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The effect of the type of hydrolysis of aluminum coagulants on the effectiveness of organic substances removal from water

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ABSTRACT

The purpose of the present study was to evaluate the effectiveness of the volumetric coagulation process in the removal of organic substances from water using polyaluminum chloride with commercial name PAXXL10 and aluminum sulfate (VI) undergoing acid hydrolysis and sodium aluminate which undergoes basic hydrolysis in water. The subject of the research was a mixture of surface water from the Obrzyca river and groundwater from quaternary formations. Analysis of the obtained results showed that regardless of the type of coagulant used, dissolved organic carbon (DOC) fractions with a high content of aromatic rings and thus a high potential for creating by-products of oxidation and disinfection were more effectively eliminated. Among the tested coagulants, the pre-hydrolyzed PAXXL10 coagulant provided the greatest efficiency of total organic carbon removal from water. Aluminum sulfate (VI) undergoing acid hydrolysis and therefore the highest pH-lowering of the water to be treated provided greater DOC removal efficiency than PAXXL10, but only in the high dose range from 4 to 5 mg Al/L and higher efficiency of removing aromatic organic substances (UV_{254}) in the whole range of tested doses. The least useful coagulant for the removal of all organic matter fractions was sodium aluminate undergoing alkaline hydrolysis in water.

Keywords: Organic substances; Coagulation; Aluminium sulfate (VI); Sodium aluminate; Polyaluminum chloride; Acid hydrolysis; Basic hydrolysis

1. Introduction

To ensure the required quality of water supplied to consumers, it is necessary to remove primary impurities and prevent secondary contamination in the treatment system as well as in the water distribution system. Pollutants and organic admixtures found in natural waters belong to the basic precursors of oxidation and disinfection products, whose presence in water due to their toxic, genotoxic, mutagenic or carcinogenic effects poses a health risk to their consumers [1–4]. Natural organic matter (NOM) is considered to be a precursor for carcinogenic disinfection by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs) that can form during chlorination [5,6] and contribute to bacterial regrowth and biofilm formation in drinking water distribution systems [7]. There is no doubt here that NOM often contributes to offensive taste and odors in potential drinking water sources and acts as a carrier for metals and various harmful organic chemicals. In addition, NOM can lead to other problems, such as increasing coagulant demand and membrane fouling [8]. Therefore, the need to remove organic matter from water is indisputable. In most water treatment systems, mainly of the surface ones, the most effective problems are the elimination of organic substances, and the most difficult ones are its dissolved fractions. The effectiveness of the coagulation process in the removal of organic substances increases with their molecular weight and degree of aromaticity, therefore hydrophobic macromolecular compounds

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with an aromatic character are best removed, and the most difficult are small molecule and non-ionic hydrophilic fractions [9–11]. High molar mass compounds are more readily removed than low molar mass compounds most likely because of the high molar matter is quite hydrophobic in nature, consisting of more aromatic compounds [12–15]. Hydrophobic NOM has been observed to carry high levels of negative charge due to the presence of ionized groups such as carboxylic and phenolic groups. Thus, the hydrophobic fraction dominates the specific colloidal charge character of water, and fractions with higher charges are more amenable to removal [16–18]. NOM absorbs light over a wide range of wavelengths (λ), whereas inorganic chemicals typically present in natural waters do not absorb light significantly at $\lambda > \sim 230$ nm. As a result, the absorbance of light by natural waters is a semi-quantitative indicator of the concentration of NOM in the water. The molecules of organic compounds that are capable of absorption in the UV and VIS range are chromophores or groups of atoms responsible for selective electron absorption. The richest fraction of natural organic substances in terms of the content of chromophore groups are humic acids, which contain aromatic rings substituted with carbonyl, carboxyl, and hydroxyl groups, as well as alkene chains containing unsaturated double bonds. In the water treatment industry, light absorbance at 254 nm has been found useful for monitoring the concentration of dissolved organic carbon (DOC) containing in its composition aromatic molecules. The UV absorbance at 254 nm is mainly exhibited by humic acids, tannins, lignins, phenols as well as other organic compounds containing aromatic rings in the molecule [19,20]. Ultraviolet absorbance at 254 nm related to the content of DOC in water makes it possible to calculate the specific UV absorbance (UV-SUVA) on the basis of which the susceptibility of organic compounds to the coagulation removal can be assessed [21,22]. $\text{SUVA}_{254} \geq 4$ m^2/gC values indicate the presence of mainly aromatic high molecular weight hydrophobic fraction in water, while $\text{SUVA}_{254} \leq 2$ m^2/gC values indicate the presence of low molecular weight hydrophilic non-humic substances. SUVA_{254} values in the range of $2 \div 4$ m^2/gC mean that both hydrophilic and hydrophobic as well as low- and high-molecular natural organic compounds are found in water [23,24]. Effectiveness of coagulation in removing organic substances from the water with a high SUVA (>4 m^2/gC), can be up to 80%, while for water with a small SUVA (<3 m^2/gC) it does not exceed 30% [1]. The use of SUVA_{254} increases the controllability of the water purification process, in particular the dosing of chemicals such as coagulants and oxidants. It also helps in assessing the effectiveness of the technological processes. Intensification of the removal of organic substances from water during volume coagulation is possible due to the use of optimal process parameters such as type and dose of coagulant, optimal pH as well as time and intensity of mixing [25–27]. Coagulants, which are aluminum and iron salts added to water are dissociated and then the hydrolysis of their cations takes place. The valency of cationic coagulants determines the number of hydrolysis stages. The most commonly used aluminum coagulants are aluminum sulfate (VI), aluminum chloride and sometimes sodium aluminate. In recent years, pre-hydrolyzed coagulants, such as basic polyaluminum chlorides or aluminum polyhydroxychlorosulfates, have become increasingly popular. Aluminum sulfate (VI) as a salt of a strong acid and a weak base undergoes acid hydrolysis in water, which results in the formation of Al(OH)_3 and sulfuric acid (VI) (reaction 1):

