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ANALYSIS OF POST-COAGULATION PROPERTIES OF FLOCS IN TERMS OF COAGULANT CHOICE

The knowledge of properties of flocs produced in coagulation may enable one to reduce effects of their breakage in a treatment system. This is particularly important in treatment of water contaminated mainly with natural organic matter; produced flocs are fragile and susceptible to rupture. The purpose of the research was to determine the influence of a coagulant type on post-coagulation suspension strength. The results show that flocs produced based on prehydrolyzed coagulants are more resistant to breakage than those produced by a hydrolyzing coagulant. Strength of post-coagulation suspension increased with the increase of polynuclear Al species (Al_b species).

1. INTRODUCTION

Prehydrolyzed coagulants have become more popular in water treatment and often replace hydrolyzing ones. These coagulants are more effective and much lower doses are required. They are also effective at low temperatures. Moreover, when prehydrolyzed coagulants are applied, the risk of decrease of chemical stability in water is avoided. The main parameter usually applied to characterize these coagulants is basicity. However, the research proved that there is no strict correlation between basicity and coagulation effectiveness. A reliable method of evaluation of coagulants may be based on the analysis of aluminum species. The knowledge of coagulant speciation makes it possible to determine the mechanisms of coagulation which decide about flocs structure and their properties including their resistance to breakage and hence treatment results [1–6].

Two fundamental approaches have been taken in measuring floc strength: a macroscopic measure of the energy required for floc breakage and a microscopic approach that measures the interparticle forces within individual flocs [7, 8]. Taking into con-

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sideration the fact that the applied shear rate determines floc size, most studies on floc strength have been focused on the macroscopic field. Under low shear rate conditions, particles are able to aggregate; under increased shear rate aggregate break-up is observed [9]. Shear-based techniques for determining floc strength allow one to predict how flocs will behave upon exposure to an increased shear rate, as could occur at water treatment works when flocs are transferred from flocculators to sedimentation tanks or to higher shear treatment processes such as dissolved air flotation or high rate filtration. Floc strength can be measured by applying an increased shear rate or a normal stress to the formed aggregates and relating the energy dissipation or velocity gradient applied to the maximum or average floc size remaining [10–12]. The results are monitored by changes in floc size over a range of shear rates. The method of determination of floc size should ensure that the technique used to measure floc size does not damage the aggregates, e.g. commercial particle size instruments that use light scattering to determine particle size or from analysis of video frames or photographs using image analysis systems. Microscopic techniques are carried out to gain a more direct measurement of floc strength by finding the force required to a floc breakage [8, 13–21].

Parker et al. [21] suggested an empirical expression which determines the relationship between the velocity gradient in the flocculating tanks and aggregate size for a stable floc size:

$$d = CG^{-\gamma} \tag{1}$$

where: d – the floc diameter [m], C – the floc strength coefficient, dependent on the method of measurement of the floc size, G – the average velocity gradient [s^{-1}], γ – the stable floc size exponent, dependent on mechanisms for the breakage of flocs under various shear conditions.

Floc strength may also be calculated or determined based on the changes of a floc size after and before breakage. By the theoretical method, flocs are exposed to hydrodynamic stress from a controllable oscillatory mixer [19]. The vibration is converted into an energy input for the system. The average strength per unit area σ in shear surface may be defined as:

$$\sigma \approx \frac{\rho_w \varepsilon^{3/4} d^{1/3}}{\nu^{1/4}} \tag{2}$$

where: σ – the floc strength [N·m^{-2}], ρ_w – the density of water [kg·m^{-3}], ε – energy dissipation at the height of floc rupture [m^2 s^{-3}], ν – kinematic viscosity [m^2·s^{-1}], d – the floc diameter [m].

The lowest σ values were noted for flocs formed in treatment of coloured waters. In comparison to humic flocs, the strength of flocs formed in flocculation of solid particles was much higher [19]. The highest σ values were calculated for flocs formed in water treated with polymer flocculants [8].

The knowledge of properties of flocs may allow one to reduce negative consequences of their breakage in a treatment system. In the paper, influence of coagulant type on resistance of post-coagulation flocs to breakage under increased shear rate conditions are presented. In the studies humic water was tested. The analysis of flocs produced in coagulation of water contaminated with high concentration mineral particles will be the subject of further studies.

