Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.27973

245 (2022) 158–166
January

The impact of *k*-value-based aluminium speciation and basicity of coagulants on flocs resistance to breakage

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Received 6 February 2021; Accepted 4 November 2021

ABSTRACT

The paper presents the results of the research on flocs resistance to breakage. In the study coagulants of various basicity and aluminium speciation were tested. It was noted that with the increase of mixing energy at flocs rupture stage, impurities concentration in water after flocs breakage and further settling of broken flocs increased. However, the values of water quality indicators decreased with the increase of coagulant basicity and the decrease of k_1/k_2 ratio which reflected the share of polymeric Al species. For aluminium chloride after flocs breakage at a rotational speed of 200 rpm followed by clarification, the values of TSS, turbidity, TOC and absorbance UV_{254} (in non-filtered samples) increased by 170%, 203%, 34% and 72%, respectively, in comparison to quality indicators measured in water after settling without flocs rupture stage before clarification. The coagulant with the highest share of polymeric Al species ($B4 = 1.47$) produced the strongest and the most resistant to shear flocs structure. The lowest increase of TSS, turbidity, TOC and absorbance UV_{254} after flocs breakage and settling was noted then in comparison to the coagulants of lower basicity. TSS, turbidity, TOC and absorbance UV_{254} increased by 42%, 93%, 19% and 27%, respectively. The results revealed the linear relationships between the increase of TSS, turbidity, TOC and absorbance UV_{254} in non-filtered samples after settling of broken flocs and the k_1/k_2 ratio values (k_1, k_2 rate constants stated in ferronometry assay indicate the presence of specific forms of aluminium). The linear relationships were also noted considering the coagulant basicity. However, k_1/k_2 ratio was a better indicator to estimate flocs resistance to stress. *R*-squared values (R^2) were higher compared to basicity values. Independently from the coagulant Al speciation, flocs rupture did not cause the desorption of dissolved organic pollutants adsorbed during the flocculation stage.

Keywords: Coagulation; Basicity; Ferronometry assay; k_1/k_2 ratio; Al speciation; Floc strength

1. Introduction

In addition to alum, many types of polyaluminium coagulants are commercially available for water treatment, including polyaluminium chlorides (PACl), aluminum chlorohydrate (ACH) and polyaluminium sulphates (PAS). Unlike alum and aluminium chloride, these products differ in their basicity and flocs strength, and can contain small amounts of other substances, such as sulphate, silica and calcium. When alum is added to rapid mixing tank, Al^{3+} rapidly undergoes hydrolysis reactions to form other dissolved Al species or Al-hydroxide precipitates. The addition of alum to water in excess of the solubility limit results in the precipitation of $Al(OH)_{3(am)}$. The solid phase formed upon precipitation with polyaluminium coagulants is different than that formed by alum. It has been stated that parts of the polymeric structure are retained when PACl precipitates. It is often designated as $Al(OH)^{*}_{3(am)}$ in the literature

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to differentiate it from the $Al(OH)_{3(am)}$ precipitate formed with monomeric Al solutions. The presence of NOM, particularly aquatic humic and fulvic acids, affects greatly the chemistry of coagulation. These aquatic humic substances are organic ligands that form complexes with dissolved Al species. Coagulants remove dissolved-phase NOM by complexation reactions followed by a phase change, that is, the NOM is removed from solution by forming a solid or adsorbing onto a solid. The coagulation mechanisms ascribed to NOM removal are: complexation of NOM with dissolved Al, leading to direct precipitation of a Al – NOM solid phase, complexation of NOM with dissolved Al, leading to adsorption of this complexed material onto precipitated $Al(OH)_3$ solids and direct adsorption of NOM onto the surface of precipitated $Al(OH)_3$ solids [1].

Natural organic matter (NOM) is a heterogeneous mixture of organic compounds, usually of medium molecular weight, consisting of many functional groups that affect their chemical properties. The key coagulation parameter during NOM removal is the pH, because this parameter affects the load of functional groups. In coagulation process, positively charged products of coagulant hydrolysis can neutralize negatively charged functional groups of organic matter. Usually, the electric charge of functional groups is 10–100 times higher than the electric charge of inorganic particles [2]. The analysis of literature data does not allow to unequivocally determine the effectiveness of PACl coagulation in natural organic matter removal. Significant discrepancies and even contradictions in the research results can be explained by the complicated structure of NOM compounds and the variety of commercial PACl products, even of the same basicity, which detailed chemical composition is unknown.

Coagulation causes a change in the nature of small particles, causing their instability, whilst flocculation promotes particle growth by gentle mixing and the consequential formation of irregularly shaped, loosely connected aggregates. During aggregation, the larger floc structure changes continually because the flocs internal bonds break under shear and reform at more favorable points where the attractive force is greater, or the repulsive force is smaller. When the balance between the rate of aggregation and the rate of breakage for a given shear condition is reached, flocs formation process completes, and the size of flocs reaches a steady plateau. The aggregation of flocs not only depends on the characteristics of solution and coagulants but also on various water quality parameters, such as the coagulation temperature, applied shear and pH, etc. It has been shown that the development and the nature of floc suspensions are governed by the prevailing shear conditions and will reach a steady state under constant shear conditions. The increased shear beyond a critical threshold cause breakage within the suspension until a new steady state is reached [3].