$$\text{Al}_2\left(\text{SO}_4\right)_3 + 6\text{H}_2\text{O} \rightleftarrows 2\text{Al}\left(\text{OH}\right)_3 + 3\text{H}_2\text{SO}_4 \tag{1}$$

The aluminum sulfate (VI) added to water can form monomers depending on the pH: Al^{3+}, Al(OH)_2^+, Al(OH)^{2+}, Al(OH)_3, and Al(OH)_4^-. In the water they may also form polymers having the general formula $\text{Al}_n(\text{OH})_y^{3n-y}$ and the pH value determines the charge of these hydroxyl complexes. The acidic environment is dominated by polycations and in basic polyanions [28–30]. The lowest solubility of Al(OH)_3 is at pH 6.5–7.5, while colloidal aluminum hydroxide, which precipitates in a colloidal form, has a positive charge in the range of pH 5.5–7.6, and at pH about 8 it dissolves to Al (OH)_4^- [31,32]. The concentration of H^+ ions affects the degree of hydrolysis which is a reversible reaction. Natural waters almost always contain HCO_3^- ions that bind H^+ ions. After taking into account the dissociation, hydrolysis, and H^+ ion reactions, the total reaction for aluminum sulfate (VI) is as follows (reaction 2):

$$\text{Al}_2\left(\text{SO}_4\right)_3 + 3\text{Ca}\left(\text{HCO}_3\right)_2 \rightleftarrows 2\text{Al}\left(\text{OH}\right)_3 + 3\text{CaSO}_4 + 6\text{CO}_2 \tag{2}$$

As a result of the hydrolysis reaction of aluminum sulphate (VI), free CO_2 is formed and the alkalinity of water is consumed. In contrast, the reaction of hydrolysis of sodium aluminate in natural waters has the following course (reaction 3):

$$\begin{aligned}&\text{Na}_2\text{Al}_2\text{O}_4 + 2\text{Ca}\left(\text{HCO}_3\right)_2 + 2\text{H}_2\text{O} \rightleftarrows 2\text{Al}\left(\text{OH}\right)_3 + \\ &\quad 2\text{CaCO}_3 + 2\text{NaHCO}_3\end{aligned} \tag{3}$$

As it results from reaction 3 sodium aluminate does not cause acidification of the purified water [33]. According to many authors [34–36], it is possible to increase the effects of coagulation due to the use of pre-hydrolyzed coagulants or acidification of water before the coagulation process, which, unfortunately, intensifies the corrosive aggressiveness of water. The greater the degree of initial hydrolysis of coagulants (higher value of the alkalinity coefficient ($r = [\text{OH}^-]/[\text{Al}^{3+}]$), the lower is the aggressiveness of the acid carbonic aggressiveness which for polyaluminum chloride explains reactions 4–7.

