



Assessment of particle size distribution for polyaluminum chloride-based coagulation–flocculation processes

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ABSTRACT

A particle counter is a very useful tool to analyse the hydrolysis and particles agglomeration processes after coagulant dosing and hence provides important data to state the optimum flocculation time and the type and dose of commercial PACl (polyaluminum chlorides) which differ in basic parameters (basicity, degree of Al polymerization of aluminum hydroxocomplexes). The aim of the research was to determine the influence of coagulant properties and process conditions on the size of particles formed during coagulation/flocculation and their distribution, which determines the subsequent course of separation of flocs. The paper presents the results of the particle size distribution changes during flocculation at different pH values. The most effective agglomeration of hydrolysis products was noted for PACl3 which is characterized by the highest share of monomeric Al species. The share of Al monomers in coagulant was decisive for floc size distribution. At the pH 7.9 resulting flocs were larger and more eager to agglomerate in relation to the pH 6.8 although there was no effective reduction in the number of fine particles. At the higher pH coagulant overdosing was observed, manifesting as the increase of particles smaller than 5 µm along with the flocculation time. It was the most noticeable for the high-polymerized PACl2. Such particles are susceptible to removal only in sweep coagulation under optimal technological conditions.

Keywords: Particle size distribution; Polyaluminum chlorides; Flocculation analysis; Al speciation

1. Introduction

In recent years, in place of hydrolysing coagulants, polyaluminum chlorides are more and more often applied. They are more effective and less sensitive to fluctuations in water pH and temperature. Due to the high positive surface charge of hydrolysis products, they have a great ability to neutralize negatively charged contaminants present in the treated water.

Along with the increase in coagulant basicity, the pH at which the precipitated forms are characterized by the lowest solubility, increases. The minimum solubility of aluminum

hydroxide formed during PACl hydrolysis occurs at a higher pH compared to aluminum sulfate. Therefore, in the acidic pH, the hydrolysis products of coagulants with a significant share of aluminum monomers contain, apart from dissolved aluminum species, also precipitated forms, which structure and properties are characteristic for monomeric forms of aluminum precipitated during the hydrolysis of aluminum sulfate. The structure of aluminum forms precipitated during hydrolysis of pre-hydrolyzed coagulants is different compared to aluminum sulfate. The studies have shown that this structure also contains polymeric forms, in contrast to the precipitated forms formed during the hydrolysis

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of aluminum sulfate, where aluminum is present in monomeric forms. To distinguish the precipitated particles formed during the hydrolysis of aluminum sulfate were assumed to be noted as $\text{Al}(\text{OH})_{3(\text{am})}'$, while for pre-hydrolyzed coagulants $\text{Al}(\text{OH})_{3(\text{am})}^*$. Therefore, not only the presence of Al_{13} polycations, but also the difference in the structure of precipitated aluminum hydroxides is decisive for the greater effectiveness of pre-hydrolyzed coagulants compared to aluminum sulfate [1].

Polyaluminum chlorides contain significant amounts of polycationic pre-hydrolysis products, which are the predominant form of dissolved aluminum at pH of approx. 6.0. The polymeric forms of aluminum are stable, whereas the monomeric forms can undergo transformation. In the case of a high-polymerized coagulant, the pH has no significant influence on the aluminum transformation processes due to the low fraction of aluminum monomers. When the process is carried out with the use of a low-polymerized reagent, monomeric species, regardless of the pH, can undergo conversion to the Al_{13} polycation, but the pH determines the intensity of the process. With increasing the pH, the monomers content decreases rapidly and reaches minimum at neutral pH, and a further increase in the pH causes the re-growth of these forms. These changes are accompanied by changes in the Al_{13} content.

Along with the decrease in the content of aluminum monomers, the proportion of polymer species increases, reaching a maximum at neutral pH, when the lowest content of monomeric forms of aluminum is recorded. The increase in the content of Al monomers at higher pH is accompanied by a decrease in the proportion of polymer forms. The changes in the content of the precipitated forms are like the polymer forms, although the scale of these changes is smaller. According to Wang et al. [2], during coagulation with aluminum sulfate, monomeric forms of aluminum, which are the only forms of aluminum in coagulant, are almost completely transformed into Al_{13} during hydrolysis in the range of 5.5–6.5. With this pH, Al_{13} polymer constituted 80%–90% of the total aluminum, while the precipitated forms were 10%–20%. Above pH 7.0, a significant amount of aluminum tridecamers further precipitated. The results of the research indicate that, under certain conditions, coagulants, which originally contain significant amounts of monomeric species of aluminum, may be even more effective than those with a small proportion. Hence, it indicates a greater ability of aluminum tridecamers produced by monomers transformation, to neutralize pollutants in water than pre-hydrolyzed tridecamers [2–8].

The research of many authors allowed to determine the basic relationships between the occurrence of individual aluminum species and the effectiveness of reducing dissolved organic carbon (DOC), UV_{254} absorbance and water turbidity. It has been shown that the degree of DOC removal depends on the Al_{13} content. On the other hand, the effectiveness of lowering UV_{254} is determined by the presence of Al_{13} and precipitated forms, and the reduction of water turbidity is mainly determined by precipitated aluminum forms. Considering the above dependencies, it is possible to optimize the pH of the coagulation process to obtain the maximum effect of removing turbidity or organic compounds [6,7]. Since the precipitated hydrolysis

products are responsible for the removal of mineral particles from the water, the maximum effect will be obtained in the pH range in which these forms of aluminum are mainly formed, that is, above the pH 7.0, regardless of the degree of polymerization of the coagulant. On the other hand, carrying out the process at a lower pH significantly worsens the obtained results, which results from the change in aluminum speciation. The degree of polymerization of the coagulant is then of great importance. In the case of polyaluminum chlorides containing mainly Al_{13} in the pH range of approx. 6, a clear increase in the turbidity of the treated water is observed resulting from the presence of stable polycationic forms of aluminum, which, although effectively neutralizing impurities causing water turbidity, do not allow the formation of flocs susceptible to sedimentation. Under such conditions, hydrolyzing and low-polymerized coagulants perform much better due to the transformation processes of monomeric aluminum forms into Al_{13} polymer, which rapidly precipitates to aluminum hydroxide. With an appropriate dose of coagulant, the flocs produced then have much better sedimentation capacity, and thus the process of removing impurities causing turbidity is more effective.

