RELIABILITY OF FERRONOMETRY ASSAYS FOR ALUMINUM SPECIATION IN PRE-HYDROLYZED COAGULANTS

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Received: 15.04.2013; Revised: 13.06.2013; Accepted: 10.12.2013

Abstract
Six prehydrolyzed commercial Al polychlorides of various basicity and aluminium sulphate (alum) were analyzed to determine the reliable method of Al speciation. The tests were carried out on the basis of colorimetric reaction of ferron with aluminum species. The analysis results were calculated based on two commonly used methods. The results have shown that the traditional ferron method may introduce errors when monomeric and polynuclear Al (Al_a and Al_b) do not react with ferron reagent within 0-2 min and 2 h, respectively. The effect of inaccuracies in the calculation assumptions appears to be significant for aluminum speciation. The method based on reaction rate constants allows determining the form of monomeric and polymeric forms, including polycation Al_{13}, which is particularly desirable in coagulation based on neutralization of the negative charge of contaminants present in treated water.

Streszczenie
W artykule zaprezentowano wyniki badań, których celem było ustalenie wiarygodnej metody analizy specjacyjnej glinu dla siarczanu glinu oraz sześciu komercyjnych koagulantów wstępnie zhydrolizowanych – polichlorków glinu, o różnej zasadowości. Testy zostały przeprowadzone na podstawie reakcji kolorymetrycznej ferronu z glinem o różnym stopniu polimeryzacji. Wyniki analizy obliczono w oparciu o dwie powszechnie stosowane metody. Na podstawie analizy wyników badań stwierdzono, że tradycyjna metoda jest niewiarygodna, gdyż jest oparta o nieścisłe przedziały czasowe. Skutkiem różnych przedziałów czasowych przyjętych do obliczeń są znaczące różnice w wynikach analizy specjacyjnej glinu. Wiarygodną metodą jest natomiast metoda oparta na analizie stałych szybkości reakcji, co pozwala na określenie udziału form monomerowych, jak i polimerowych, w tym polikationu Al_{13}, który jest szczególnie pożądany podczas koagulacji realizowanej w oparciu o neutralizację ujemnego ładunku zanieczyszczeń obecnych w wodzie.

Keywords: **Prehydrolyzed coagulants; Speciation characteristics; Ferronometry; Basicity.**

1. INTRODUCTION

Coagulation as the primary surface water treatment process is still the subject of vast research on how the improvement of the efficiency of this process makes it possible to improve the quality of treated water in the whole technological system. It is practically the only process unit, which allows increasing the efficiency of removal of organic matter from water, which is especially very important in terms of risk of the formation of disinfection by-products. The easiest way, which is often sufficient to obtain the required water quality, is to change the type of coagulant. At present, polyaluminium chlorides (PACls) are applied at many water treatment plants, because they are usually more effective, also at low temperatures, than aluminum sulfate [1-4].

The basic information provided by the manufacturers to characterize pre-hydrolyzed coagulants is basicity and aluminum concentration, whose the parameters are not clear guideline to determine the effectiveness of these coagulants. The key information that allows determining the mechanisms of coagulation and hence optimum coagulation parameters, especially coagulant dosage, is aluminum speciation. It is defined as the share of monomeric and polymeric, especially Al_{13}, species [5].

The aim of the research presented in the paper was to determine a reliable method of aluminum speciation in pre-hydrolyzed coagulants. The tests were carried out on the basis of colorimetric reaction of ferron with aluminum species. The analysis results were calculated based on two commonly used methods.

2. METHODS

2.1. Reagents

The characteristics of tested coagulants are shown in Table 1.

Table 1.
Coagulants characteristics

coagulant	OH/Al	Al^{3+} %	Al_2O_3 %	Cl^- %
PACl1	2.4	11.0	20.79	7.0
PACl2	2.4	6.0	11.34	4.0
PACl3	2.55	12.5	23.6	8.5
PACl4	2.55	8.5	16.0	5.5
PACl5	2.1	11.0	20.79	10.0
PACl6	1.95	8.5	16.0	9.0
Alum	0	4.2	7.9	0

Speciation analysis was calculated based on two methods: k-value ferron assay and traditional ferron assay [6-10].

