/flocculant particle size on the coagulation rate constants

According to the theory of fast coagulation kinetics [9], the probability of collision between two particles of the same radius can be determined by the following formula:

$$k = 4\pi AD \quad (4)$$

where A is the radius of attraction, nm, and D is the diffusion coefficient, m²·s⁻¹.

Attraction radius A is approximately equal to particle diameter

$$A = 2r \quad (5)$$

By substituting $A = 2r$ into Eq. (4) and inserting the diffusion coefficient D from Einstein's equation

$$D = \frac{RT}{N} \times \frac{1}{6\pi\eta r} \quad (6)$$

where R is the gas constant, J·mol⁻¹·K⁻¹, T – absolute temperature, K, N – Avogadro's number, η – viscosity, Pa·s, we finally arrive at:

$$k = 8\pi r \left(\frac{RT}{N} \times \frac{1}{6\pi\eta r} \right) = \frac{4RT}{3N\eta} \quad (7)$$

In this equation, the particle radius is not present, which means that for a monodisperse system, the coagulation rate does not depend on the particle size. In the conducted simulation, particles of a constant radius $r_s = 2$ nm were present alongside coagulant/flocculant particles with a radius r_c ranging from 1 to 10 nm. The monodisperse system became polydisperse. When using coagulants with $r_c = 1-5$ nm, the system behaved like a monodisperse one, and the rate constant (k) remained at a similar level Fig. 2. Only a 3–5-fold increase in the coagulant/flocculant particle size relative to the sol particle size had a significant impact on the coagulation rate constant. According to Müller's theory, an extended version of the Smoluchowski theory for polydisperse systems, the probability of collision between two particles of different sizes is greater than that between particles of the same size. The effective attraction radii are equal to the sum of the radii of the larger and smaller particles:

$$A = r_1 + r_2 \quad (8)$$

Therefore,

$$K_1 = 2\pi(r_1 + r_2)(D_1 + D_2) \quad (9)$$

where: K_1 is the probability of collision between two particles of different sizes; D_1, D_2 – diffusion coefficients for particles of radii r_1 and r_2

Substituting Eq. (7) into Eq. (9), we get:

$$K_1 = \frac{RT}{3N\eta} \frac{r_1 + r_2}{r_1 r_2} \quad (10)$$

It follows that the coagulation rate in polydisperse systems depends on the degree of dispersion. An increase in the radius of coagulant/flocculant particles leads to an increase in the radius of the attraction zone, resulting in an increased probability of particle collision and aggregation. Consequently, the reaction rate increased, as observed in the simulated coagulation process.

Figure 3 (series II) illustrates the dependence of the rate constants of the colloidal coagulation on the size and mass of coagulant/flocculant particles. The ratio of the mass of coagulant/flocculant particles to the mass of colloidal particles increased from $m_c/m_s = 0.125$ (with a coagulant/flocculant particle radius of $r_c = 1$ nm) to $m_c/m_s = 125$ (with a coagulant/flocculant particle radius of $r_c = 10$ nm). In this case, the density of the coagulant is equal to the density of the colloidal particles ($d_c = d_s$). For comparison, series I is also presented, where the ratio of the mass of coagulant particles to the mass of colloidal particles remained constant ($m_c/m_s = 1$), meaning that as the size of the coagulant/flocculant particles increased, their density decreased ($d_c < d_s$). In the case where the size and mass of the coagulant particles increased (series I), a tenfold increase in the coagulant particle radius from $r_c = 1$ nm to $r_c = 10$ nm resulted in an over fourfold

increase in the rate constant of the reaction, from $k = 2.27\text{E-}05 \text{ s}^{-1}$ to $k = 8.59\text{E-}05 \text{ s}^{-1}$. Comparing both graphs, it can be observed that for larger particles ($r_c > 5 \text{ nm}$), when the size increased along with the mass of the coagulant/flocculant particles ($d_c = d_s$), the reaction rate (k) was higher than when using a coagulant of the same size but of lower mass ($d_c < d_s$). The particle mass directly affects its sedimentation rate, with heavier particles settling down faster than lighter ones. Different sedimentation rates for particles of varying masses and sizes increase the number of collisions, resulting in acceleration of the coagulation.