DOC removal mechanism is different from that of turbidity. Yan et al. [7] found that the maximum effectiveness is obtained at pH of about 6 and is due to the presence of Al_{13} species. Both the reduction and the increase in the pH above this value resulted in a reduction in the efficiency of removal of organic compounds designated as DOC. Since the effectiveness of the process was determined by aluminum tridecamers, better effects in terms of neutral pH were observed when high-basicity coagulants were used during coagulation. At a slightly acidic pH low-basicity coagulants were more effective in DOC removal. As the monomer content increased, the transformation processes played an increasingly important role in the removal of impurities, hence the higher efficiency of low-polymerized PACl was noted.

The range of optimal pH for the reduction of UV_{254} absorbance varied depending on the type of coagulant and its dose and was wider than during the removal of DOC. The effectiveness of reducing UV_{254} absorbance was higher than that of DOC, which resulted from the greater susceptibility of organic matter, determined as UV_{254} absorbance, to removal in the coagulation process. The studies of Xu et al. [9] show that the use of a hydrolysing coagulant in the acidic pH range changes the properties of flocs in relation to the neutral pH due to the transformation processes of Al monomers to tridecamers. The flocs produced by coagulation based on Al_{13} produced in situ, although larger, they were characterized by lower strength ($\gamma = 0.72$), had a less stable and less compact structure (smaller fractal dimension D_f) than those produced based on pre-hydrolyzed Al_{13} ($\gamma = 0.53$).

Moreover, during coagulation with pre-hydrolyzed coagulants, the structure of flocs strengthened over time, while when using hydrolyzing coagulants, Al transformation processes weakened the structure of flocs. The authors of the research explain the obtained results by changes in the structure of the precipitated flocs. At pH 5.5, when AlCl_3 was applied, Al_{13} species were formed in situ. The main task of these forms was to neutralize the negative charge

of humic acids and/or to complex with these acids. As the Al_{13} - KH complexes were transformed into Al_m - KH complexes, the number of intermolecular bonds decreased, which negatively affected the strength of the flocs and, consequently, their size [9,10].

The study of the floc growth kinetics indicates that hydrolyzing coagulant allows for the formation of flocs of larger sizes than the reagent containing pre-hydrolyzed forms of aluminum. This is due to the different precipitation and flocculation mechanisms of the coagulant hydrolysis products, determined by the size and distribution of the surface charge. It was found that at optimal doses of the coagulant, the flocs formed during $AlCl_3$ coagulation were greater than those generated during coagulation with the use of PACl with a very high content of tridecamers. At the same time, it was noticed that time, in which the flocs reached their maximum size was significantly shorter when a coagulant containing pre-hydrolysis products was used. Extending the flocculation time had a negative effect on the size of the flocs, their gradual disintegration was noted. In the case of $AlCl_3$, after reaching their maximum size, there was no constant downward trend, but the phenomenon of continuous disintegration and re-growth of the flocs was observed. This was because large flocs are more prone to breakdown [3,11].

This paper presents the results of research on the application of particle counter to the analysis of the flocculation process and the selection of the coagulant dose.

2. Scope and methodology of research

2.1. Water quality

The research was carried out on the basis of tap water.

The values of the basic water quality indicators were as follows:

- turbidity: 0.5 NTU,
- total number of particles (0.5–100 μm): 200 cm^{-3} ,
- total organic carbon measured by the spectrophotometric method (TOC): 2.3 $\text{mg}\cdot\text{C}/\text{dm}^3$,
- dissolved organic carbon measured with the spectrophotometric method (DOC): 2.1 $\text{mg}\cdot\text{C}/\text{dm}^3$,
- ultraviolet absorbance UV_{254} – unfiltered samples: 3.2 m^{-1} ,
- ultraviolet absorbance UV_{254} – filtered samples using 0.45 membrane filters: 2.2 m^{-1} ,
- alkalinity: 5.1 meq/dm^3 ,
- pH: 6.8.

2.2. Reagents

Commercial reagents widely available on the market, widely used in water treatment for municipal and industrial purposes, were used in the research. To assess the impact of the properties of these coagulants on the course of coagulation, data obtained from the manufacturers' laboratory for a given coagulant batch were used. The selection of reagents for the study was carried out considering previous results and experience with this type of reagents [14].

Due to the inability to use trade names, three pre-hydrolyzed coagulants were labeled as PACI1, PACI2, PACI3 and their basic characteristics are presented in Table 1.

In addition, considering the previous experience with this type of reagents, suggesting a different mechanism of the coagulation process for PACI1 and PACI3, despite similar value of basicity, the tests were carried out to assess the degree of polymerization of aluminum species using Ferronometry method.

2.3. Al species analysis – Ferron complexation timed spectrophotometry

Table 2 shows aluminum speciation determined according to Ferron complexation timed spectrophotometry. A new Al-Ferron kinetics method was developed to monitor and calculate Al speciation. Al-Ferron complexation timed spectrophotometry is the commonly used method of determining Al speciation, but this new Al-Ferron kinetics calculation method shows different species distributions. The method is based on the complexation reaction of the monomeric forms of aluminum with Ferron (8-hydroxy-7-iodo-5-quinoline-sulfonic acid) with the formation of a complex compound of probable composition $Al(\text{Ferron})_y$, at $\text{pH} = 5.0 \pm 0.2$, which has a maximum absorption at 370 nm. Ferronometry makes it possible to evaluate the amount of aluminum that is bound to the monomeric, oligomeric and polymeric ions on the basis of the different rate of $Al(\text{Ferron})$ complex formation. The higher degree of

Table 1
Characteristics of the tested coagulants

	PACI1	PACI2	PACI3
Specific gravity, g/mL	1.245	1.275	1.350
pH	3.94	4.21	3.5
Al, % wt.	9.32	11.46	12.5
Cl, % wt.	5.53	5.69	9
Basicity, %	85.69	77.81	85.0

Table 2
Al species distribution of coagulants determined by “modified” Ferronometry

Al speciation, %	PACI1	PACI2	PACI3
Al_1^*	12.6	2.3	40.8
Al_2^*	36.7	10.2	59.2
Al_3^*	50.6	87.5	0

* Al_1 – monomeric Al species, the presence of which in the solution is determined in the first 60–70 s of the reaction. In the standard interpretation of the results of Ferronometry they are denoted as Al_a ;

* Al_2 – low polymerized Al species, mainly in the form of dimers and trimers. In the standard interpretation of the Ferronometry they are denoted as Al_{b1} (species that react quickly with Ferron);

* Al_3 – medium and highly polymerized Al species, in the form of tridecamers and oligomers. In the standard interpretation of the Ferronometry, they correspond to the forms of aluminum designated as Al_{b2} (species slowly reacting with Ferron) and Al_c (precipitated Al forms and as colloidal compounds), if the reaction is not completed within 2 h.

polymerization the lower rate of the Ferron reaction with aluminum hydrocomplexes is noted.