Ferron method can distinguish various forms of Al by their different rates of reaction with the ferron reagent (8-hydroxy-7-iodo-5-quinoline sulfonic acid). In traditional method 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 slower than Al_a (1–120 min) are thought to include polynuclear Al species (Al_b). Polynuclear species is regarded to ensure high coagulation efficiency. The fraction of Al that does not react with the ferron reagent within the time of experiment (typically 120 min), i.e. a non-reactive fraction (Al_c), is assumed to represent colloidal, solid-phase or polymeric Al. The total concentration of aluminum (Al_T) can be calculated according to formula:

$$Al_T = Al_a + Al_b + Al_c \quad (1)$$

In recent years, ferron complexation timed spectrophotometry has become the main method to measure aluminium speciation. However, the classification of Al_a, Al_b, and Al_c is based on the arbitrary reaction time of hydrolyzed aluminum complexation with ferron. Therefore, the results are somewhat random and cannot accurately reveal the chemical species generated and transformed during aluminum salt hydrolysis, coordination and polymerization. Therefore, using the ferron method to measure aluminium species may introduce errors when monomeric and polynuclear Al (Al_a and Al_b) do not react with ferron reagent within 1 min and 2 h, respectively. Kinetics curves provide a more accurate method of identifying the Al speciation and include information about all phases of the Al-ferron reaction [6].

The second method to analyze aluminium species is based on the assumption that the mononuclear Al and ferron react instantaneously and the mononuclear Al contribute all its absorbance at t = 0, i.e., A_0. The subsequent increases of absorbance comprise of absorbance resulting from parallel reactions between ferron and polynuclear species [7]. The reactions between polynuclear Al species and ferron conform to pseudo-first-order, so the whole model can be expressed in the following equation:

$$A_t = A_0 + \Sigma_x (A_x - c) (1 - exp(-k_x t)),$$

where:

A_t, A_0 –the absorbance measured at any time and zero time, respectively

A_x (x = 1,2) – the absorbance resulting from the reaction between ferron and polynuclear Al species that would be measured at infinite time

k_x (x = 1,2) – kinetic constants (k values) for various Al species

c – constant value depending on experiment system.

In this method, the polymeric species can be identified by its k value and its fraction can be calculated from A_x.

3. RESULTS

The figures 1-7 presents the kinetics curves for 7 tested coagulants.

