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EFFECT OF POLYALUMINIUM CHLORIDES OVERDOSAGE ON EFFECTIVENESS OF COAGULATION AND FILTRATION

PACls overdosage has negative impact on the operation and the effectiveness of coagulation and separation of post-coagulation suspensions. The results of the pilot study revealed that a sharp increase of fine particles was observed at reaching and exceeding the isoelectric point. Based on the full-scale research with PACl_1 ($B = 2, 4$) it was stated that these particles did not cause deterioration of standard quality parameters (turbidity, absorbance UV_{254}, colour, TOC, COD_{Mn}) of water purified in conventional treatment. However, the particles not retained in sedimentation tanks supplied rapid filters and caused their overloading, and hence shortening of filtration cycles.

1. INTRODUCTION

Coagulation is a basic unit process used in surface water treatment, mainly for the removal of mineral particles and dissolved organic matter. Generally, coagulation is based on two fundamental mechanisms: charge neutralization of negatively charged colloidal particles by the positively charged hydrolysis products as well as on so-called sweep coagulation, based on the phenomenon of "capture" of pollutants by the precipitated aluminum hydroxide particles, the latter being mainly responsible for the efficiency of aggregation of neutralized particles and production of flocs of the desired properties. It also enables the creation of optimal conditions for the removal of dissolved organic compounds causing the colour of water by their sorption on the surface of the precipitates of post-coagulation suspension [1, 2].

The effectiveness of the process is evaluated by a number of parameters, the most important being the type and the dose of coagulant. They largely determine both the mechanisms of coagulation and the achieved effects of pollutants removal. In recent years, on a large scale, pre-hydrolyzed coagulants (e.g. polyaluminium chloride

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– PACl) have been used. PACls are often more effective than hydrolyzing coagulants, especially at low temperatures and in a wide range of pH. Tridecameric Al_{13} species with the formula $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ (abbreviated as Al_{13}) has been shown to be the dominant polymeric species in partially neutralized Al solutions when PACl is used under certain pH conditions [3, 4]. The common opinion about the lack of possibility of PACls overdosing, resulting in deterioration of water quality, led to their application in place of hydrolyzing coagulants.

The paper presents the results of the pilot and the full-scale research which aimed to determine the effects of pre-hydrolyzed coagulants overdosing on coagulation mechanisms and treatment effectiveness.

2. MATERIALS AND METHODS

Experimental procedures. A pilot study was conducted to evaluate the effect of PACls dose on coagulation mechanism based on streaming current (SC) values and measurements of particles number and particle size distribution (PSD). SC measurements allow characterizing the effect of a coagulant dose on the zeta potential which describes the stability of colloids. Based on this relationship, the ranges of a coagulant dose which are dominated by various coagulation mechanisms (charge neutralization, sweep coagulation) may be specified.

In the full-scale research, the impact of PACl overdosing on coagulation, sedimentation and filtration effectiveness was analyzed. Treatment effectiveness was assessed based on turbidity, COD_{Mn}, UV absorbance at 254 nm (UV_{254}), TOC, DOC, and additionally the measurement of particles number and particle size distribution as supplementary indicators of turbidity measurement. Turbidity is especially suitable for monitoring changes in water quality, in which the particle size is lower than 1 μm, and does not reflect the actual content of particles of a larger size [5]. The measurement of particles number is a better indicator for evaluating the effectiveness of filtration due to the high sensitivity to any disruptions that may occur in the operation of the filters.

In the pilot testing, the number of particles was analyzed by a particle size analyzer (ARTI WPC21, Hach). In the full-scale research, the samples were collected after unit processes and analyzed by an analyzer IPS LCW, Kamika Instruments (each measurement was repeated three times and the average value was calculated). Turbidity was detected by Turbimax W CUS41, Endress+Hauser. The UVAS plus sc process probe (Hach) measured absorbance at 254 nm. The probe was simply submerged in the fluid, without taking samples. TOC and DOC were detected by TN/TN Multi N-C, Analytik Jena. SC value was measured by the SC analyzer, SEEN Technologie.