So, this method is based on kinetic analysis of the formation of the Ferron-aluminum complex. In standard Ferronometry the fraction of Al designated as Al_r , which reacts with Ferron almost instantaneously (0–2 min), is assumed to include primarily monomeric species. The species that react with Ferron rapidly but slower than Al_a (1–120 min) – Al_p , are thought to include polynuclear Al species of superior quality and possess structures that are fairly stable to further hydrolysis and solution chemistry, resulting in higher coagulation efficiency. The fraction of Al that does not react with the Ferron reagent within 120 min, that is, a non-reactive fraction (Al_i), is assumed to represent colloidal, solid-phase Al. When low-polymerized coagulants are considered, the methodology presented above is reliable, because the content of polymers is so low that reaction with Ferron is completed within 2 h. However, the other research proved that for high-polymerized coagulants, all Al hydroxocomplexes are in a dissolved form, and the reaction of coagulants with Ferron is longer than 2 h and results from the presence of high-polymerized species. Interpretation of the results allowed to divide polymerized species Al_b into two groups: quickly reacting with Ferron (Al_{b1}) and slowly reacting (Al_{b2}) with Ferron [12–14].

2.4. Particles size distribution measurements

The tests were carried out at the pH of 6.8 for all three tested coagulants. For comparison purposes, tests were carried out at pH 7.9 to assess the effect of aluminum species on the size of flocs and their quantity formed during flocculation.

The coagulant was applied into the water samples at a volume to obtain doses of 1, 2, 3 mg·Al/dm³, respectively. The coagulation process was carried out according to the jar test methodology, using a steel reactor instead of standard beakers, the construction of which was adapted to the continuous sampling of samples to the particle counter.

After dosing and rapid mixing at 270 rpm for 10 s, the number of particles was measured along with the flocculation time using the Kamika Instruments IPS LCW analyzer. The particles were measured in two ranges: 0.5–30 μm and 30–100 μm for a period of max 570 s, every 240 s, starting the measurement after 90 s of flocculation. The volume of a single sample taken for analysis ranged from 10 to 20 cm³, depending on the number of particles in the sample.

The measurement method of the particle counter used in the testing is based on the theory of geometric optics and on measuring particles in a parallel beam of light. The analyzed particles moving in the air or liquid cause, due to the phenomenon of scattering, the weakening of the luminous flux received by the photodiode. The magnitude of this attenuation is measured by the amplitude of the electrical signal formed by the electronic system. The pulse amplitude corresponds to the maximum particle size in spherical calibration. After sieve calibration in accordance with the patented Elsieve method (patent no. PL-P205738), the collection of particles can be presented in accordance with the traditional measurement method on mechanical sieves.

The measuring sensors comply with the ISO 13322-2:2006 standard. The measurement solutions used in the device allow for the assessment of spatial changes in particle size during flocculation much better than typical devices operating based on the phenomenon of laser diffraction. An additional advantage of the applied solution is the connection of the coagulation reactor with the probe feeding the sample to the analyzer, which eliminated errors resulting from, for example, the sampling process and the transfer of samples from one device to another device.

3. Discussion

Figs. 1–3 show the course of changes in the size and number of aggregates formed after application of various doses of the tested coagulants to the treated water at pH 6.8. In all cases, after adding the reagent, regardless of the degree of polymerization of the coagulant, a significant increase in the number of particles ranging from 0.5 to 30 μm was observed in relation to the number of these particles in water before the addition of the coagulant (approx. 200 cm⁻³). The presented figures show that it is possible to determine the influence of three parameters on the properties of particles formed during the precipitation process of various aluminum polymer species. These parameters are the reaction time, the coagulant dose and Al speciation (determined according to Ferronometry assay).

Analyzing the influence of precipitation reaction time on the aggregate size in the range of 0.5–30 μm, it was noted that along with the flocculation time the number of particles in that range decreased significantly, regardless of the type of coagulant. After dosing of PAC11, which contained monomeric, low-, medium- and high-polymerized species of aluminum, it was noticed that with the increase of the coagulant dose, the floc size distribution curve shifted to the right (Fig. 1). With increasing PAC11 dose, the size of flocs produced in maximum concentration increased regardless of the flocculation time, while the number of particles in the analysed range decreased with time. In the initial phase of flocculation only small number of particles ranging from 30–100 μm were noted. No flocs rupture during flocculation period was observed, which confirmed by no increase in the number of smaller particles in relation to the shorter flocculation time.

There was a clear tendency that the number of particles decreased with the flocculation time, but the size distribution was strictly dependent on the dose of the coagulant. At the dose of 1 mg·Al/dm³ of PAC11 the highest number of particles, that is, 22,000 cm⁻³ was recorded for particles 1–2 μm in size after 90 s flocculation time, decreasing to 11,000 cm⁻³ in the final stage of flocculation time. At the dose 2 mg·Al/dm³ the highest number of particles was noted for the largest particle size was 4 μm, with the number 32,000 cm⁻³ after 90 s, which decreased at the end of flocculation to 10,000 cm⁻³. At the dose of 3 mg·Al/dm³, the size of flocs, which were the most numerous, increased to 7 μm in comparison to the lower coagulant dose, and their maximum number, that is, 20,000 cm⁻³ was recorded at the beginning of flocculation, and at the end of flocculation it dropped to approx. 5,000 cm⁻³. Along with flocculation time, a decreasing number of particles with a size of 30–50 μm was also