Flocs are highly porous fractal-like aggregate composed of many primary particles. The flocs properties, such as density and settling velocity, are non-integral function of size, but exhibit the structure of flocs. Fractal dimension is an important parameter that characterized flocs structure. It corresponds to the space-filling capacity of an object. Floc strength is another important parameter to describe flocs properties. Flocs must resist stresses, to which flocs are exposed, if they are to avoid being broken into smaller particles, which generally have lower removal efficiencies. Therefore, flocs strength is a particularly important operational parameter in solid/liquid separation techniques for the efficient removal of aggregated particles [4–6].

The flocs aggregation process largely depends on coagulation mechanisms, that is, charge neutralization, sweep and bridging. The kaolin floc strength shows a hierarchy as follows: bridging > charge neutralization > sweep while the structure of flocs formed under sweep is thought to be the most compact [7]. Floc strength could be measured by applying an increasing shear rate to the preformed flocs and relating the energy dissipation to the broken floc size [8–11]. The research has shown that the broken flocs are difficult to re-grow and only limited re-growth of flocs occurred both for alum and PACl [12–16].

According to Shu-xuan et al. [3] and Yan et al. [4] the mechanism of NOM removal is different for various Al species. Monomeric Al species (Al_a) shows high ability to satisfy some unsaturated coordinate bonds of NOM to facilitate particle and NOM removal but most of the flocs formed by Al_a are small and difficult to settle. Medium polymerized Al species (Al_b) can destabilize particle and NOM efficiently, while some flocs formed by Al_b are not large and not easy to precipitate in comparison to those formed by colloidal or solid Al species (Al_c). Thus, Al_c could adsorb and remove NOM efficiently. The removal of contaminant by species of Al_a, Al_b and Al_c follows mechanisms of complexation, neutralization, and adsorption, respectively. Unlike preformed Al_b in PACl, in-situ-formed Al_b can remove NOM and particle more efficiently according to the mechanism of further hydrolysis and transfer into Al_c during coagulation. While the presence of NOM would reduce Al_b formed in-situ due to the complexation of NOM and Al_a. As the flocs formed by Al_a are thought to be quite small and weak, the high residual dissolved Al in treated water is observed. The flocs formed by Al_c are large and compact, the residual dissolved Al is much lower accordingly [17,18]. However, the results presented by Wang et.al. [5] are different and show that the monomeric and dimeric aluminum species form the largest and strongest HA (humic acids) flocs with longest growth time. The HA flocs formed by Al_{13} is the smallest and weakest. It was confirmed by Xu et al. [6] who tested flocs formed during coagulation using a coagulant that contained more than 90% of Al_{13}. For the given optimum coagulation condition, the flocs formed by Al_{13} polymer were more fragile and weaker than those of PACl with lower Al_{13} participation, while the flocs of Al_{13} polymer had a better recoverability. For Al_{13} polymer and PACl, the flocs formed in acidic HA solution were stronger and better able to re-form than those formed in neutral and alkaline solutions. The pH values had much less effect on the breakage and re-growth of flocs formed by Al_{13} polymer than those formed by PACl. However, the other research results have shown that as compared to PACl, Al_{13} produced smaller flocs, but of higher strength, better re-growth abilities and compacter structures. HA-Al_{13} flocs displayed better resistance ability to the increasing shear than HA-PACl flocs [19].

General trends emerge showing that smaller flocs tend to have greater strength than larger flocs, whilst the use of polymer seems to give increased strength to only some types of floc. The largest flocs have been observed when coagulation process was carried out using hydrolysing coagulant. The size of flocs formed during flocculation increased with the increasing content of monomeric aluminium species [20–23].

The paper presents the results of the research on the impact of coagulant characteristics in terms of basicity, aluminium speciation, k_1/k_2 ratio on the strength of the flocs subjected to various shear force. The susceptibility of the flocs to desorption of impurities because of their breakage was also analysed.

2. Materials and methods

2.1. Raw water

The tests were carried out using model water to ensure stable water quality during the tests. Peat extract solution was added to dechlorinated and degassed tap water to obtain a specific concentration and properties of natural organic compounds. Humic acid extract was prepared by extraction with 0.1 N NaOH based on different solubility of humic substances at different pH values. The mixture was left for 1 week, then the clarified solution was decanted. Water was prepared every time in such an amount that its volume was sufficient to carry out one jar test series.

The model water quality indicators in the research were as follows:

- turbidity: 1.7–2.6 NTU,
- total suspended solids (TSS): 24–31 mg/dm^3,
- total organic carbon (TOC): 6.9–8.0 mg C/dm^3,
- dissolved organic carbon (DOC): 6.0–7.5 mg C/dm^3,
- UV absorbance at 254 nm – non-filtered samples: 0.302–0.348 cm^{-1},
- UV absorbance at 254 nm – filtered samples: 0.279–0.328 cm^{-1}.