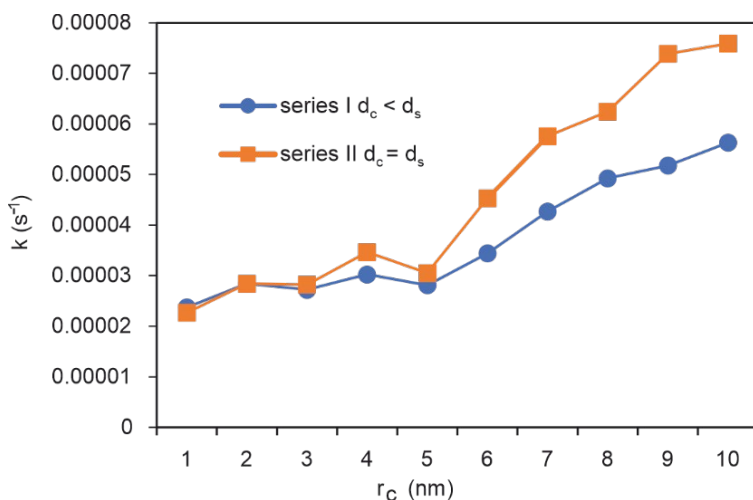


Fig. 3. Dependences of the coagulation rate constants on the coagulant particles size and mass: series I – increasing coagulant/flocculant particle size, series II – increasing coagulant/flocculant particle size and mass

Further research focused on a simulated system in which the density of the coagulant/flocculant was changed while keeping its size constant, investigating the impact on the coagulation rate constant. Initially, the density of the coagulant in the system was equal to the density of the colloidal particles, $d_c/d_s = 1$, and then it was increased ($d_c > d_s$) from 2 to 6, applied to r_c of 2, 4, 6, 8, 10 nm. For coagulant/flocculant particles of a small size ($r_c = 2 \text{ nm}$), increasing density and, therefore, mass did not significantly affect the rate constant of the reaction (Fig. 4). For a coagulant with $r_c = 4 \text{ nm}$, the highest rate constant, $k = 4.51\text{E-}05 \text{ s}^{-1}$ was obtained at its maximum density relative to the density of the colloidal particles, $d_c/d_s = 6$. A similar dependence was not observed for coagulants of larger sizes, where the maximum values of coagulation constants were achieved at different coagulant densities. Specifically, the highest rate constant, $k = 9.09\text{E-}05 \text{ s}^{-1}$ was obtained for a coagulant with $r_c = 10 \text{ nm}$ at a density of $d_c/d_s = 2$. Further increase in density did not improve efficiency but, on the contrary, reduced the reaction rate.

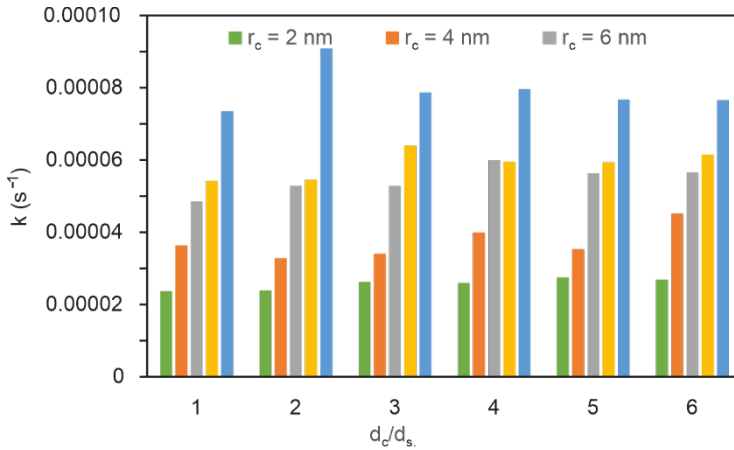


Fig. 4. Dependences of the density and coagulant mass (at constant size) on the coagulation rate constant

Thus, there exists an optimal point beyond which increasing the mass and density of the coagulant/flocculant does not lead to further acceleration of the coagulation process. Particles with excessively high density and mass, which are hard and compact, likely underwent too rapid sedimentation and had limited penetration capacity into the solution, making it challenging for them to effectively interact with pollutant particles.

3.3. INFLUENCE OF SIZE AND MASS OF THE COAGULANT ON THE INITIAL COAGULATION AND TRANSITION HALF-LIFE

An important phase in the coagulation-flocculation process is the so-called initial coagulation, during which there are no visible changes, such as turbidity. Another significant value for the kinetics of the coagulation process is the half-life, during which the number of all colloidal particles in the system decreases by half compared to the initial value. Figure 5 illustrates the dependence of the time required to destabilize 10% (Fig. 5a) and 50% (Fig. 5b) of the system on the size and mass of the coagulant/flocculant particles. Each time the particle radius increases, regardless of whether its mass increased ($d_c = d_s$) or remained constant ($d_c < d_s$), the time needed to destabilize the system decreases. The maximum fit of the obtained results, with $R^2 > 0.95$ was achieved for an exponential relationship represented by $y = a \exp(bx)$ (Fig. 5). The values of the coefficient b fall within a relatively narrow range from -0.106 to -0.113 , and -0.143 to -0.149 . This may indicate that this parameter is independent of the degree of system destabilization, as well as the size, mass, and density of the coagulant/flocculant used in the studied system. The changes in the curve profiles are attributed to the parameter a , which, for 50% destabilization, equals 49 and is 5 times larger than the value for 10% destabilization ($a = 9$).