Coagulants characteristics. Coagulation was carried out using four selected pre-hydrolyzed coagulants, representing the most commonly used reagents. PACl_1, PACl_2, PACl_3, PACl_4 were used in pilot-scale tests. PACl_1 was applied in full-scale research. The characteristics of the reagents are given in Table 1.

Table 1

Characteristics of coagulants

Parameter	PACl_1	PACl_2	PACl_3	PACl_4
Specific gravity, g/cm^3	1.28	1.20	1.22	1.24
pH	4.2	4.2	4.2	2.6
Al, wt. %	11	6.0	8.5	5.5
Cl, wt. %	7	4.0	5.3	13.1
Al/Cl	1.57	1.50	1.60	0.42
Basicity (OH/Al), %	80	80	84	71

Raw water. In the pilot study, water of low turbidity, mainly polluted by dissolved organic matter, was tested (Table 2, series 2). The research in the technical scale was made in two several months' period, characterized by different quality of raw water. In the first period, water of low turbidity (of maximal value 5 NTU) was tested. In the second period, of the research, water turbidity reached a maximal value of 45 NTU. In the paper, the results of one exemplary series in each research period have been presented. The detailed analyses of the raw water quality for two selected series are presented in Table 2.

Table 2

Characteristics of feed water

Parameter	Turbidity [NTU]	Total particles No. [1/cm^3]	COD_{Mn} [mg O_2/dm^3]	TOC [mg C/dm^3]	DOC [mg C/dm^3]	Absorbance [m^{-1}]
Series 1	45	2806	6.2	5.46	4.9	11
Series 2	5	388	5.5	5.47	5.27	5.6

Pilot-scale experiment. The study was conducted in the pilot system with a capacity of about 1 m^3/h. It was installed at the treatment plant supplied with water from the dam reservoir. The installation comprised a double section flocculation tank and a lamella sedimentation tank, preceded by rapid mixing conducted using a hydraulic mixer. The proper volume of commercial PAC_l product was supplied to the system to get the required dose. The testing was carried out in the range of doses of 0–11 mg Al/dm^3. After 6 and 28 s of rapid mixing, in collected samples SC, particle number and particle size distribution were measured.

Full-scale experiment. On the technical scale, the treatment system of surface water was designed as a conventional system (a hydraulic tank of rapid-mixing, vertical sedimentation tanks combined with rotational flocculators and rapid filters). Coagulation was carried out with PACl_1. The last unit process of separation of post-coagulation suspension was rapid filtration carried out on five identical double-layer beds (anthracite–sand) filters (F1, F2, F3, F4, F5) operating with a hydraulic load in the range of 4–5 $m^3/(m^2\cdot h)$. Because each filter was backwashed at different time, during sampling at a strictly designed time each filter was at a different moment of the filtration run.

3. RESULTS AND DISCUSSION

3.1. THE EFFECT OF PACls DOSE ON COAGULATION MECHANISM. PILOT STUDY

Figure 1 shows the dependences of SC values on PACls doses. The course of these curves is typical of pre-hydrolyzed reagents. It depends largely on the surface charge of hydrolysis products, which is used to determine the ability of a coagulant to neutralize the charge of colloidal compounds present in water. The data shows that the highest surface charge was noted for PACls of high basicity (PACl_1 and PACl_2). The isoelectric points of PACl_1 and PACl_2 were achieved at the dose of about 2 mg Al/dm^3. For PACl_4 of the lowest basicity, the dose required to obtain neutralization of negative charge of the pollutants was significantly higher and it was about 9 mg Al/dm^3.