Absorbance UV_{254} in non-filtered samples is an indicator of the content of natural organic compounds as well as colloidal particles and fine suspensions in water, while in filtered samples it is an indicator of dissolved organic matter, mainly humic acids. During the tests, the water was characterized by high alkalinity, ranging from 230 to 250 mg $CaCO_3$/dm^3, and the pH was 7.0–7.2.

The SUVA (specific ultraviolet absorbance) was also measured. The specific UV absorbance is an operational indicator of the nature of NOM and the effectiveness of coagulation in removing NOM, TOC and DBP precursors. SUVA values offer a simple characterization of the nature of NOM based on measurements of UV absorbance at 254 nm and DOC. The SUVA of the model water exceeded 4 m^3/gC m. According to the guidelines on the nature of NOM and expected TOC removals the water contained mostly aquatic humics of high hydrophobicity and high molecular weight, susceptible to removal during the coagulation process [1].

2.2. Jar test procedures

Coagulation was performed by jar test procedure using a six-beaker flocculator SW1 Stuart Scientific. Three types of pre-hydrolyzed coagulants (polyaluminium chlorides of various basicity) and aluminium chloride were tested. The research was carried out in two stages. In the first stage, optimal doses of coagulants were determined. The coagulant was injected directly above the liquid surface. Rapid-mixing for 1 min at rotational speed of 200 rpm was followed by 30 min slow-mixing at 30 rpm and 60 min settling. Three series of coagulation tests were performed for each coagulant at the doses: 1.0, 2.0, 3.0, 3.5, 4.0 and 5.0 mg Al/dm^3. The selection of optimal doses was carried out based on visual observations of flocculation process and the values of water quality indicators after sedimentation. Measurements of total suspended solids (TSS), TOC, absorbance UV_{254} – in non-filtered and filtered samples (using 0.45 μm membrane filter) were made using a Pastel UV analyzer, QBD1200 Hach analyzer and HACH DR5000, respectively. Turbidimeter 2100P ISO was used to measure turbidity.

In the second stage of the research, the strength of flocs formed during flocculation at previously selected optimal doses of coagulants was determined. Three series were carried out for each coagulant in accordance with the methodology used in the first stage of the testing. However, in five beakers, after slow mixing stage, prior to sedimentation, flocs were subjected to rupture within 1 min at various rotational speeds: 60, 90, 120, 150 and 200 rpm. In one beaker break-up stage was skipped and technological parameters of coagulation/flocculation stated in the first stage of the testing were applied. It was a comparative sample. After settling all six samples were analysed.

Before each analysis, the measuring cuvette was first rinsed with distilled water, then with a small sample volume, and finally filled with the sample and analysed. Each sample was analysed in triplicate. The average value was calculated as a result.

2.3. Reagents

Coagulants with different species distribution were prepared by the slow base titration method in the laboratory. At the first stage aluminium foil was used, which was dissolved in a 35% hydrochloric acid at 50–55°C while stirring the sample continuously. $AlCl_3$ solution was transferred into a 300 cm^3 glass reactor, and NaOH was applied into the Al solution under rapid stirring. The amount of NaOH added varied with the target OH/Al molar ratio (simplified as B values). Three laboratory prepared coagulants were as follow: PAC04, PAC08, PAC15 with OH/Al molar ratio of 0.42, 0.84 and 1.47, respectively. $AlCl_3$ solution was applied in this study as a special PAC with a B value of 0.

Coagulants were subjected to Al speciation analyzes using the ferronometry assay. The kinetics of the reaction of aluminium hydro-complexes with ferron (8-hydroxy-7-iodoquinoline-5-sulfonic acid) was measured, in which coloured complexes with a simplified structural formula Al – $(\text{ferron})_3$ were formed at pH 5.0 ± 0.2. They are characterized by a maximum absorbance at 370 nm. Measurement results were developed using two methods. The first one determined various Al species based on the rate of the ferron reaction with aluminium hydro-complexes [24]. The fraction of Al designated as Al_a, which reacts with ferron almost instantaneously (0–1 min), is assumed to include primarily monomeric species. The species that react with ferron rapidly but slower than Al_a (1–120 min) – Al_b, 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_c), is assumed to represent colloidal, solid-phase Al.

The second applied method of Al species calculation was the least squares method [25,26]. It is assumed that all monomeric species of aluminium react with ferron immediately after mixing the solutions ($t = 0$). The subsequent increases of absorbance results from parallel reactions between ferron and polynuclear species.