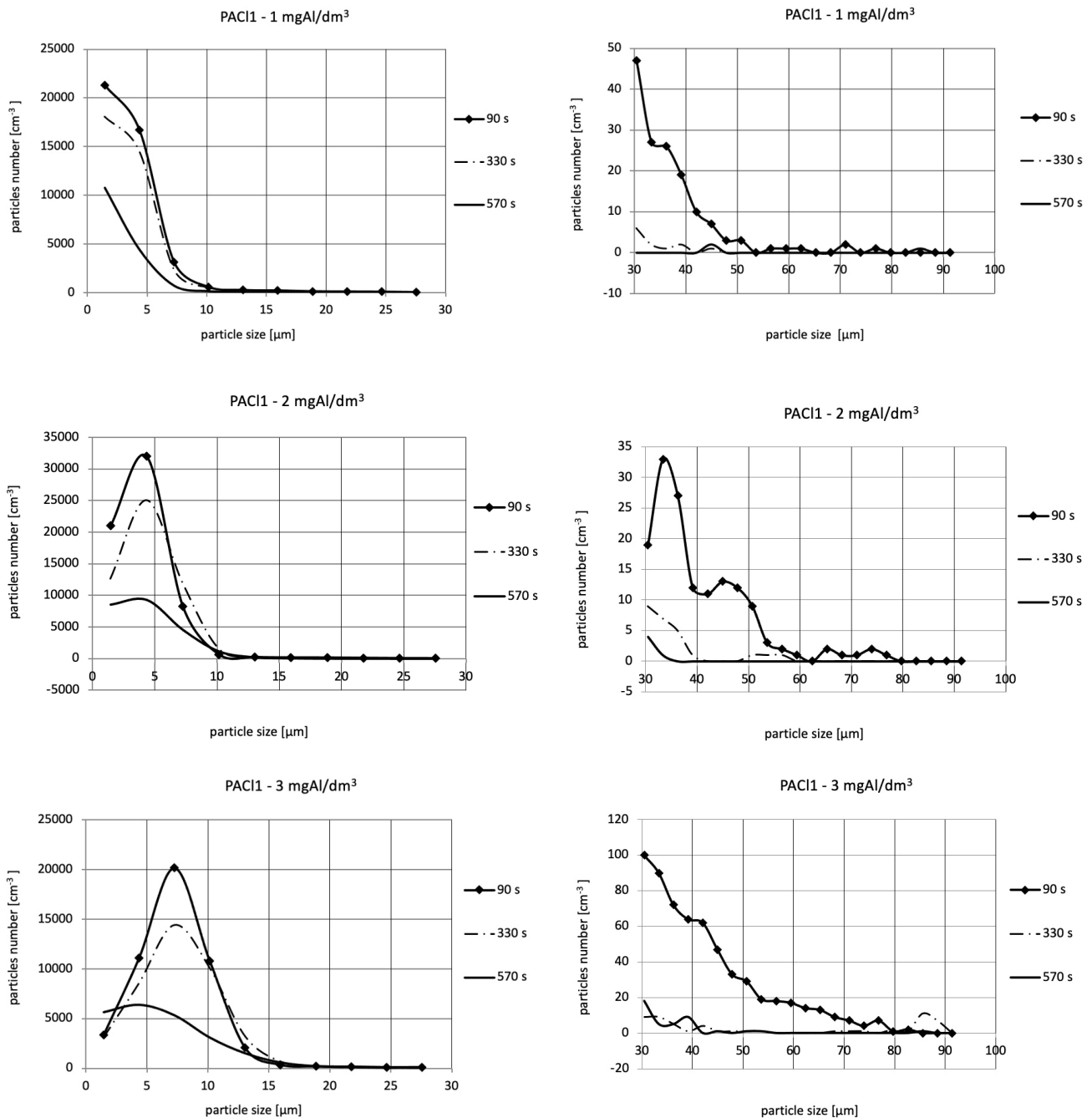


Fig. 1. Particle size distribution along with the flocculation with PACI1 at the doses: 1, 2, 3 mg-Al/dm³, pH 6.8.

observed (Fig. 1) which indicated that the size of produced flocs was outside the measuring range (above 100 μm).

A very similar to PACI1 particle size distribution during flocculation was observed for high-polymerized PACI2. It proves that the share of Al_2 and Al_3 species was decisive for the size of flocs (Figs. 1 and 2).

The test results for PACI3 at the dose of 1 mg-Al/dm³ are shown in Fig. 3. The analysis of changes in the number and size of particles for the three analysed flocculation periods, that is, 90, 330 and 570 s, indicates the lack of effective fine flocs aggregation. The number of the smallest particles

in the range 1–2 μm decreased from 7,000 cm^{-3} after 90 s flocculation to 5,000 cm^{-3} after approx. 10 min. flocculation, but it was not accompanied by an increase in the number of larger size particles that would be prone to sedimentation. Only single particles in the range of 30–60 μm were observed, however, such a small number of these particles prevents their agglomeration. The analysis of the flocculation process showed that the applied dose of the tested coagulant did not allow for effective agglomeration of precipitated particles. The main reason for such difficulties was mainly because the process was analysed for water of very