2. EXPERIMENTAL

Characteristics of tested coagulants. Since the study was aimed at understanding the shearing characteristics of flocs formed with different coagulants, four reagents were tested: three commercial prehydrolyzed coagulants (PACl1, PACl2, PACl3) and aluminum sulphate (ALS). The prehydrolyzed reagents used in the research are water solutions of complex aluminum chlorohydroxide at a stated polymerization degree supersaturated with $Al(OH)_3$ being in a metastable equilibrium in the solution. PACl1 is produced in "sulphate modification". The characteristics of the coagulants are given in Table 1.

Table 1

Characteristics of tested coagulants

Parameter	Coagulant			
	PACl1	PACl2	PACl3	ALS
Density [g/cm^3]	1.245	1.275	1.350	1.59
pH	3.94	4.21	3.5	3.4
[Al] [wt. %]	9.32	11.46	12.5	9.2
[Cl] [wt. %]	5.53	5.69	9	0
[Al]/[Cl]	1.69	2.01	1.0	0
Basicity [%]	85.69	77.81	85.0	0

The degree of polymerization of aluminum hydroxocomplexes in the coagulant solutions may be determined by the ferronometry method. It 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 $Al(ferron)_3$, at pH = 5.0 ± 0.2, which has a maximum absorption at 370 nm. Ferronometry makes it possible to evaluate the amount of aluminum bound to monomeric, oligomeric and polymeric ions based on the different rates of Al(ferron) complex formation. The higher degree of polymerization, the lower rate of the ferron reaction with aluminum hydro complexes is [22–27]. Thus, the method is based on kinetic analysis of the formation of the ferron–aluminum complex. In traditional ferron assay, 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 form polynuclear Al species of superior quality with structures fairly resistant to further hydrolysis, resulting in higher coagulation efficiency. The fraction of Al that does not react with the ferron reagent within 120 min, i.e. a non-reactive fraction (Al_c), is assumed to represent colloidal, solid-phase Al (Table 2).

T a b l e 2

Aluminum speciation of coagulants tested
by traditional ferron assay

Al fraction [%]	Coagulant			
	PACl1	PACl2	PACl3	ALS
Al_a	4	4	38	92
Al_b	28	53	39	8
Al_c	67	43	23	0

When coagulants of low polymerization degree are considered, the assay presented above is reliable, because the amount of polymer forms is so low that reaction with ferron is completed within 2 h. However, 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, resulting from the presence of high-polymerized fraction. Interpretation of these results allowed dividing polymerized forms Al_b into two groups: quickly reacting with ferron (Al_{b1}) and slowly reacting (Al_{b2}) with ferron [26, 27].

Water sample. Peat extract was mixed with tap water to form water samples. A stock solution of humic substances was obtained by extraction with 0.1 M sodium hydroxide. After 1 week ageing, the clarified solution of humic acids was collected. Testing samples were prepared by diluting the stated volume of aquatic humic extract in 0.7 dm^3 of tap water to simulate coloured water sample. So that to prepare a homogeneous sample while extract diluting it was mixed at 200 rpm for 120 s.

The ranges of raw water quality parameters for bench-scale testing were:
- pH 7.0–7.2,
- total organic carbon (TOC): 4.2–5.0 mg C/dm^3,
- dissolved organic carbon (DOC): 3.5–4.6 mg C/dm^3,
- absorbance $UV_{251\ nm}^{1\ cm}$ – unfiltered samples: 0.21–0.253,
- absorbance $UV_{251\ nm}^{1\ cm}$ – filtered samples (0.45 μm membrane filters): 0.147– 0.224.

There was no possibility to measure absorbance at 254 nm in the designed laboratory system, because the device (Pastel UV Secomam) applied in the system could only measure absorbance at 251 nm. However, comparative measurements made with

a UV-VIS spectrophotometer proved that absorbances measured at 251 nm met the values recorded at 254 nm.