Since the reactions between individual forms of aluminium and ferron are the first order reactions, the kinetics of these reactions can be represented in the form of an exponential function (1):

$$A_t = A_0 + A_1\left(1-\exp\left(-k_1 t\right)\right) + A_2\left(1-\exp\left(-k_2 t\right)\right) \quad (1)$$

The first component of the sum A_0 relates to the reaction of mononuclear Al with ferron, and the second and third components represent the transformation of polymeric forms. Ye et al. [25,26] experimentally determined constant values that indicate the presence of specific forms of aluminium. They selected three types of rate constants k: the rapid kinetics around 0.01 s^{-1}, the moderate kinetics around 0.001 s^{-1} and the slow kinetics around 0.0001 s^{-1}, which are responsible for three categories of polymeric Al–OH complexes corresponding to their kinetics: rapid species – oligomers, moderate species – Al_{13} and slow species – other large polymers or colloidal aluminium species, respectively. It was stated that the rapid species does not disappear until $B < 1.2$ ($k \approx 0,01$ s^{-1}). The moderate species start to appear at $B = 0.5$. As $B \geq 1.5$, the rapid species is replaced by the slow species ($k \approx 0.001$ s^{-1}) [26].

The traditional approach to the ferrronometry assay based on arbitrarily defined reaction times of aluminium species with ferron or determining the breakpoints of the curve is not always appropriate [27,28]. At present, many manufacturers produce mixtures of different types of coagulants to adjust their products to the market requirements. For such mixtures, the standard approach may give unreliable results in relation to homogeneous products synthesized under strictly stated conditions. If the traditional ferronometry method is not reliable, a comparison of the quotient of the constant values k_1 and k_2 can be applied.

3. Results and discussion

3.1. Relationship between the coagulant basicity and kinetic constants

In the study, the coagulants synthesized in a laboratory, were characterized by various basicity in the range from zero to moderate values. Based on traditional ferron method and k-value-based ferron assay Al speciation was calculated (Table 1, Fig. 1). In the case of PAC0 (aluminium chloride) approx. 75% of aluminium species were measured as monomers. The k_1/k_2 ratio value was very high (245). With the increase of the coagulant basicity from 0 to 0.84, the decrease of the k_1/k_2 value from 245 for PAC0 to 110 for PAC08 was noted. The share of polymeric Al_b species (calculated on traditional ferronometry assay) was 9% and 12% for PAC0 and PAC08, respectively. It is confused that the slow species can be found as $B = 0$. According to Ye et al. [25,26] the self-hydrolysis might be responsible for this phenomenon. The further increase of basicity to approx. 1.5 and the decrease of k_1/k_2 ratio to 55 for PAC15, resulted in the increased amount of Al_b species to 19%.

The presented analysis confirms the observations of Ye et al. [25,26] that the basicity of pre-hydrolyzed coagulants should not be directly related with aluminium speciation [26]. Fig. 1 shows the relationship between the value of constants k_1, k_2, k_1/k_2 ratio and the basicity of coagulants used in the study.

3.2. Impact of aluminium speciation on the strength properties of flocs

Strength tests were conducted at optimal doses of coagulants, which were determined in jar tests. The coagulation process was carried out at the pH of about 7.0. The dose of aluminium chloride was 5 mg Al/dm^3. For pre-hydrolyzed coagulants they were much lower, that is, 2.5–3 mg Al/dm^3. The quality of treated water was similar regardless of the type of coagulant.

The results of the strength tests illustrating the impact of the agitator rotational speed during the phase of breaking the flocs on the increase of turbidity, TSS, TOC and absorbance UV_{254} (non-filtered samples) after flocs rupture and settling stage are presented in Figs. 2–5.

The results show that the type of coagulant has a decisive impact on flocs strength. With the increase of rotational speed during the breakage phase, the quality of treated water deteriorated, however, the effects were different depending on the tested coagulant. A very large difference was noted between the stress resistance of flocs formed

Table 1
The tested coagulants aluminium speciation, k-values and basicity

Coagulant	[OH]/[Al]	k_1	k_2	k_1/k_2	Al species based on traditional ferronometry assay		
		s^{-1}	s^{-1}		Al_a	Al_b	Al_c
PAC0	$B1 = 0$	0.019233	0.000079	244.8297	75%	9%	15%
PAC04	$B2 = 0.42$	0.023621	0.000154	153.7808	79%	6%	13%
PAC08	$B3 = 0.84$	0.018146	0.000164	110.4725	79%	12%	9%
PAC15	$B4 = 1.47$	0.009463	0.000173	54.54987	41%	19%	40%