For $r = 1$

$$\text{Al}\left(\text{OH}\right)\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Al}\left(\text{OH}\right)_3 + 2\text{HCl} \tag{4}$$

$$2\text{HCl} + \text{Ca}\left(\text{HCO}_3\right)_2 \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O} + 2\text{CO}_2 \tag{5}$$

For $r = 2$

$$\text{Al}\left(\text{OH}\right)_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{Al}\left(\text{OH}\right)_3 + \text{HCl} \tag{6}$$

$$\text{HCl} + 0.5\text{Ca}\left(\text{HCO}_3\right)_2 \rightarrow 0.5\text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2 \tag{7}$$

Controlled initial hydrolysis of aluminum salts occurring during the production of polyaluminum chloride causes that they contain more polymerized aluminum forms with a high positive charge than those generated during rapid and uncontrolled hydrolysis of aluminum sulfate (VI) [37–39]. Coagulation, the aim of which is the highly effective removal of disinfection by-products precursors is known as intensified coagulation. It has been shown that the effectiveness of total organic carbon (TOC) removal from water increases with increasing its content and together with lowering the pH in raw water [40]. In the case of organic substances with increasing pH value, their degree of dissociation increases and the dose of coagulant required for their effective removal is greater. In general, the pH value to a greater extent affects the stability of organic colloids (more difficult to remove) than inorganic ones [41,42]. Colloid stability is determined by the value of the electrokinetic potential ζ, which is defined as the electrokinetic potential occurring at the boundary between the bound and free liquid, between the ionic bound motionless in the adsorption layer and the free counterions of the diffusion layer. As the electrokinetic potential increases ζ the stability of the colloidal system increases, so the repulsive forces acting between the particles are greater [39]. It was also shown that the electrokinetic potential ζ is proportional to the charge density on the surface of the colloid, which depends on the pH. Therefore, the value of electrokinetic potential ζ will vary depending on pH and electrolyte concentration [43]. Lowering the pH value of purified water, which is equivalent to an increase in the positive charge of coagulant hydrolysis products, increases the neutralization efficiency of the removed organic substances, and as a result, the degree of removal of DOC is also increased. The increase in pH intensifies the hydrolysis of coagulants, thus the hydroxides of coagulant cations ($Al(OH)_3$ and $Fe(OH)_3$), are formed faster, whose destabilizing force negative electrokinetic potential of removed colloids is much smaller than the products of hydrolysis with positive electric charge [44–48]. As a result, a larger dose of coagulants is required to achieve the same colloid destabilization effects. In the case of unhydrolyzed coagulants initially (eg, aluminum sulfate (VI) or iron (III) sulfate (VI)), the condition for obtaining the right amount of positive hydrolysis products is lowering the pH value, below 6, which, unfortunately, intensifies the corrosivity of water [49–51]. According to Pernitsky and Edzwald [36,37], the use of pre-hydrolyzed polyaluminum chloride ensures the introduction of polymeric aluminum forms (produced during the production of these coagulants) into the purified water regardless of the pH of the water. The stability in water of aluminum polycations depends to a much lesser extent on the pH of the water to be purified than the hydrolysis products of non-hydrolyzed coagulants. The goal of the present study was to try to clarify the role of the type of hydrolysis of classical hydrolyzing aluminum coagulants undergoing in water during coagulation acid hydrolysis or basic hydrolysis and the role of prehydrolysis of polyaluminum chlorides which they undergoing during production in the removal of organic substances from the water. The efficiencies of three commercial coagulants in different characteristics were compared: aluminum sulfate (VI) undergoing acid hydrolysis, sodium aluminate undergoing basic hydrolysis in water during coagulation and prehydrolysed polyaluminum chloride with commercial name PAXXL10. Controlled initial hydrolysis of aluminum salts occurring during the production of polyaluminum chlorides causes that they contain more polymerized aluminum forms with a high positive charge than those generated during rapid and uncontrolled hydrolysis of aluminum sulfate (VI) or sodium aluminate in water during coagulation.