The specific UV absorbance (SUVA) of the raw water was higher than 4.0 dm^3/mg C·m. SUVA is an operational indicator which on one hand allows one to determine the characteristics of NOM and on the other hand – the effectiveness of coagulation in removal of NOM, TOC and DBPs (disinfection by-products) precursors. The SUVA values indicate that natural organic matter in tested water mainly consisted of hydrophobic fractions of a high molecular weight.

Methods. The study in a laboratory scale was carried out with the usage of a six-beaker Flocculator SW1 (Stuart Scientific). In five beakers, rapid-mixing (1 min at the rotational speed of 200 rpm) was followed by 30 min slow mixing (at 30 rpm). Then, produced flocs were ruptured at various rotational speeds (60, 90, 120, 150, 200 rpm) for 1 min and followed by 60 min settling. After settling, the absorbance (in filtered and unfiltered samples), TOC and DOC measurements were taken (Pastel UV Secomam). The sixth beaker was a comparative one (without the stage of flocs rupture after flocculation). All the tests were carried out at the optimum coagulant doses which were stated before. The coagulant dose was optimized for minimum absorbance and TOC values using conventional jar testing procedures. The optimum doses for ALS were in the range 1.5–2.0 mg Al/dm^3. For prehydrolyzed coagulants, the doses were much lower, i.e. 0.2–0.6 mg Al/dm^3. For these doses, treatment resulted in the decrease of absorbance $UV_{251\ nm}^{1\ cm}$ (in unfiltered samples) from 0.21–0.253 to 0.13–0.19 and for TOC from 4.2–5.0 mg C/dm^3 to 2.8–3.9 mg C/dm^3. Each coagulant was tested in six series. The pH of the coagulated water solution ranged from 6.9 to 7.2 depending on a coagulant type.

Additionally, the influence of coagulant dose on flocs resistance to breakage was studied (flocs were ruptured at 90 rpm). The doses for ALS and PACl2 were 1–5 mg Al/dm^3 and 0.2–1.2 mg Al/dm^3, respectively.

3. RESULTS

The presented values were the average ones calculated from six series. The analysis was made based on changes of UV absorbance as an indicator of concentration of organic matter. A strict relationship was found between UV absorbance and TOC values in tested samples (Fig. 1). The results show the discrepancy of flocs properties produced in flocculation with the usage of various coagulants (Figs. 2, 3).

At all tested rupture speeds flocs produced with ALS were the most sensitive to breakage. In comparison to the effectiveness of coagulation without rupture of post-coagulation suspension, UV absorbances increased linearly from 4.2% at 60 rpm to 37.5% at maximum speed of breaking-up (200 rpm).
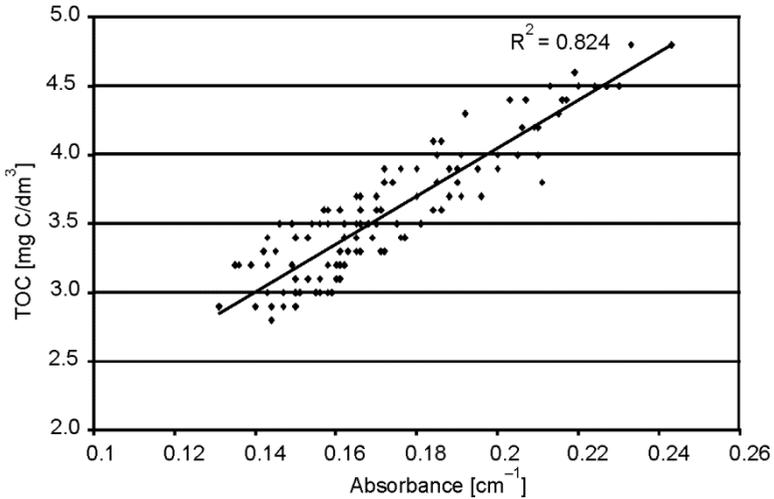
Fig. 1. Dependence of TOC in treated water on the UV absorbance (in unfiltered samples)
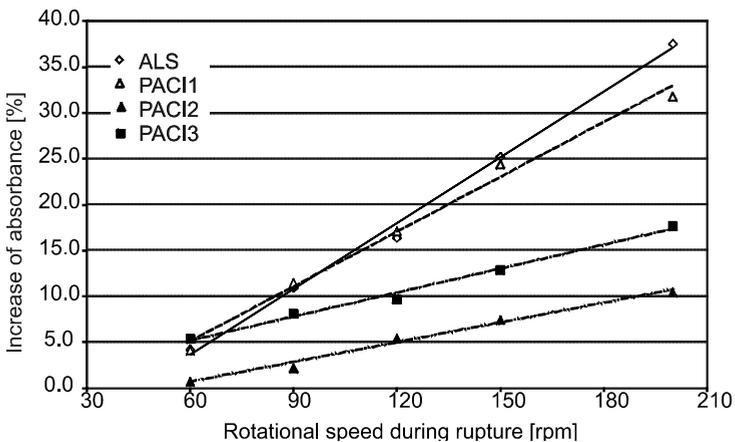