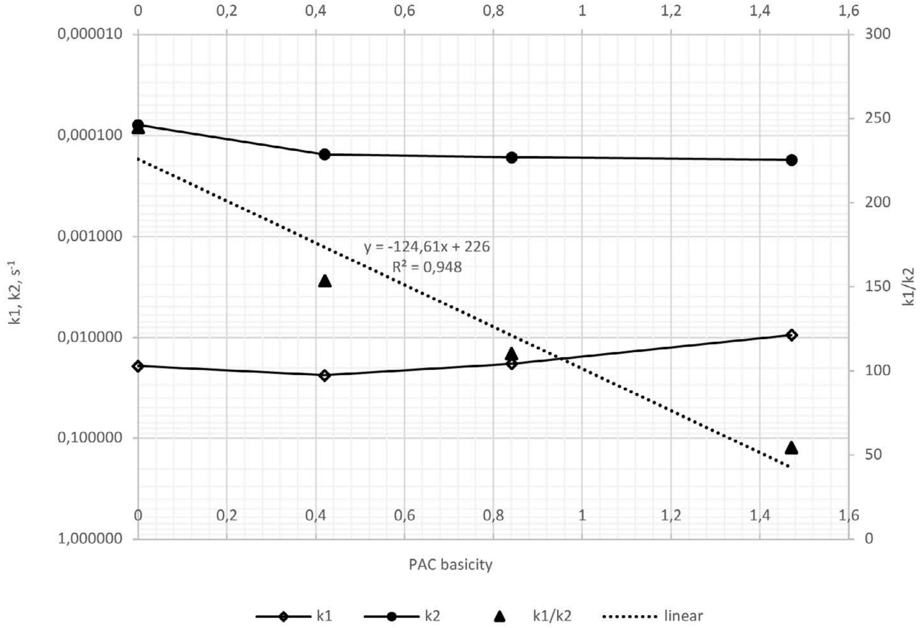

Fig. 1. Relationship between the tested coagulant basicity and k-values and k_1/k_2 ratio.

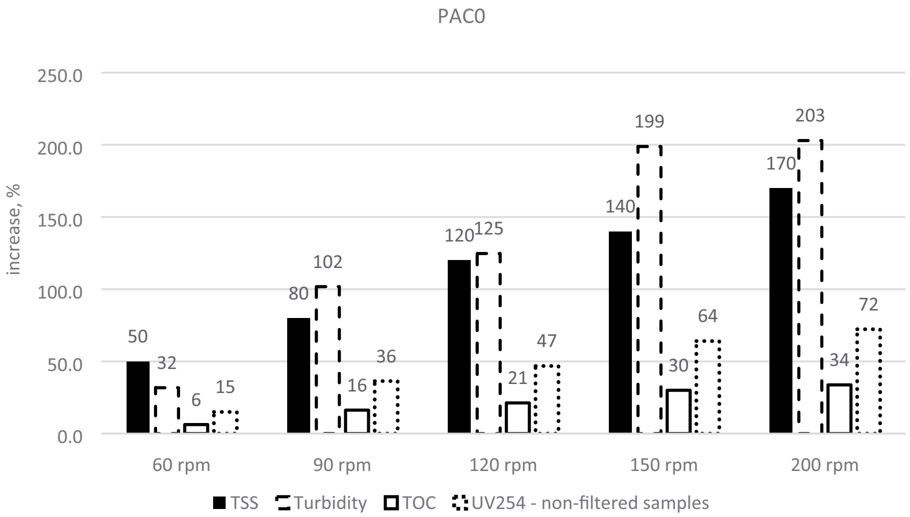

Fig. 2. The impact of mixing rate applied in breaking stage on the increase in the value of water quality parameters after sedimentation of broken flocs in comparison to treatment without breakage stage – PAC0.

based on aluminium chloride (PAC0) and the resistance of flocs formed during flocculation with pre-hydrolyzed coagulants, and this difference increased with the increase of the mixing gradient at flocs breakage stage.

In the case of aluminium chloride (PAC0), at all stirring speeds much higher turbidity of water after breakage and partial regrowth (at the settling stage) was observed in relation to pre-hydrolyzed coagulants. At a rotational speed of 200 rpm, the turbidity of water after sedimentation of broken flocs increased by 203%, TSS and absorbance values (in non-filtered samples) increased by 170% and 72%, respectively, in relation to the values after treatment without flocs rupture. The increase in the values of these indicators were accompanied by the increase in TOC by 34%. This increase was the smallest in relation to the changes in total suspended solids, absorbance UV_{254} and turbidity.

This means that the floc structure was so weak that there was a very strong dispersion of flocs resulting in higher number of particles smaller than 1 μm, which are responsible for turbidity measurement, and the increase of larger aggregates, which are reflected by TSS value.

Based on the results of testing with pre-hydrolyzed coagulants, it was observed that as the coagulant basicity increased, the mechanical strength of flocs also increased.

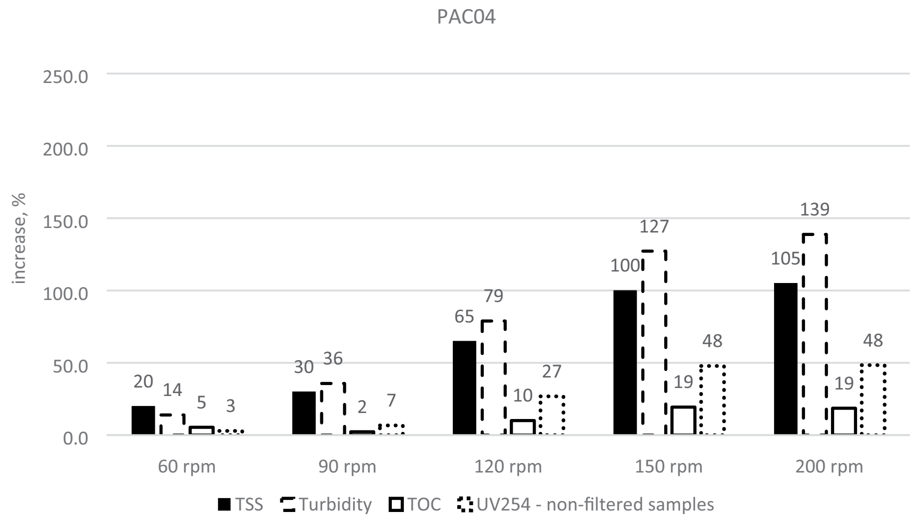

Fig. 3. The impact of mixing rate applied in breaking stage on the increase in the value of water quality parameters after sedimentation of broken flocs in comparison to treatment without breakage stage – PAC04.