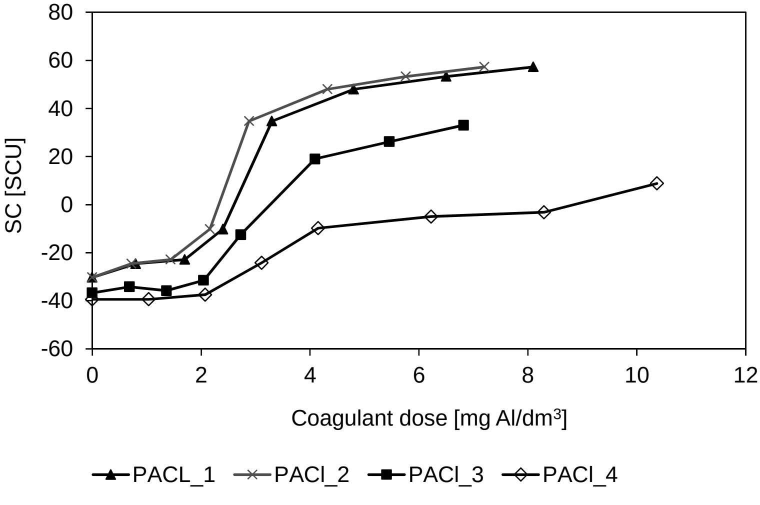

Fig. 1. The effect of PACls dose on SC [SCU]

Simultaneously to SC values, the measurements of particles number in water were made. The results revealed that the amount of particles underwent significant fluctuations. Figure 2 shows the dependence of the number of 1 μm particles after 28 s of rapid mixing (after 6 s no changes have been observed yet) on various PACls doses. For all tested coagulants, the increase of particles number was observed when reaching and exceeding the isoelectric point. The only significant difference was the dose of coagulant, especially PACl_4, required for the charge neutralization.

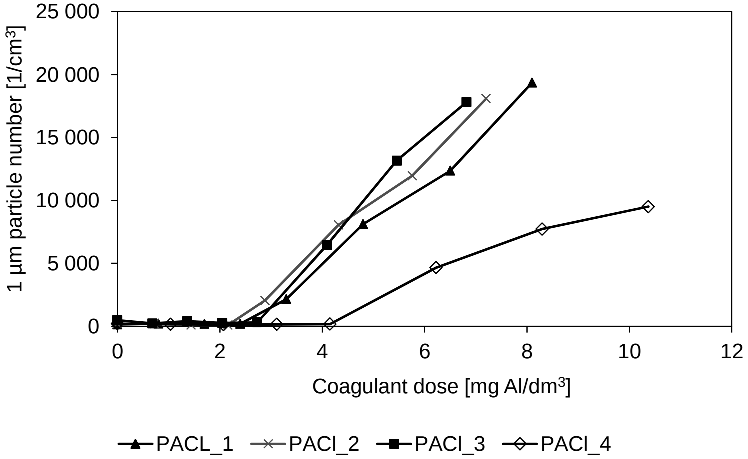

Fig. 2. The effect of coagulants dose on the number of 1 μm particle after 28 s of rapid mixing

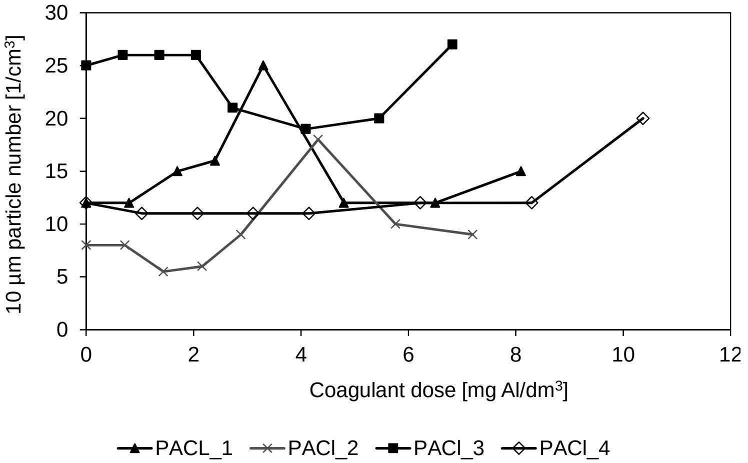

Fig. 3. The effect of coagulants dose on the number of 10 μm particle after 28 s of rapid mixing

The measurements of particles number of a larger size (2, 5 and 10 μm) did not show such changes. Figure 3 shows the results for 10 μm particles. Similar results were observed for the particles of 2 and 5 μm.