Fig. 2. Influence of rotational speed during flocs rupture on water quality after treatment;
changes of UV absorbance in unfiltered samples

Linear dependences of absorbance changes on the rupture speed were also observed for prehydrolyzed coagulants. For PACl2 and PACl3, the range of changes was distinctly lower. When PACl3 was tested, absorbance increased by 5.4% at 60 rpm and by 17.6% at 200 rpm. The most resistant to breakage were flocs formed when PACl2 was applied, absorbance increased by 0.7% at the lowest rupture speed to 10.4% at the highest stress value. Surprisingly, in tests with PACl1, flocs were very sensitive to stress. Absorbance increased from 4.1% at 60 rpm to 31.8% at 200 rpm. It was concluded that strength properties of flocs produced by that coagulant were similar to these formed in coagulation with ALS. It may result from the fact that PACl1 is,

as the only one, produced in sulfate modification. It has already been proved that the presence of sulphate ions may influence the mechanism of formation of flocs. However, further research is required to find out its significance for flocs strength. The results recorded for TOC were similar to those noted for absorbance $UV_{251\ nm}^{1\ cm}$.
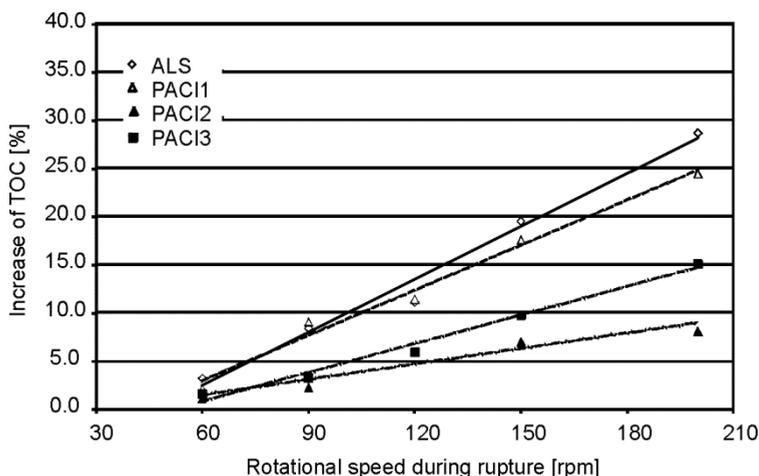

Fig. 3. Influence of rotational speed during flocs rupture
on water quality after treatment; TOC changes

Absorbance $UV_{251\ nm}^{1\ cm}$ and DOC values measured in filtered samples in the comparative beaker for all tested coagulants were the same as values noted in testing when flocs breakage stage was applied. For example, in the series with ALS after conventional treatment (without flocs rupture) absorbance in filtered samples and DOC values were 0.14 and 3.3 mg C/dm^3 (0.16 and 3.6 mg C/dm^3 in unfiltered samples, respectively). In rupture tests the values in filtered samples also were 0.14 and 3.3 mg C/dm^3 for all rupture parameters. In unfiltered samples absorbance $UV_{251\ nm}^{1\ cm}$ and TOC values were 0.17 and 3.8 mg C/dm^3 at 60 rpm and 0.23, 4.8 mg C/dm^3 at 200 rpm, respectively. In the exemplary series with PACl2 absorbance (after membrane filtration) and DOC values after conventional treatment were 0.13 and 2.6 mg C/dm^3 (0.14 and 2.8 mg C/dm^3 in unfiltered samples), respectively. In rupture tests the values in filtered samples did not change for all rupture parameters. In unfiltered samples, $UV_{251\ nm}^{1\ cm}$ absorbance and TOC values were 0.14 and 2.9 mg C/dm^3 at 60 rpm and 0.16 and 3.1 mg C/dm^3 at 200 rpm, respectively. Similarly, no changes of absorbance in filtered samples and DOC values were observed for PACl1 and PACl3 (at the optimum doses). Hence, it was concluded that organic matter once incorporated in flocs matrix is not desorbed into treated water after flocs rupture.