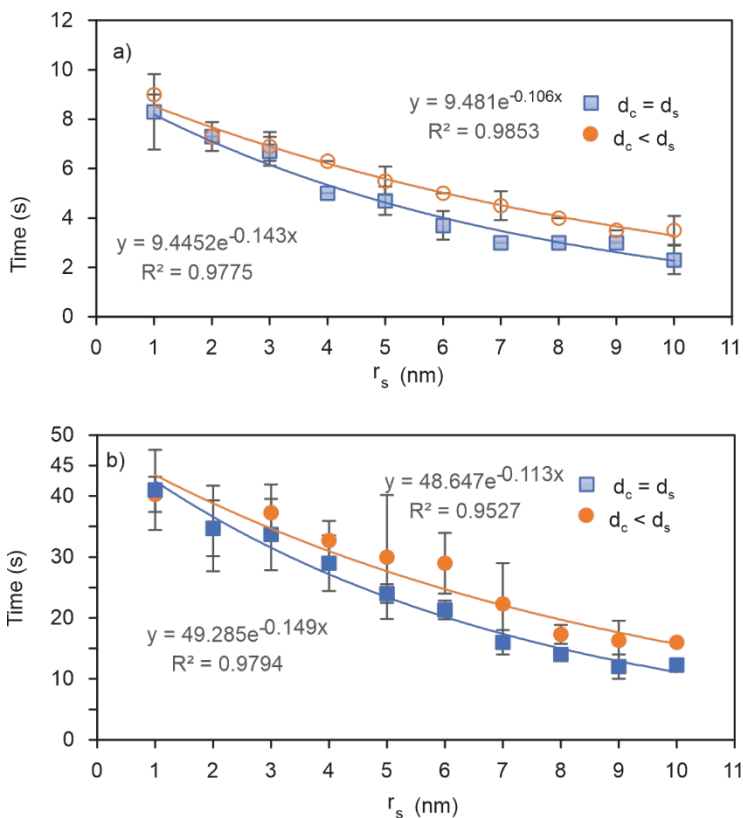


Fig. 5. The time necessary for destabilisation of: a) 10% of the system particles, b) 50% of the system particles depending on the size and mass of the coagulant

This suggests that the particle size, mass, and density of the coagulant have a minimal effect on the initial coagulation rate, which is consistent with Smoluchowski's theory [9] that during rapid coagulation, its rate constant does not depend on the size of aggregates. It seems that this assumption holds during the initial phase of coagulation.

4. SUMMARY AND CONCLUSION

The obtained results of the kinetic studies of the simulated coagulation process were tested against the classical Smoluchowski–Müller equations and exhibited high compatibility. The rate of the simulated coagulation process, where the size, mass, and density of the coagulant/flocculant were varied, satisfied both first-order ($R^2 = 0.97$) and second-order kinetic equations ($R^2 = 0.98$). The relationships $1/N(t)$ and $\ln 1/N(t)$ had linear characteristics supported by a high coefficient of determination (R^2).

The particle size, mass, and density of the coagulant/flocculant have a significant impact on the kinetics and efficiency of the coagulation process. An increase in the size of the coagulant/flocculant particles within the studied range resulted in an increase in the coagulation process rate expressed as an increase in the rate constant of the reaction. A tenfold increase in the radius of coagulant/flocculant particles with decreasing density led to a twofold increase in the rate constant of the process. When the radius increased along with the mass (with density remaining constant), a tenfold increase in the radius resulted in an almost fourfold increase in the coagulation rate. Coagulant/flocculant particles with larger size and mass showed a tendency to settle faster onto the pollutant particles, which accelerated the coagulation process. However, the research indicated that there is an optimal point beyond which increasing the mass of the coagulant/flocculant does not further accelerate the coagulation process. For particles with small sizes, an increase in density and mass did not significantly alter the rate constant of the reaction.

The size of the coagulant particles, their mass, and density (within the tested range) had a minor effect on the initial coagulation rate. In contrast, a clear influence of the coagulant/flocculant particle size and mass was observed for the half-life of coagulation. The influence of the coagulant/flocculant particle size and mass on the coagulation process kinetics is related to the mechanism of interaction between pollutant particles and coagulant/flocculant particles. Coagulant/flocculant particles must have the appropriate size, mass, and density to efficiently interact with pollutant particles.

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