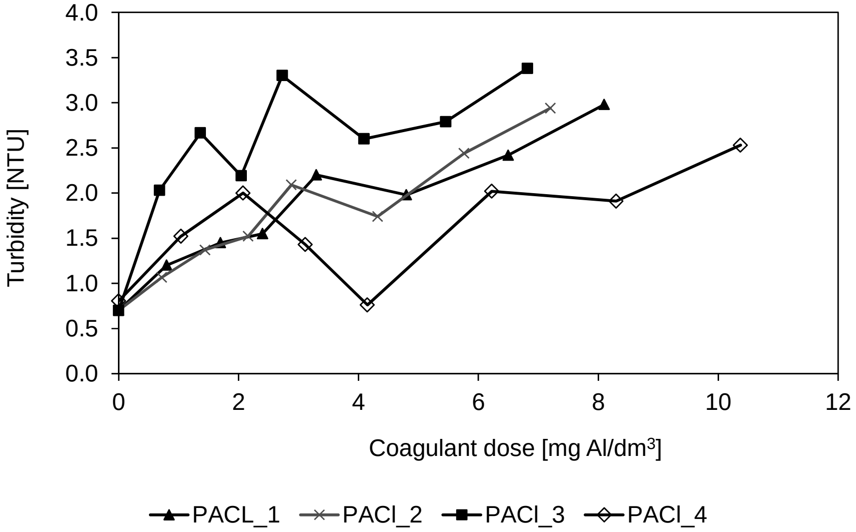

Fig. 4. The effect of coagulants dose on turbidity after 28 s of rapid mixing

Turbidity analysis did not reflect the change in the amount of 1 μm particles (Figs. 2, 4). Only for PACl_1 and PACl_2 a slight increase in turbidity after crossing the isoelectric point was noted but the trend was not as distinct as for particles number. The observed differences in the number of particles and turbidity were caused by two different factors. First of all, performance of the turbidimeters was strongly influenced by 0.2 μm particles. Besides, various coagulants differed in effectiveness to aggregate neutralized colloids and fine particles (below 1 μm). PACl_3 showed a poor ability to aggregate impurities, probably resulting from its high basicity but at the same time low share of Al_{13} species. The obtained results show that coagulants of lower basicity, e.g. PACl_4, were more effective.

Coagulant overdosing was stated in two stages. At the first stage, the range of the effective coagulant dose based on the curve of coagulant dose and SC value (Fig. 1) was determined. At the second stage, the analysis of particle number was made. In the range of the effective dose, the number of particles of 1 μm increased, what reflected a significant amount of un-agglomerated particles produced by Al precipitation. These particles did not agglomerate due to the same surface charge.

3.2. THE EFFECT OF PACl OVERDOSING ON TREATMENT EFFECTIVENESS. FULL-SCALE RESEARCH

Particle behaviour in the early stages of granular media filtration is complex. Generally, in the very early stage of a filter run, larger particles and particles with lower surface charge are captured to a greater extent than smaller ones. Particles capture is strongly influenced by the previously retained particles and their improved removal occurs with increasing cumulative hydraulic loading [6].