Additionally, the influence of coagulant dose on flocs resistance to breakage was investigated (flocculation was followed by flocs rupture at 90 rpm and 60 min settling period). The results for ALS and PACl2 are presented in Table 3. The optimum coagulants doses for water treated in conventional coagulation (without flocs breakage) were: 1.5 mg Al/dm^3 of ALS and 0.2 mg Al/dm^3 of PACl2. The further increase of reagent doses did not influence on significant improvement of water quality after sedimentation.

Table 3

Characteristics of water after rupture tests at different coagulants doses

ALS dose [mg Al/dm^3]	Raw water	1	1.5	2	3	4	5
TOC	4.3	4.0 (3.6*)	3.8 (3.3*)	3.8 (3.3*)	3.8	3.8	3.6
DOC	4.0	3.4 (3.4*)	3.3 (3.2*)	3.3 (3.2*)	3.2	3.2	3.2
Abs$_U$ (unfiltered samples)	0.24	0.22 (0.2*)	0.21 (0.18*)	0.21 (0.18*)	0.2	0.2	0.19
Abs$_F$ (filtered samples)	0.22	0.18 (0.18*)	0.17 (0.17*)	0.17 (0.17*)	0.17	0.16	0.16
PACl2 dose [mg Al/dm^3]	Raw water	0.1	0.2	0.4	0.6	0.9	1.2
TOC	4.7	3.9 (3.8*)	3.0 (2.9*)	2.9 (2.9*)	2.9	2.9	2.8
DOC	4.1	3.2 (3.2*)	2.9 (2.9*)	2.8 (2.8*)	2.8	2.7	2.7
Abs$_U$ (unfiltered samples)	0.22	0.18 (0.17*)	0.12 (0.12*)	0.12 (0.12*)	0.12	0.12	0.11
Abs$_F$ (filtered samples)	0.18	0.13 (0.13*)	0.12 (0.12*)	0.12 (0.12*)	0.12	0.12	0.11

*Exemplary results for conventional treatment (without flocs rupture).

The results presented in Table 3 show that ALS (2–5 mg Al/dm^3) and PACl2 (0.4–1.2 mg Al/dm^3) overdosing did not affect effectiveness of the treatment in the series with rupture stage. If in the rupture test too low dose of ALS (1 mg Al/dm^3) was applied, the values of TOC and absorbance in unfiltered water were higher than those at the optimum ALS dose. ALS flocs were very small and fragile and after breakage they were much less susceptible to reagglomeration and settling than PACl2 flocs. PACl2 flocs easier reagglomerated even when too low reagent dose (0.1 mg Al/dm^3) was applied. However, flocs rupture had no influence on absorbance and DOC values in filtered samples in comparison to conventional treatment for all tested coagulants doses.

4. INFLUENCE OF COAGULANTS SPECIATION ON FLOCS STRENGTH

Significant differences of strength of post-coagulation suspension formed during coagulation by tested coagulants occurred. The most distinct difference was observed between flocs produced by hydrolyzing ALS and the highest-polymerized PACl2. Therefore, for all those reagents an attempt was made to find the relationship between coagulants characteristics, including Al speciation and flocs strength. Figures 4–6

show relationships between the increase of UV absorbance (in unfiltered samples) after flocs rupture at 200 rpm and contents of Al fractions in tested coagulants. Absorbance increase was assumed to be an indicator of flocs strength.