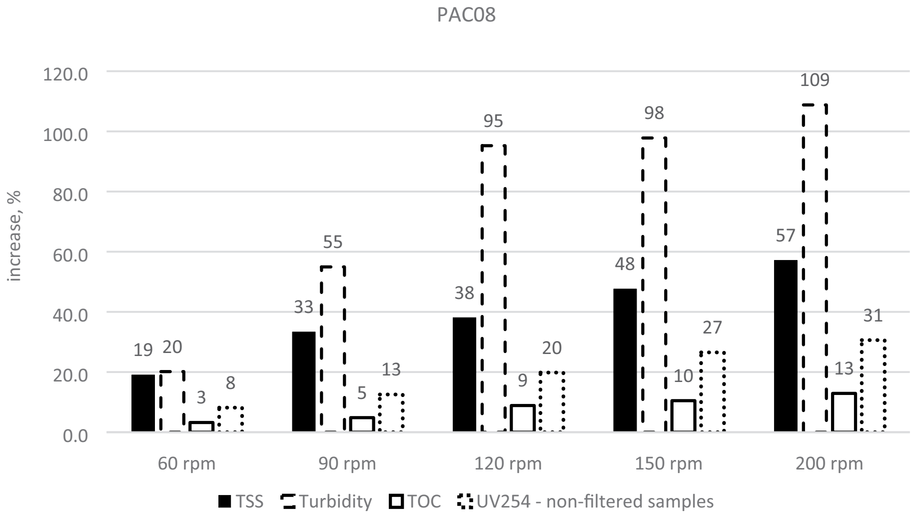

Fig. 4. The impact of mixing rate applied in breaking stage on the increase in the value of water quality parameters after sedimentation of broken flocs in comparison to treatment without breakage stage – PAC08.

After flocs rupture at increasing rotational speed, turbidity, TSS and absorbance UV_{254} in non-filtered samples were higher in all cases in relation to samples without flocs breaking.

The relationship between the increase of water quality indicators values and the rotational speed during breakage stage for PAC0 was almost linear. Similar relationships were observed for pre-hydrolyzed reagents. However, it should be noticed that the impact of the increasing rotational speed at flocs rupture stage on the worsening of water quality, decreased with increasing coagulant basicity, and thus the degree of coagulant polymerization. It may be concluded that the coagulant with a high content of polymerized Al species ($B4 = 1.47$) produced the strongest and most resistant to shear flocs structure.

For PAC04 ($B = 0.42$), at 200 rpm rotational speed at flocs breakage stage resulted in the increase of TSS, turbidity, TOC and absorbance UV_{254} after settling by 105%, 140% 19% and 48%, respectively.

For PAC08 ($B = 0.84$), at the same rotational speed the increase of TSS, turbidity, TOC and absorbance UV_{254} after breakage and settling was by 57%, 109%, 13% and 31%, respectively.

For PAC15 ($B = 1.47$) – the coagulant with highest share of Al_{13}, flocs rupture resulted in the lowest increase of TSS, turbidity and absorbance UV_{254} after breakage and settling stage, that is, by 42%, 93%, 19% and 27%, respectively.

To sum up, for all PAC, with increasing stirring speed during flocs rupture stage, the increase in TSS, turbidity and absorbance UV_{254} was accompanied by an increase in TOC.

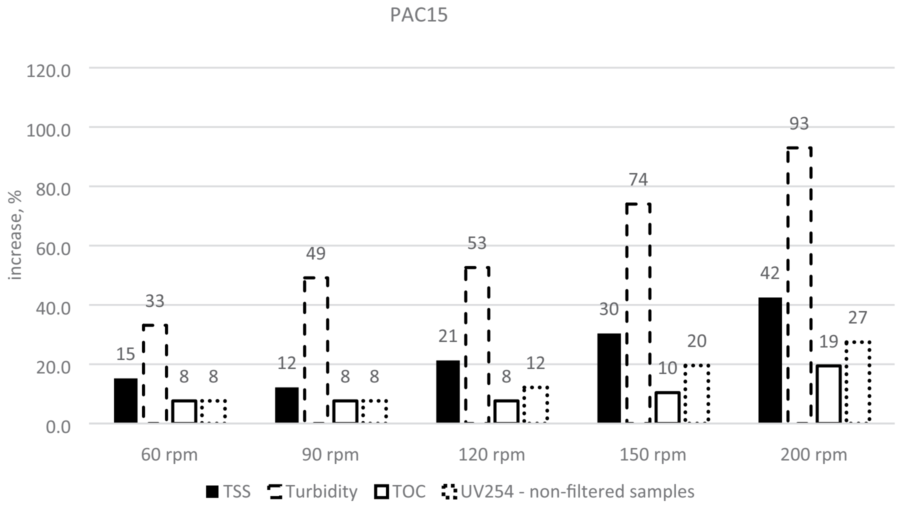

Fig. 5. The impact of mixing rate applied in breaking stage on the increase in the value of water quality parameters after sedimentation of broken flocs in comparison to treatment without breakage stage – PAC15.