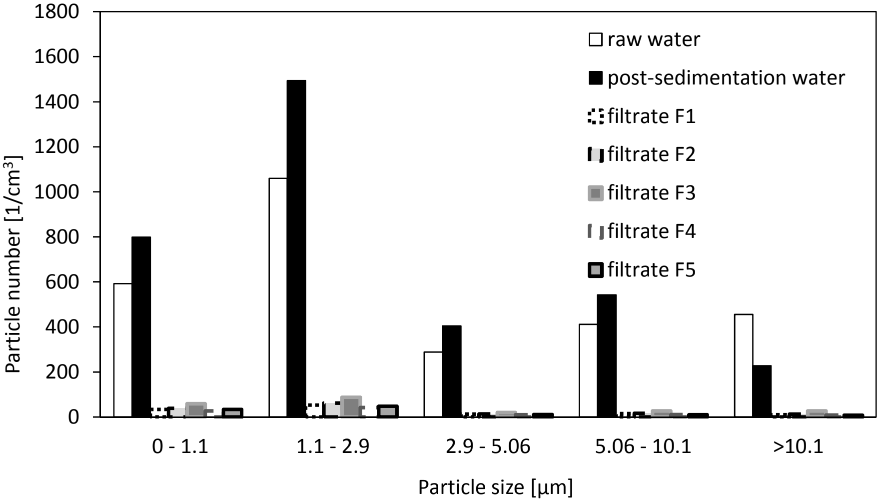

Fig. 5. Particle size distribution in raw water of high turbidity (series 1)
and after unit treatment processes

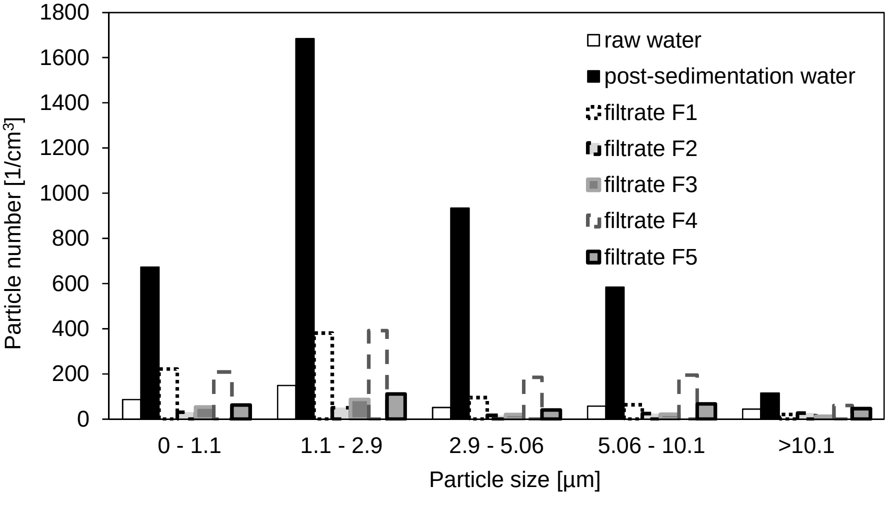

Fig. 6. Particle size distribution in raw water of low turbidity (series 2)
and after unit treatment processes

Figures 5 and 6 show the particle size distribution recorded during the treatment process of water of high (the series 1) and low turbidity (the series 2). The measurements were made in samples collected after unit process (sedimentation, filtration).

PACl_1 dose was 4.7 mg Al/dm^3 in the series 1 and 3 mg Al/dm^3 in the series 2. The doses were stated in jar-testing by the operators of the technological system.

Table 3

Characteristics of treated water

Parameter	Turbidity [NTU]	Total particles No. [1/cm^3]	COD_{Mn} [mg O_2/dm^3]	TOC [mg C/dm^3]	DOC [mg C/dm^3]	Absorbance [m^{-1}]
Series 1						
Post-sedimentation water	3.3	3468	0.9	2.5	2.3	2.7
Filtrates F1–F5	0.08–0.32	96–219	0.2–0.3	2.2–2.4	2.1–2.2	2.1–2.4
Series 2						
Post- sedimentation water	2.1	3991	2	2.4	2.3	2.1
Filtrates F1–F5	0.21–0.47	150–1040	0.9–1.2	2.2–2.3	2.1–2.2	1.2–1.7