No strict correlation was visible between the contents of Al_a and Al_c fraction and floc resistance to rupture (Figs. 4 and 6). However, there was high influence of Al_b species on flocs strength. The higher Al_b fraction in coagulant was noted, the higher floc resistance to breakage was observed ($R^2=0,93$). Figure 5 shows that the highest deviation from the linear model of relationship between Al_b fraction and absorbance increase in rupture tests was noted for PACl1.
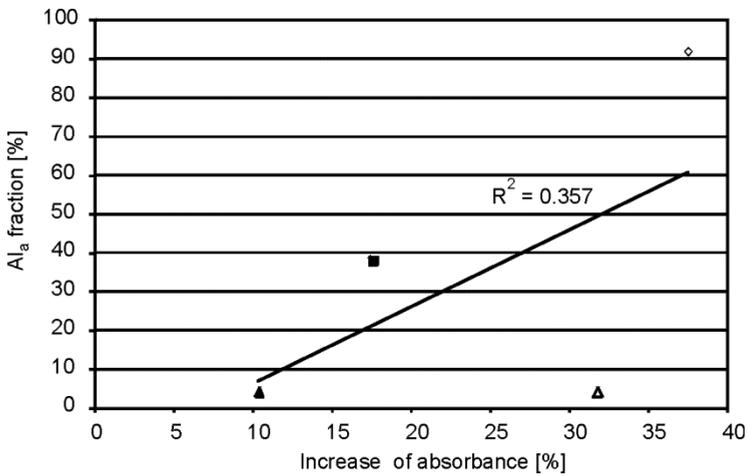

Fig. 4. Dependence Al_a fraction contents in tested coagulants on increase of UV absorbance (unfiltered samples) after flocs rupture at 200 rpm
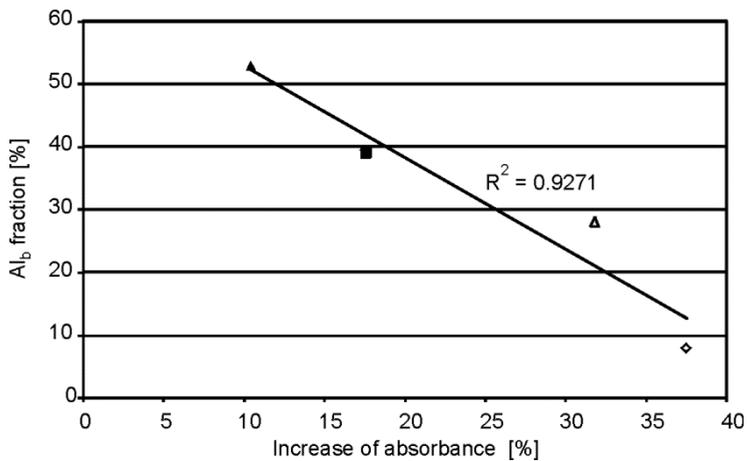

Fig. 5. Dependence Al_b fraction contents in tested coagulants on increase of UV absorbance (unfiltered samples) after flocs rupture at 200 rpm
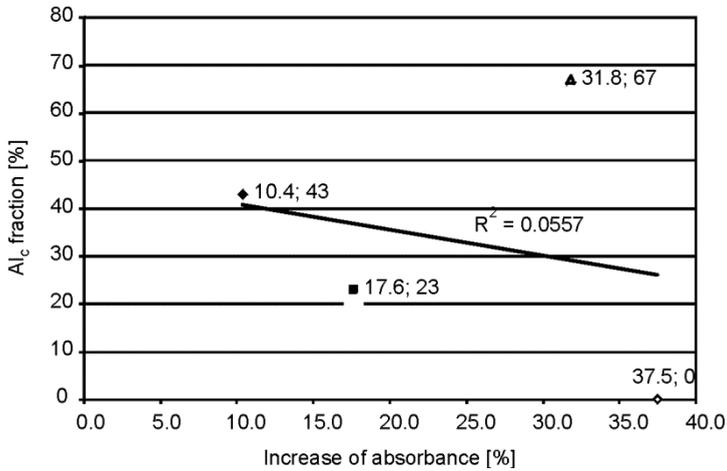
Fig. 6. Dependence Al_c fraction contents in tested coagulants on increase of UV absorbance (unfiltered samples) after flocs rupture at 200 rpm