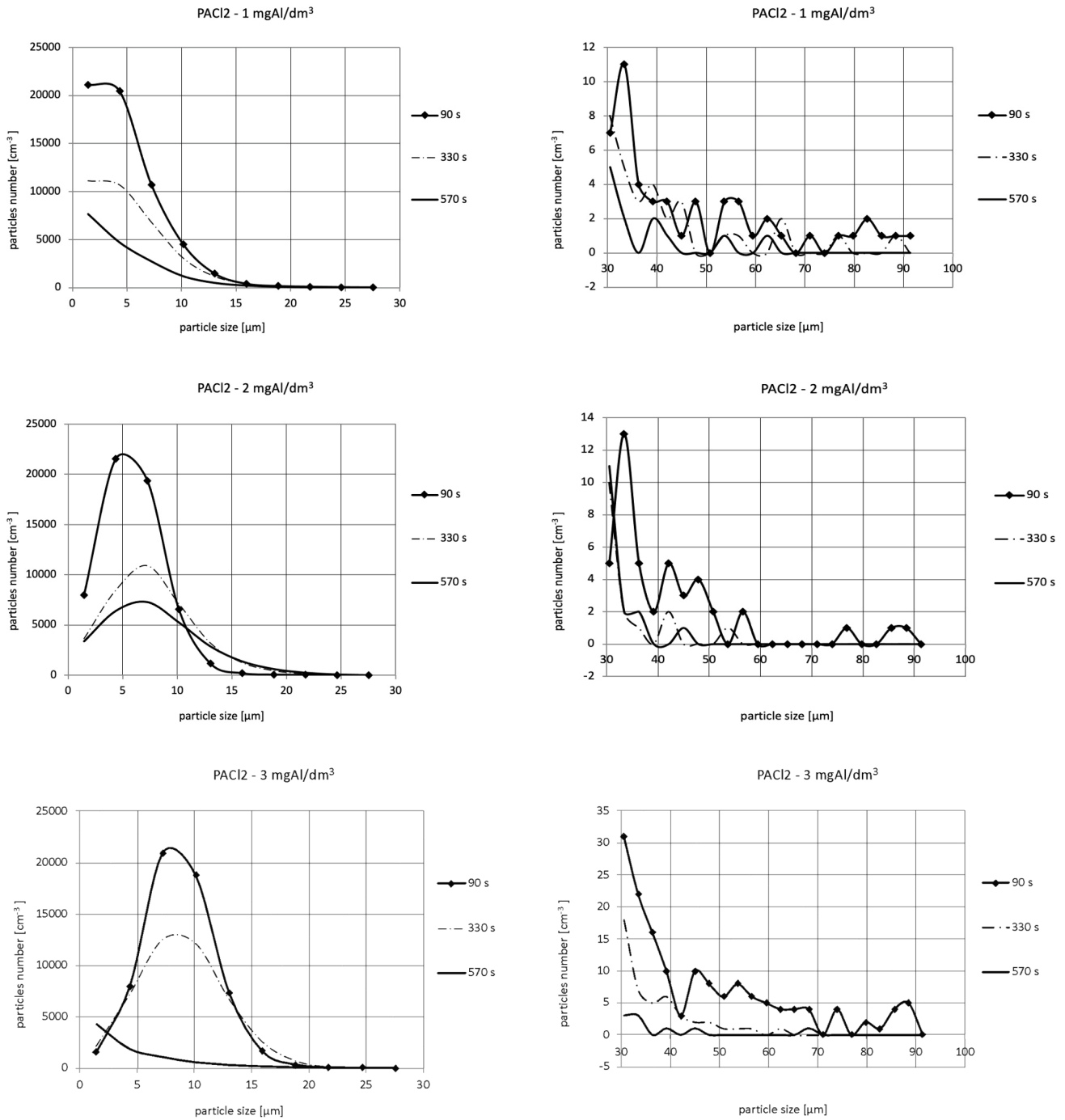


Fig. 2. Particle size distribution along with the flocculation with PACl2 at the doses: 1, 2, 3 mg·Al/dm³, pH 6.8.

low turbidity, that is, unsusceptible to effective flocculation. In such a situation, in practice, flocculants are used, which enable agglomeration of small particles.

Increased PACl3 dose to 2 mg·Al/dm³ changed the course of flocculation. There is clearly a reduction in the number of fine particles in relation to the dose 1 mg·Al/dm³. After 90 s flocculation the number of the particles in the range 1–2 μm was 2,000 cm⁻³, while it increased to 7,000 cm⁻³ after 10 min. flocculation. Such a phenomenon

indicated that the process of coagulant hydrolysis still continued, and new particles were formed which were unable to agglomerate. At the same time, larger particles were recorded. The most numerous were particles of 7 μm in size, the number of which was 15,000 cm⁻³ after 90 s, and after 10 min flocculation it dropped to 4,000 cm⁻³. The decrease in the number of particles should have been accompanied by an increase in the number of larger particles. However, in the range of 30–100 μm, such a phenomenon was not

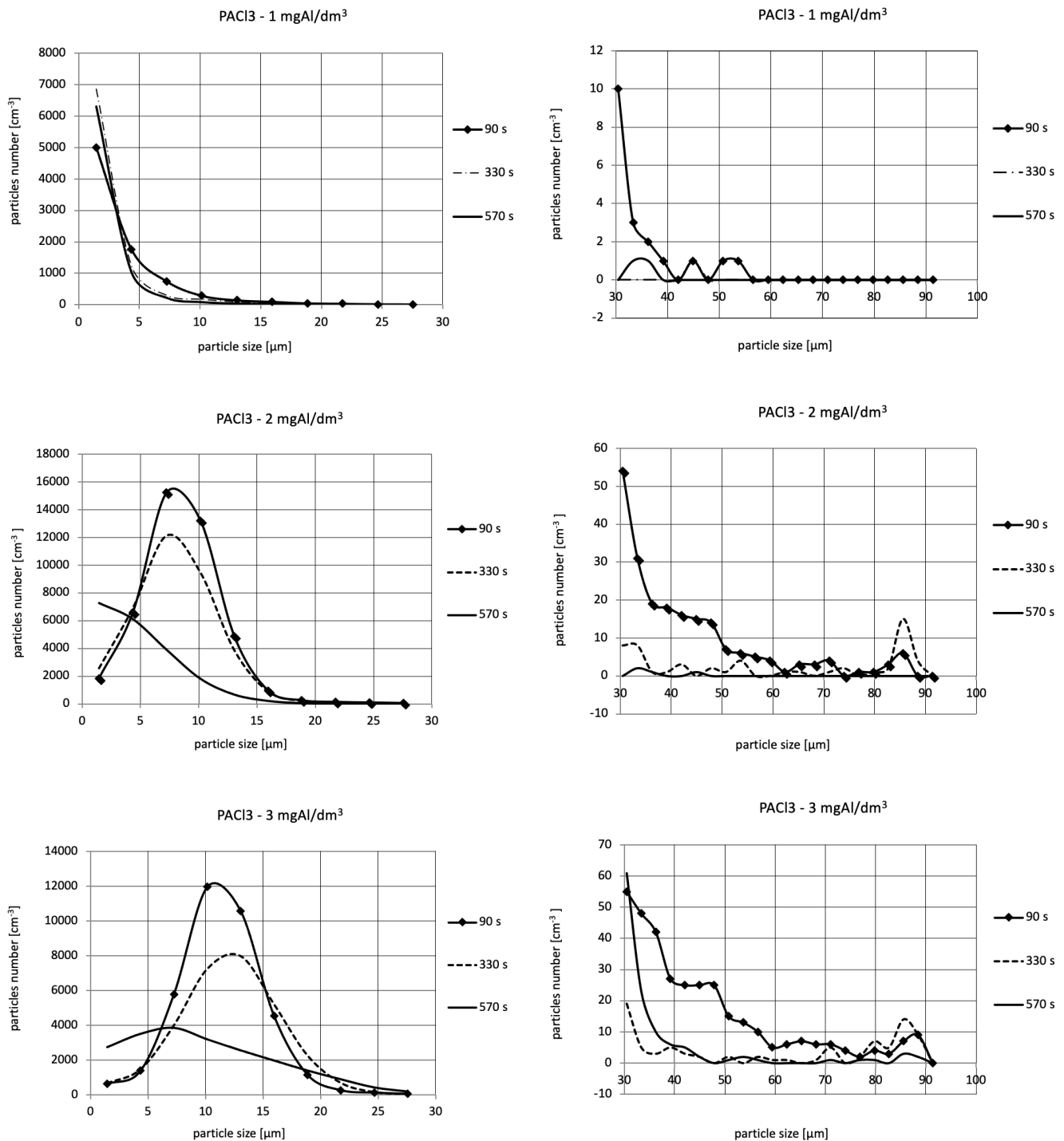


Fig. 3. Particle size distribution along with the flocculation with PACI3 at the doses: 1, 2, 3 mg·Al/dm³, pH 6.8.

recorded. The decrease in the number of particles with a size of 5–10 μm was probably accompanied by an increase in the number of particles larger than 100 μm , which were not able to be noted in the measuring size range. A similar course of particle size changes was observed at higher dose of PACI3, that is, 3 mg·Al/dm³. The only difference, compared to the lower dose, was that produced particles were larger. The highest number of particles was recorded

in the range of 7–13 μm , with the maximum size of 10 μm with the concentration 12,000 cm^{-3} after 90 s flocculation. The decrease in the number of 10 μm particles after 570 s of flocculation was accompanied by an increase in the number of particles with a size of 1–2 μm , which indicated further PACI3 hydrolysis. It results from the maladjusted dose of coagulant to the pollutant load present in treated water.