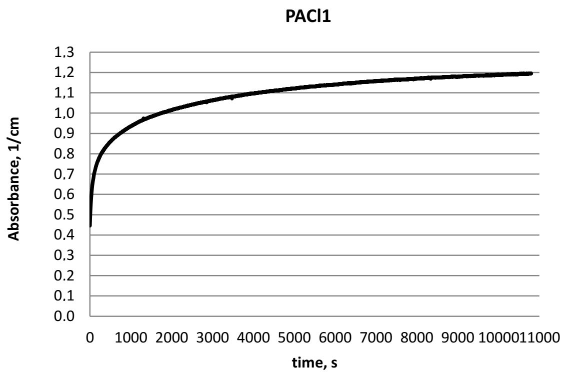

Figure 1.
Timed colorimetric analysis of PACl1

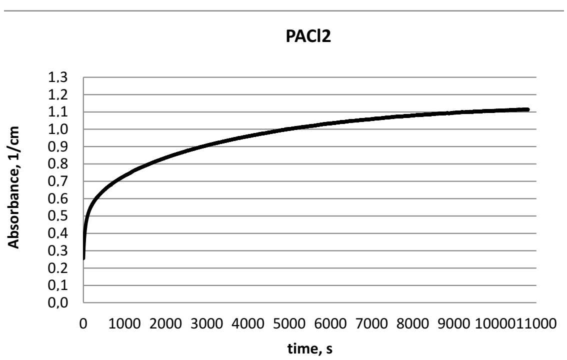

Figure 2.
Timed colorimetric analysis of PACl2

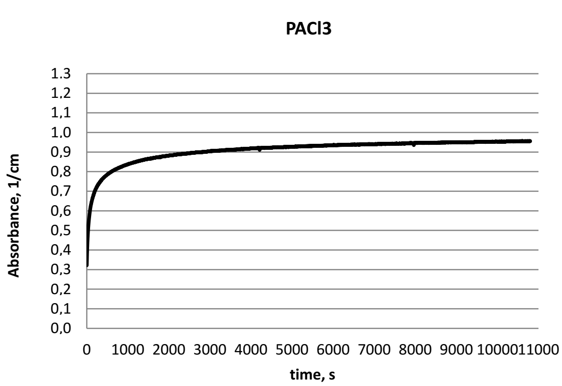

Figure 3.
Timed colorimetric analysis of PACl3

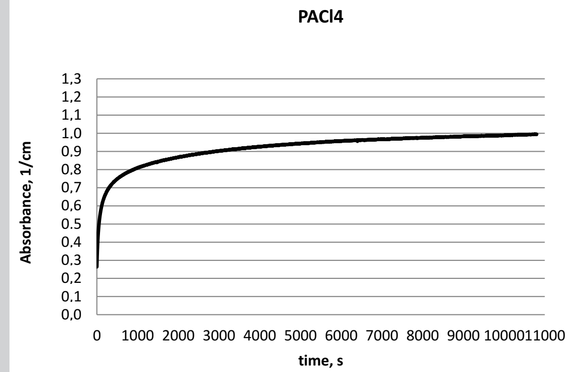

Figure 4.
Timed colorimetric analysis of PACl4

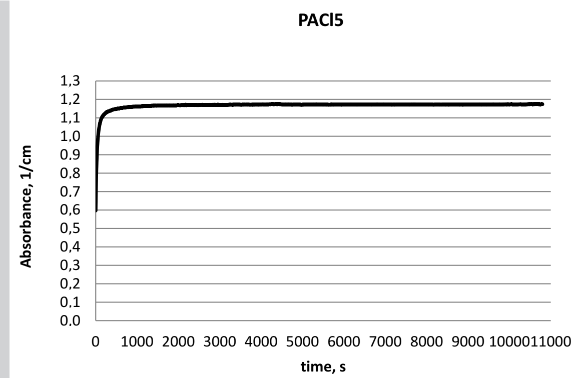

Figure 5.
Timed colorimetric analysis of PACl5

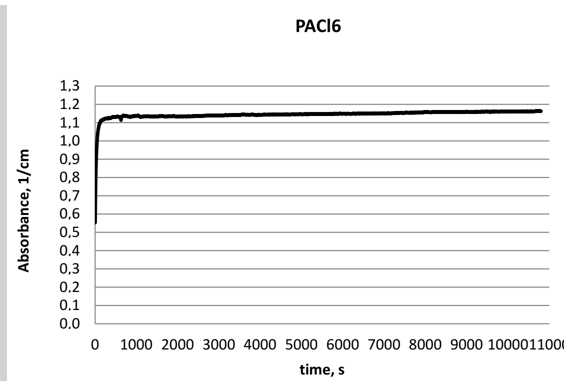

Figure 6.
Timed colorimetric analysis of PACl6

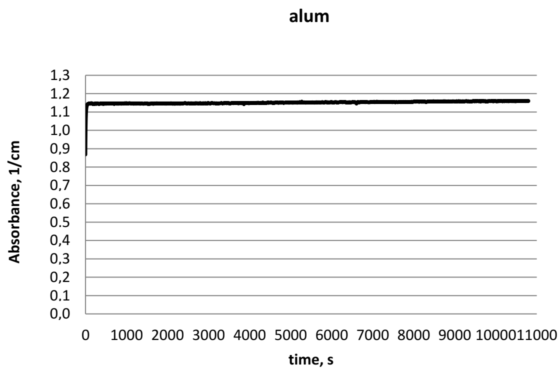

Figure 7.
Timed colorimetric analysis of alum

During the measurements, it was found that, the reaction time between ferron and aluminium species was longer than 2 hours. It was due to the presence of polymeric forms slow-reacting with ferron. Disregarding the results of increase in absorbance after 120 minutes in traditional method was one of the reasons for the differences in the resulting coagulant speciation analysis using both measurement methods (Table 2., Table 3.)