So that to pre-estimate strength of flocs produced by prehydrolyzed coagulants, besides determination of Al species, basicity and Al/Cl ratio were also considered. Figures 7 and 8 show the relationship between the increase of absorbance after flocs breakage which was assumed to be an indicator of flocs strength, and [Al]/[Cl] ratio and basicity. Taking into consideration these results, no linear correlation between flocs resistance to rupture and [Al]/[Cl] ratio ($R^2 = 0.12$) and basicity ($R^2 = 0.65$) were found. This confirms that [OH]/[Al] ratio, being a commonly used parameter to characterize prehydrolyzed coagulants, is not a suitable criterion for prediction of flocs properties. [Al]/[Cl] ratio cannot also be used as a reliable parameter to estimate flocs strength.
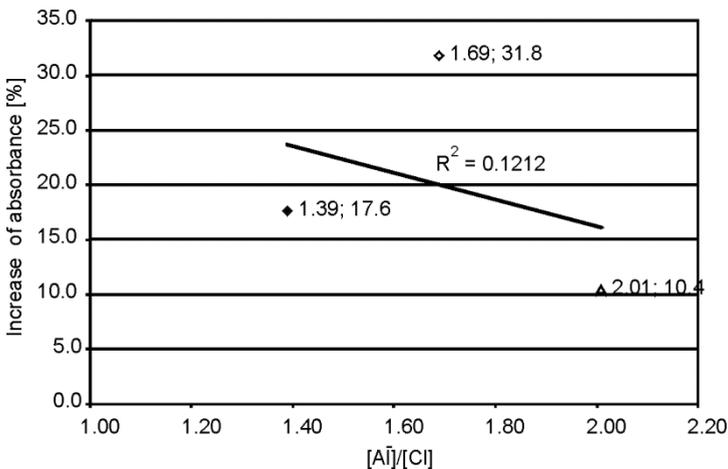

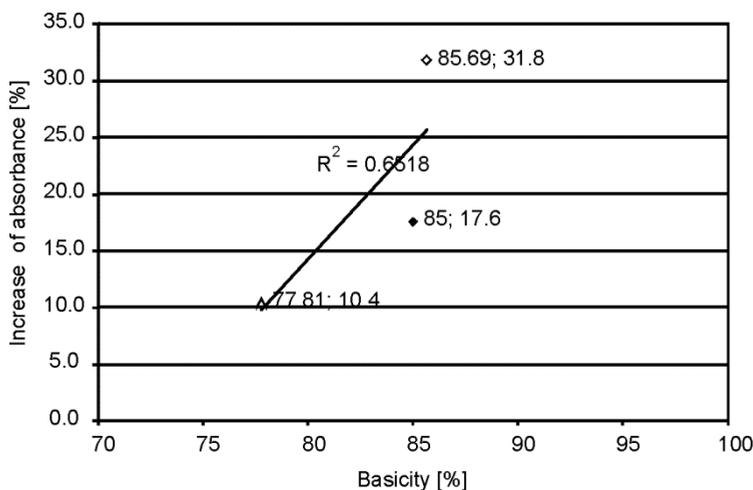Fig. 7. Dependence of increase of absorbance on [Al]/[Cl] ratio after flocs breakage (at 200 rpm)

Fig. 8. Dependence of increase of absorbance on basicity after flocs breakage (at 200 rpm)

Further studies should be focused on examination of more detailed coagulant properties. It is well known that the technology of coagulant production is very important and a coagulant characteristic presented by the producer is not sufficient to gain knowledge about its chemical composition.

5. CONCLUSIONS

Flocs strength should be an important criterion in a coagulant choice. Flocs produced based on prehydrolyzed coagulants were more resistant to breakage than those produced by alum coagulation.

A strict correlation between the presence of Al_b fraction in coagulants and flocs strength was found. Strength of post-coagulation suspension increased with the increase of contents of Al_b species.

The highest resistance to rupture was noted for flocs formed in coagulation by PACl2, less resistant were flocs produced by PACl3. Much more sensitive were flocs formed by PACl1. The least resistance was noted when alum was applied, and the results were comparable to those for PACl1.

For tested coagulants, there was no correlation between their basicity and flocs resistance to rupture.

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