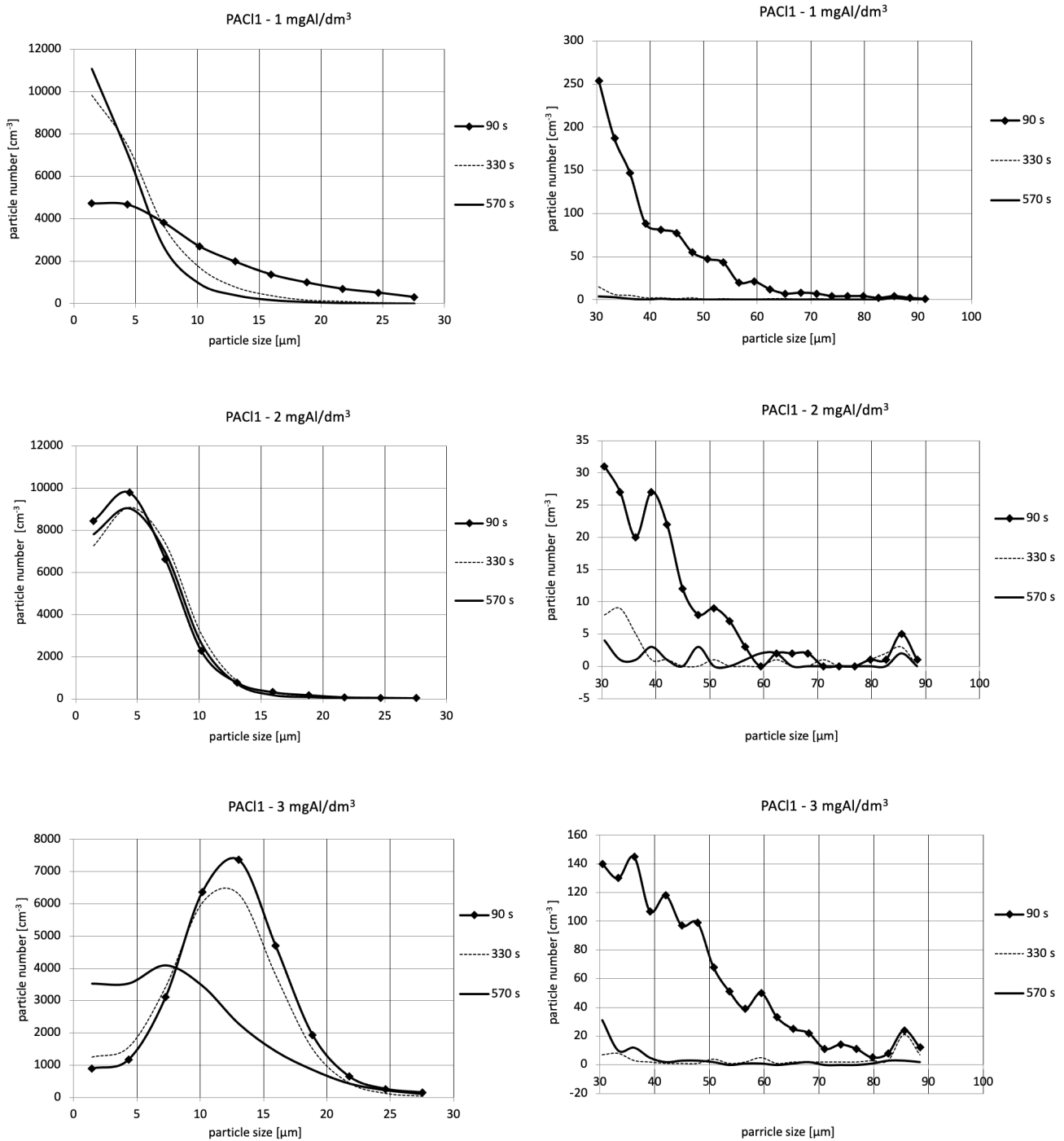


Fig. 4. Particle size distribution along with the flocculation with PAC11 at the doses: 1, 2, 3 mg·Al/dm³, pH 7.9.

The analysis of the particle size distribution for the same doses of coagulant shows that in the case of PAC13, the mean particle size obtained was larger compared to PAC11 and PAC12 (Figs. 1–3).

In conclusion, for PAC11 and PAC12, which out of three tested coagulants are characterized by the highest share of Al polymer species, similar changes in the particle size distribution during flocculation were found. The reagent dose was an accompanying variable for the reaction time. In

most samples, as the dose and flocculation time increased, not only the mean particle size but also the total number of particles decreased significantly. Regardless of the Al speciation, it could also be noticed that with the increase of the reagent dose, the size of the aggregates increased in the initial phase of flocculation. The largest aggregates were formed for PAC13 with the highest fraction of monomeric Al species (about 41%), that is, for coagulant with the lowest degree of polymerization. The second largest aggregates