However, the TOC increase was the lowest in comparison to other water quality indicators and similar for three pre-hydrolyzed coagulants. It shows that the same factors cause a deterioration of the water quality independently from the coagulant basicity, though the degree of flocs disintegration was different.

The comparison of the increase in the value of basic water qualitative indicators observed in the floc breakage tests (flocs rupture at 200 rpm) and Al speciation does not allow to state simple relationship in the aspect of flocs strength. This is due to the limitations of the interpretation of the ferronometry results. A linear relationship was stated between k_1/k_2 ratio values and the increase of water quality indicators after settling of broken flocs (Fig. 6). The deteriorating flocs resistance to mechanical stress was observed with the increase of k_1/k_2 value. The results suggest that it is appropriate to apply k_1/k_2 ratio analysis to determine flocs strength and it is more useful than relying on Al speciation analysis.

Considering the relationship between the coagulant basicity or k_1/k_2 ratio value and the increase of TSS, turbidity, TOC and UV_{254} after flocs breakage, both basicity and k_1/k_2 ratio can be used for the assessment of coagulants properties in the aspect of flocs strength. However, in the case of B values, as indicated in Fig. 7, the R-squared value (R^2) was lower than for the k_1/k_2 ratio.

The analysis of indicators related to the concentration of dissolved organic compounds in water after the rupture of post-coagulation aggregates, showed that when flocs were broken, there was no desorption of dissolved organic pollutants adsorbed at flocculation stage (no increase of absorbance UV_{254} in filtered samples and DOC were observed). Absorbance UV_{254} values in filtered samples without flocs breakage stage for PAC0, PAC04, PAC08 and PAC15 were 0.092, 0.095, 0.093, 0.097 cm^{-1}, respectively. The similar absorbance UV_{254} values were also noted in samples where flocs rupture stage was incorporated. DOC values noted in the tests without flocs breakage for PAC0, PAC04, PAC08 and PAC15 were 3.7, 4.0, 3.8, 3.9 mg C/dm^3, respectively. Similar to absorbance UV_{254}, no significant influence of flocs rupture on DOC changes were observed. No increase in the values of absorbance UV_{254} (in filtered samples) and DOC indicate that flocs rupture did not result in desorption of dissolved natural organic pollutants into water. It proves the mechanical breakdown of the flocs.

However, due to the flocs rupture, the previously agglomerated NOM colloids were released from the flocs back to the treated water. They were in the form of very fine particles, which did not pass through the membrane filters 0.45 μm. Taking into account the difference between the changes in absorbance UV_{254} (non-filtered samples) and turbidity values, it could be concluded that those particles were probably about 1–2 μm in size. It results from stronger influence of fine particles on nephelometric turbidity measurement than on spectrophotometric absorbance UV_{254} measurement.

Although the differences in flocs size and their strength are caused by the course of hydrolysis during coagulation with hydrolyzing and pre-hydrolyzed coagulants, the presence of humic acids (HA) is very important. If the hydrolysis products are aluminium monomers (Al_m), then they are complexed with humic acids. Al_m-HA complexes are very strong, so they are resistant to breakage. Floc precipitation is delayed until a sufficiently large dose of coagulant is reached that will lead to the adsorption of these complexes on the precipitated hydroxides or to the direct aggregation of Al_m-HA complexes. The resulting aggregates can then attach to larger flocs by charge neutralization mechanism. However, the structure formed during the aggregation of strong Al_m-HA complexes is already much weaker. The presence of Al_{13} polymers leads to co-precipitation with HA in the form of Al_{13}-HA complexes. Due to the large size of the Al_{13} polymer, the precipitated particles can serve as nuclei of the flocculation process, accelerating the collision of particles in water, and thus the growth of flocs. Therefore, the growth rate of these flocs is higher compared