Table 2.
Aluminium speciation based on traditional ferron assay

Traditional method		
coagulant	Monomery %	Polimery %
PACl1	54.07	45.93
PACl2	40.74	59.26
PACl3	57.61	42.39
PACl4	57.18	42.82
PACl5	85.62	14.38
PACl6	89.23	10.77
Alum	98.65	1.35

Table 3.
Aluminium speciation based on k-value ferron assay

k-value-based ferron assay			
coagulant	monomers %	rapid species (oligomers) %	tridecamers %
PACl1	11.08	41.70	47.21
PACl2	15.49	32.47	52.04
PACl3	14.25	53.07	32.68
PACl4	12.71	56.12	31.17
PACl5	22.37	49.69	27.94
PACl6	8.02	85.93	6.06
Alum	90.65	4.09	5.35

The data obtained by means of the two ferron methods of aluminium speciation are significantly different from each other. The largest difference is the content of monomeric forms. The monomers fraction calculated on k-value-based ferron assay is in the range 8.02-22.37% for pre-hydrolyzed coagulants, and 90.65% for aluminum sulphate. At the same time the content of monomeric species determined according to traditional method varied over a wide range from 40.74% to 89.23%, for alum it was 98,65%. Such a significant difference in the results obtained using both methods results from the fact that a traditional assay does not take into consideration the actual kinetics rate.

The changing value of a constant rate means that other aluminium species began to react with ferron. However, in a traditional method, the aluminum fraction of a particular form is determined based on arbitrary reaction time of hydrolyzed aluminum complexation with ferron, which is not equivalent to the fact that only one aluminium species have been detected. According to the traditional method the first 60 seconds of reaction corresponds only to monomers, but the analysis of kintetics constants in this period indicates that they have undergone changes, which is tantamount to the fact that not only monomers, but also oligomers have reacted with ferron.

Additional inaccuracy obtained on the basis of traditional assay stems from the fact that in the literature the monomers are determined based on various assumptions. For their calculation three different time periods, i.e. 30 s, 60 s, 120 s are adopted. No clear criteria means that for the same sample fraction of the monomers may differ significantly.

The analysis of polynuclear species confirms a significant difference between the results obtained by traditional method and the k-value-based method. Speciation analysis of aluminum, based on the reaction rate constants allows specifying the fraction of monomers, oligomers and polynuclear species. It has been stated that the slow-reacting species with ferron (constant k_2) is tridecamer Al_{13}, as confirmed by the results of studies using NMR (Nuclear Magnetic Resonanse). The content of polymeric species of aluminum determined by the two methods is definitely different. The results calculated based on the traditional method shows that the fraction of tridecamer Al_{13} varies in the range 10.8-59.26%, while based on the reaction rate constants 77.6-92%.

4. CONCLUSIONS

- Speciation analysis of pre-hydrolyzed coagulants is crucial for determining the coagulation mechanisms and their effectiveness in removing impurities.
- The traditional ferron method to measure aluminium species may introduce errors when monomeric and polynuclear Al (Al_a and Al_b) do not react with ferron reagent within 1 min and 2 h, respectively.
- Kinetics curves provide a more accurate method of identifying the Al speciation and include information about all phases of the Al-ferron reaction.
- The method based on reaction rate constants allows determining the form of monomeric and polymeric forms, including polycation Al_{13}, which is particularly desirable in coagulation based on neutralization of the negative charge of contaminants present in treated water.

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