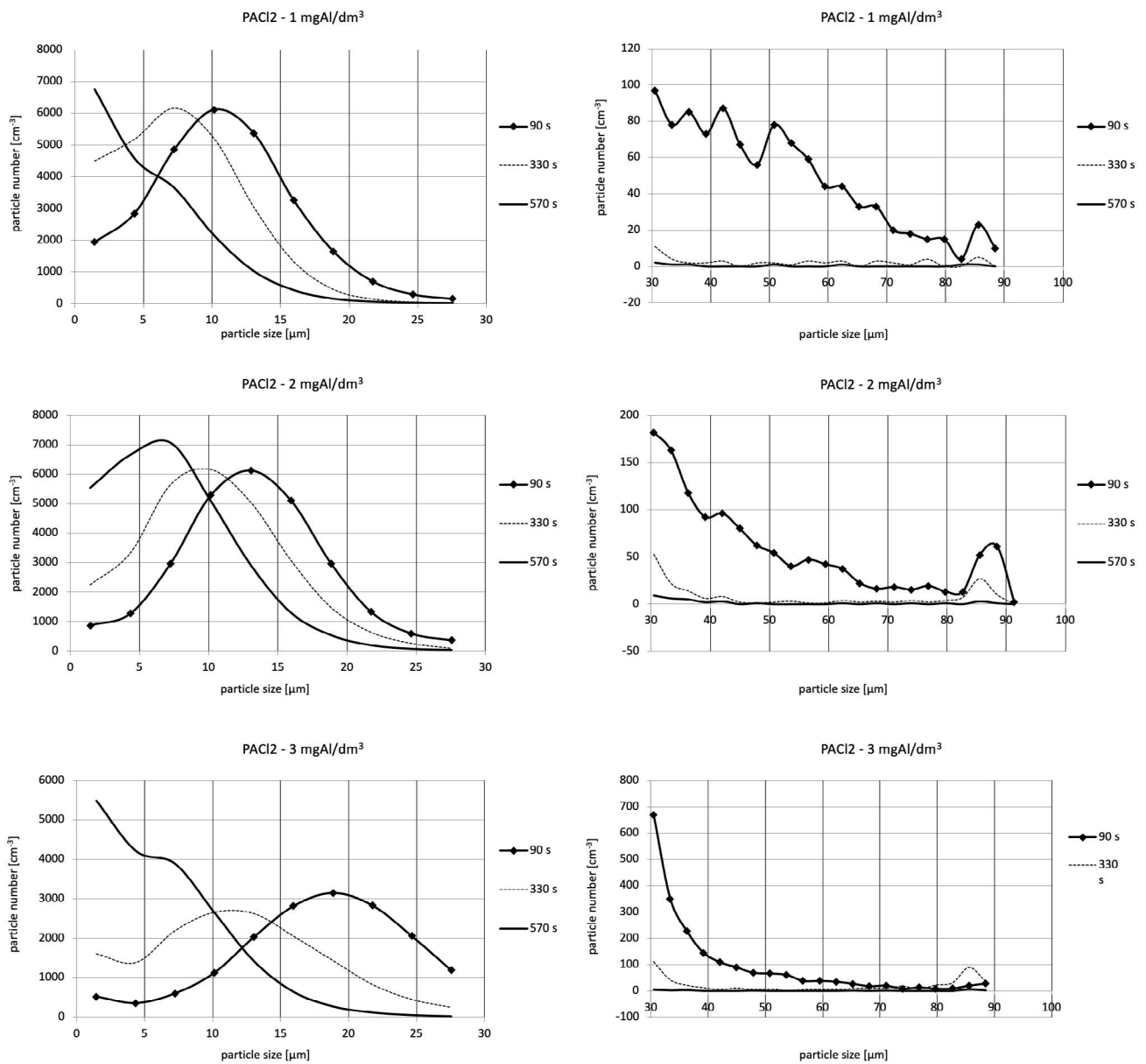


Fig. 5. Particle size distribution along with the flocculation with PACl2 at the doses: 1, 2, 3 mgAl/dm³, pH 7.9.

were recorded for PACl2, and the smallest for PACl1, which was the reagent produced in the sulfate modification (approx. 13% of Al monomers).

Along with the flocculation time, and thus further changes in aluminum species, the aggregates stopped growing until the residual aluminum in the sample was mostly in dissolved or colloidal form (aggregates smaller than 0.5 µm). Increasing the doses caused an increase in the number of polymeric species in the sample, which due to their surface properties (electrically heterogeneous surface of the aggregates, allowing them to be combined into larger clusters) could form large particles. Over time, these forms converted to aluminum hydroxide, which resulted in the inability to form larger, stable structures. Therefore, it is very important to precisely determine the dose of the coagulant in relation

to the number of impurities present in the water. Where these ratios are inadequate, there was a sharp increase in the number of very fine particles (<5 µm). This means that also when using pre-hydrolyzed coagulants, PACl overdosing may occur.

At the higher pH value, that is, pH 7.9 (Figs. 4–6), it was noted the shift to the left of particle size distribution curves during flocculation, especially for PACl2 and PACl3. The effect of the dose on the size of aggregates formed in the initial phase of flocculation, depending on the type of coagulant, was similar to the lower pH 6.8. The largest aggregates were produced for PACl3 which was characterized by the highest share of Al monomers. However, at the pH 7.9 there was no effective reduction in the number of fine particles (smaller than 5 µm), especially it was noted at the