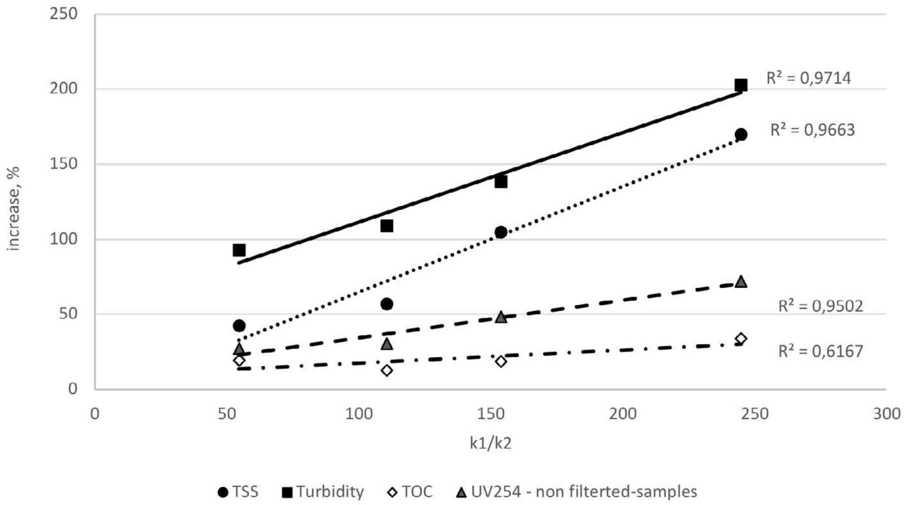

Fig. 6. Relationship between the rate of the basic impurities increase and k_1/k_2 ratio.

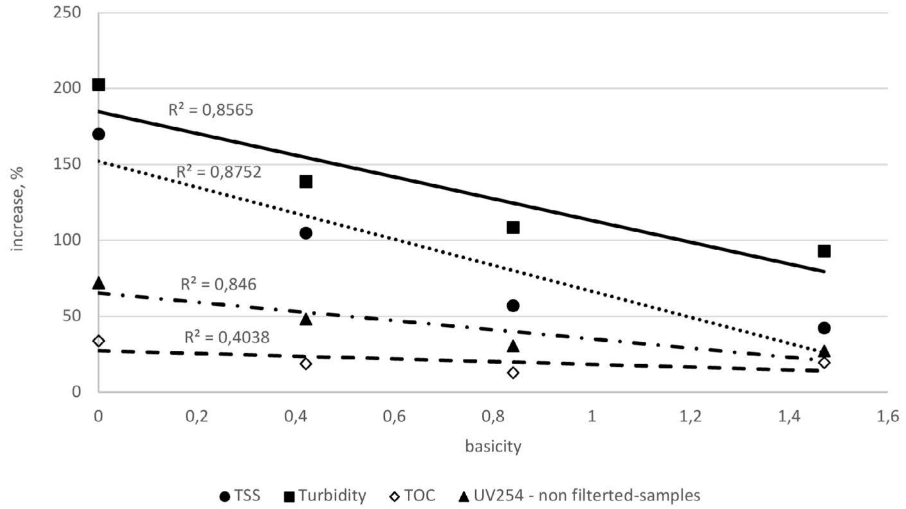

Fig. 7. Relationship between the rate of the basic impurities increase and coagulant basicity.

to hydrolyzing coagulants. However, Al_{13}-HA complexes have a limited number of adsorption sites, hence there are a limited number of bonds that allow flocs to grow. With the time, these complexes decompose, but the time is too long to negatively affect the strength of the flocs [6,21,29].

These differences between the growth rate and stability of Al_m-HA and Al_{13}-HA complexes explain why the flocs produced by hydrolysing coagulants were more prone to rupture and less prone to solid/liquid separation than flocs based on Al_{13} polymer-containing coagulants.

4. Conclusions

The relationships between the basicity, Al speciation, the values of k_1, k_2 and the k_1/k_2 ratio on the flocs strength were analysed. Based on the results of traditional ferronometry it was stated that the basicity of tested coagulants should not be directly related with the aluminium speciation.

The deteriorating flocs resistance to mechanical stress was observed with the increase of k_1/k_2 value and the decrease of PAC basicity. The linear relationships between the increase of TSS, turbidity, TOC and absorbance UV_{254} in non-filtered samples (noted as indicators of flocs strength) in the breakage tests and the k_1/k_2 ratio value or the PAC basicity were observed. It has been shown that k_1/k_2 ratio is a better parameter to estimate flocs properties under stress than basicity. *R*-squared value (R^2) was higher compared to basicity.

The greater the mixing gradient was applied during the floc breaking phase; the worse water quality was obtained after the sedimentation of the broken flocs. A large difference was noted between the resistance to rupture of flocs formed based on aluminium chloride (PAC0, $B = 0$), and the resistance of flocs formed by medium-basicity coagulants. While testing with PAC0, after flocs rupture at 200 rpm and further settling; TSS, turbidity, TOC and absorbance UV_{254}

increased by 170%, 203%, 34% and 72%, respectively, in relation to the results achieved in the tests without breakage stage.

For PAC15 (B = 1.47) – the coagulant with highest share of Al_{13} (which corresponded to the lowest value of the k_1/k_2 ratio compared to the other coagulants) the slightest deterioration in water quality after settling of broken flocs was observed. TSS, turbidity, TOC and absorbance UV_{254} increased by 42%, 93%, 19% and 27%, respectively.

Regardless of the type of coagulant, the flocs rupture did not cause the desorption of dissolved organic pollutants adsorbed at the flocculation stage (no increase in the values of absorbance UV_{254} in filtered samples and DOC was observed referred to the samples treated without breakage stage).

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