The characteristics of treated water collected after unit processes shows that treatment was very effective (Table 3). However, in both series, the effects of coagulant overdosing were observed. In water after sedimentation, the increase of fine particles in comparison to raw water was noted. In the raw water, primarily contaminated with mineral particles (series 1), the total number of particles was 2806 in 1 cm^3. As a result of coagulant overdosing, the total amount of particles was 3468. The number of small particles (max. 1.1 μm) increased from 592 in 1 cm^3 in the raw water up to 799 after sedimentation. The higher amount of larger particles (1.1–10.1 μm) was also observed. Only the amount of the largest particles (>10.1 μm) dropped after sedimentation from 455 to 228 in 1 cm^3. The presence of those particles had a positive impact on treatment effectiveness, because they shortened the stage of filter bed ripening. In the effluent samples, total particle number was very low and ranged from 96 to 144 in 1 cm^3. From the chemical point of view, those particles were polymeric products of PACl_1 hydrolysis which were produced in the excess amount in relation to the pollutant load in the feed water. The effluent turbidity ranged from 0.08 to 0.32 NTU, despite the fact that the amount of particles in filtrates was similar.

In the series 2, the feed water was mainly contaminated with dissolved organic matter. Turbidity was 5 NTU. The total number of particles in the raw water, supernatant and filtrates were 388, 3991 and 150–1040 in 1 cm^3, respectively. Filtration effectiveness depended on the phase of filter operation (each of five filters was at a different stage of a filtration run). Particles number in the effluent was the highest for F4 which was at the early stage of filtration after its backwashing. The filter bed was then characterized by the highest porosity and small particles could not be stopped. The number of particles up to 1.1 μm was 208 in 1 cm^3, whereas after sedimentation 673 in

1 cm^3. The increase in the number of larger size particles was also observed. Contrary to the series 1, the amount of the largest size particles (>10.1 μm) increased from 44 in the feed water to 116 in 1 cm^3 after sedimentation but it was still less than in the series 1. The longer filtration time the fewer particles in filters effluents were measured due to the ripening effect being more dominant than detachment of flocs. Filtrates turbidity ranged from 0.21 to 0.47 NTU. In both series, no correlation between the particles number and the value of turbidity ($R^2 = 0.36$) was found.

The results once again deny the colloquial idea that pre-hydrolyzed coagulants cannot be overdosed. The effects of PACls overdosing result in the increase of the number of fine particles and very rarely this effect is accompanied by the deterioration of standard water quality parameters such as turbidity, colour, COD_{Mn} and absorbance UV_{254}. This means that the adopted procedure for monitoring and the control of a coagulant dose should take into account this phenomenon [7, 8]. The analysis of the changes of the amount and particle size suggests that these particles are precipitated products of PACls hydrolysis (Al_C, by standard ferron assay) [9–12]. Because of their high surface charge they have a strong effect on the electrokinetic potential and participate in sweep coagulation. The most important problem is their separation. This phenomenon is particularly troublesome in the systems of water treatment prior to ultrafiltration. Schulz et. al. [13] found that one of the main factors that cause fouling of ultrafiltration membranes is aluminum in the form of suspensions of particles of a very small size (<0.2 μm). The fine suspension is also a problem in water treatment for drinking purposes because it causes overloading of rapid filters and impacts on deterioration of disinfection effectiveness based on UV radiation.

4. CONCLUSIONS

The effective treatment of water of variable quality, which is contaminated both with mineral particles and dissolved organic compounds, should be based on sweep coagulation. It is important to apply a coagulant dose that ensures the best possible removal of impurities from treated water, while maintaining a low number of fine un-agglomerated particles.

The study showed that there is a need to adapt the existing treatment system control to the properties of pre-hydrolyzed coagulants. The excessive amount of hydrolysis products of pre-hydrolyzed coagulants has negative impact on the operation and the effectiveness of coagulation and separation of post-coagulation suspensions resulting from the formation of large quantities of fine un-agglomerated particles. The results of the pilot study revealed that a sharp increase of 1 μm particles was observed when reaching and exceeding the isoelectric point. Based on the full-scale research with polyaluminium chloride – PACl_1 it was stated that these particles did not cause any negative effects on standard quality parameters (turbidity, absorbance UV_{254}, TOC, COD_{Mn}) of water collected after sedimentation and filtration, however, not retained in sedimentation tanks, supplied rapid filters and caused their overloading. In the initial phase of filtration cycles these particles were also detected in filtrates.

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