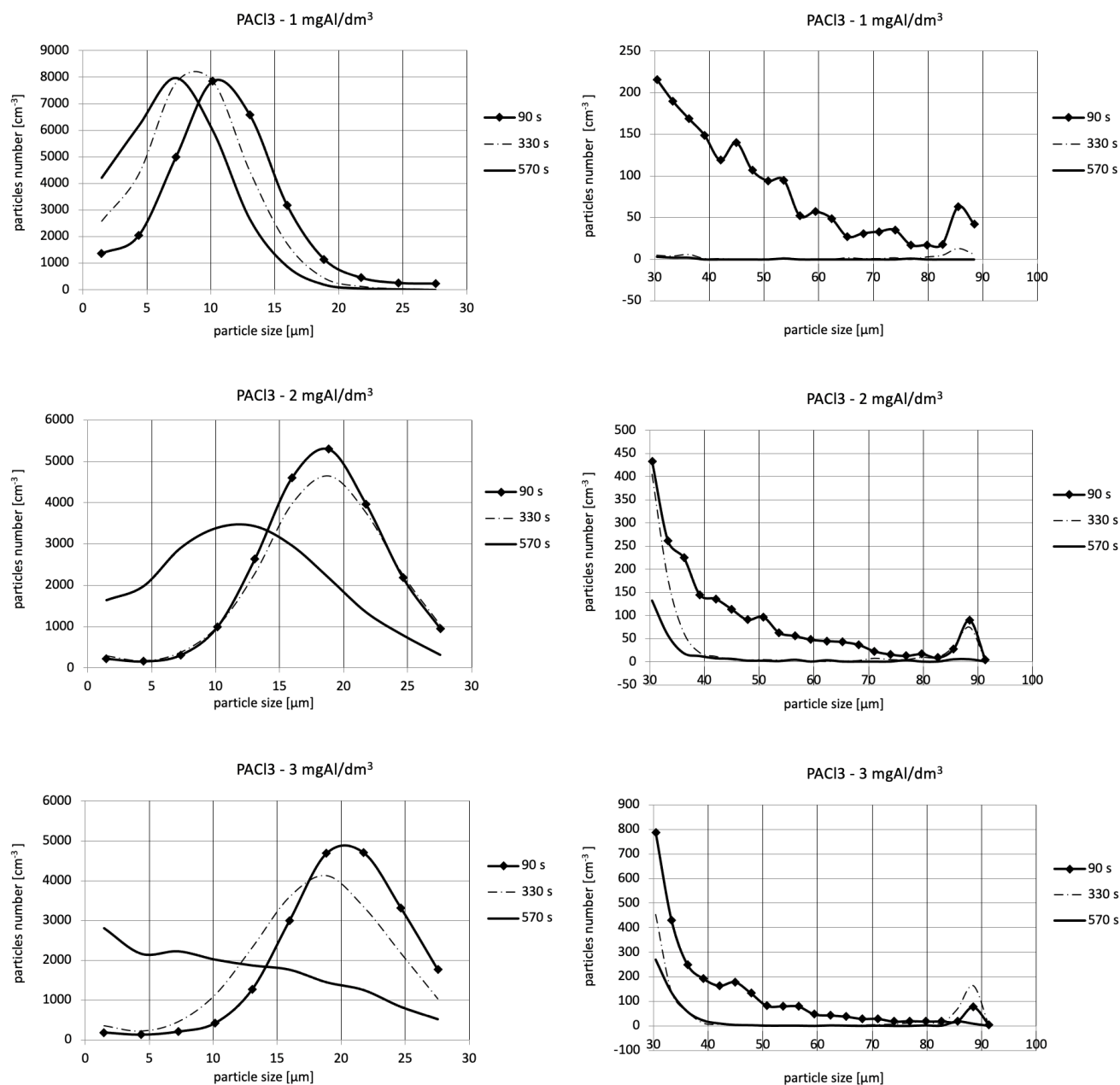


Fig. 6. Particle size distribution along with the flocculation with PACl3 at the doses: 1, 2, 3 mg·Al/dm³, pH 7.9.

lowest PACl3 dose. In the measuring range of 0–30 μm , the maximum particle sizes after 90 s flocculation were 10, 18 and 20 μm for the dose of 1, 2 and 3 mg·Al/dm³, respectively. At the same time, a significantly lower number of particles was recorded compared to the pH 6.8. At pH 7.9 with the dose of 1 mg·Al/dm³ after 90 s of flocculation, the number of the largest particles (10 μm) was 5,000 cm⁻³, that is, it was more than two times lower than at the pH 6.8. Along with the flocculation time, agglomeration of flocs was noted, which was confirmed by the particle size distribution analysed in the range of 30–100 μm (Fig. 4). At the end of flocculation time, there was a clear reduction in the number of particles in the analysed range, which might indicate their agglomeration and the increase of floc size above 100 μm . However,

simultaneously to these changes, irrespective of PACl3 dose, at the end of flocculation time the effect of overdosing was observed, as manifested by the formation of many fine particles, mainly smaller than 5 μm . It should be emphasized that turbidity measurements in samples after coagulation, flocculation, and sedimentation in tested samples, did not result in an increase of turbidity, which means that the measurement of the particle counter is a more reliable tool for selecting the PACl optimal dose.

When analysing the particle size distribution for PACl1, it was observed that only at the highest dose of this reagent, that is, 3 mg·Al/dm³, resulted in the reduction of the number of particles. The lower doses were completely ineffective. The effects of overdosing of the coagulant with the

highest share of polymeric species (PACI2) were observed already at the lowest dose, that is, 1 mg-Al/dm³. It was manifested by the formation of many fine particles during flocculation time.

The obtained results are consistent with the results of the research conducted by McCurdy et al. [15] on the influence of aluminum speciation on the size of the flocs. The researchers pointed to the clear differences between the properties of flocs formed during coagulation with aluminum sulfate and PACI (depending on the zeta potential value). Based on the analysis of the relationship between the zeta potential and the fraction of particles formed during rapid mixing, it was found that in coagulation with aluminum sulfate, the highest number of flocs was formed at the value of the potential close to zero, that is, the highest coagulation efficiency by charge neutralization. For polyaluminum chloride at zero value of zeta potential, the fraction of precipitated particles was very small. The highest number of flocs was noted at a much higher value of ζ potential. In practice, it causes the need to use a higher PACI dose than it results from the load of pollutants in treated water, in order to produce an appropriate number of particles capable for agglomeration and subsequent sedimentation. It is especially important during the coagulation of low turbidity waters. When analyzing the properties of post-coagulation flocs that did not sediment, a clear shift of the zeta potential distribution curve was found in the case of aluminum sulfate, which means that the properties of flocs formed during rapid mixing and those that did not sediment were different. It was evidenced by the morphological analysis of the flocs, which showed differences in their size, geometry, and surface charge. On the other hand, the properties of polyaluminum chloride flocs were the same, which was confirmed by the same zeta potential distribution curve both for flocs formed during rapid mixing and those that did not sediment [15].

The above information is very important from the point of view of optimizing the coagulant dose ensuring not only the correct course of colloid destabilization, but also the production of an appropriate number of particles susceptible to agglomeration and further sedimentation.

4. Conclusions

- The properties of particles formed during the precipitation process depend on the reaction time, coagulant dose, and Al speciation.
- At the pH 6.8 the size of flocs in the range 0.5–30 μm increased with the coagulant dose, regardless of the flocculation time, while the number of particles in an analysed range decreased with time. In the initial phase of flocculation only a small number of particles ranging from 30–100 μm was noted. No flocs rupture in time was observed.
- There was a clear tendency that the number of particles decreased with the flocculation time, but the floc size distribution was strictly dependent on the dose of the coagulant.
- PACI1 and PACI2 showed similar particle size distribution during flocculation. It proves that the share of Al₂ and Al₃ species was decisive for the size and the amount of flocs.
- The analysis of the particle size distribution for the same doses of PACI3 showed the mean particle size was larger compared to PACI1 and PACI2.
- At the pH 6.8, the most effective particle agglomeration was obtained for the coagulant with the highest share of Al monomer species (PACI3) which was confirmed by the formation of the largest flocs.
- At the dose 2 and 3 mg-Al/dm³ of PACI3 after 570 s of flocculation an increase in the number of fine particles with a size of 1–2 μm started, which indicated an overdose of the coagulant. It results from the maladjusted of coagulant dose to the pollutant load in treated water and their particles inability to agglomerate.
- At the higher pH value, that is, pH 7.9, the effect of the dose on the size of aggregates formed in the initial phase of flocculation, depending on the type of coagulant, was like the lower pH 6.8. The largest aggregates were produced for PACI3. However, at the pH 7.9 there was no effective reduction in the number of fine particles (smaller than 5 μm).
- At pH 7.9. the resulting flocs were larger and more eager to agglomerate in relation to pH 6.8. However, the overdosing was observed, manifesting as the increase of fine particles during flocculation. It was the most visible for the high-polymerized PACI2.
- The measurements of particles size and their number along with the flocculation time enable to analyse the process and to adjust PACI dose based on the changes of fine particles number which may reflect improper coagulant dose application.

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