2. Materials and methods

2.1. Water used to coagulation

The subject of the study was a mixture of surface water from the Obrzyca river and the groundwater after the aeration process from Quaternary formations. The mixture of the surface and groundwater was made as a matrix for the experiments because the presence of iron in water makes it difficult to remove organic matter from water due to the formation of chelate complexes and formation of the so-called protective colloids of hydrophilic character [31,32]. The groundwater after the aeration process in forced airflow cascades was mixed with surface water after the microfiltration process on microsites with a pore diameter of 10 µm in a 1: 2 volume ratio. Raw water is a mixture of groundwater and surface water was characterized by an increased content of general iron from 1.40 to 1.60 mg Fe/L, iron (II) from 0.07 to 0.08 mg Fe/L and increased turbidity from 11 to 15 NTU, intensity of the color from 18 to 20 mg Pt/L, pH from 7.60 to 7.84, electrokinetic potential (ζ) from –14.00 to –14.60 mV. TOC varied in the range from 6.50 to 7.30 mg C/L, DOC from 6.30 to 6.90 mg C/L, and the UV_{254} absorbance between 14.25 to 16.49 m^{-1}, which indicates, that the treated water of dissolved organic matter-containing organic compounds occur rings aromatic with a high potential to create by-products of oxidation or disinfection. In raw water, the particle diameter was in the range from 24 to 122 nm. The calculated $SUVA_{254}$ value was from 2.46 to 2.66 m^2/gC, which in turn indicates that in both raw waters there were both hydrophilic and hydrophobic as well as low and high molecular weight organic compounds to remove the coagulation process [23,24].

2.2. Experimental procedure of coagulation

In the research of the effectiveness of volumetric coagulation in water treatment was determined. The tests were carried out by a 1 L six-place paddle stirrer (Flocculator Kemira 2000, Sweden). Coagulation was carried out in water samples of 1 L through 1 min. fast mixing at a speed of 250 rpm and 25 min. flocculation with an intensity of mixing of 30 rpm. As a coagulant, the commercial pre-hydrolyzed polyaluminum chloride PAXXL10 with a basicity of 70% and alkalinity ratio $[OH^-]/[Al^{3+}] = 2.10$ and two classical hydrolyzing coagulants: aluminum sulfate (VI) undergoing acid hydrolysis and sodium aluminate undergoing basic hydrolysis in water during coagulation were tested (Table 1). The doses of coagulants were expressed in mg Al/L and varying from 1 to 5 mg Al/L. After coagulation, the samples were subject to the sedimentation process for 1 h. The jar tests were repeated three times and the presented

Table 1
Selected properties of the coagulants tested [52]

Indicator	Type of coagulant		
	PAXXL10	Aluminum sulfate (VI)	Sodium aluminate
Alkalinity ratio, $(OH^-)/(Al^{3+})$	2.1	–	–
Alkalinity, %	70	–	–
Al^{3+}, %	5	4.3	9.5
Fe_{tot}, %	–	<0.007	0.003
Cl^-, %	11.5	<0.1	–
SO_4^{2-},%	–	22.5	–

results are the average value. Table 1 shows the characteristics of the aluminum coagulants tested.

2.3. Analytical methods

The physical-chemical composition was determined by the International Standard methods. The NOM in all samples was determined by measuring TOC and DOC concentration, color (absorbance of 410 nm wavelength) and absorbance at 254 nm. TOC concentration is the most reliable method for determining the total amount of NOM, UV absorption at 254 nm monitors the number of NOM fractions containing aromatic structures in their molecules [40]. The TOC and DOC were measured using the thermal method and a Shimadzu TOC Analyzer. DOC was analyzed by the TOC Analyzer after filtration through 0.45 μm pore diameter membranes. UV absorbance at 254 nm (UV_{254}) was measured by a UV-VIS spectrophotometer Agilent Cary 60 using a quartz cell with a 1 cm path length after filtration through 0.45 μm membrane. DOC and UV_{254} are used in the calculation of the SUVA.

$$\text{SUVA} = \frac{\text{UV}_{254\text{nm}}}{\text{DOC}}\left[\text{m}^2 / \text{g}\, C\right] \tag{8}$$

where SUVA is specific UV absorbance at 254 nm (m^{-1}) and DOC (g C/m^3) [53].

True color was indicated in accordance with ISO 7887-Method C [54], using a spectrophotometer Agilent Cary 60. Quartz cuvette with a path length of light 50 mm was used. It was determined after filtration of the water sample through a membrane filter of pore size 0.45 μm. Colour of the sample was calculated using the following equation:

$$C = \frac{A_{410}}{ad}\left[\text{mg Pt} / \text{L}\right] \tag{9}$$

where C is true colour of the sample, A_{410}-absorbance of the sample at $\lambda = 410$ nm, a is the specific absorption coefficient of the calibration solution of potassium hexachloroplatine and cobalt chloride (mm^{-1} (mg Pt/L)$^{-1}$), d is the optical pathlength (mm) [54].

The total iron and iron (II) concentrations were determined with the Dr 3900 (HACH Lange) spectrophotometer. Iron (II) was measured using the 1,10 phenanthroline method. Total iron was measured using the same method. As a reducing agent of ferric ions to the ferrous ions, hydroxylamine hydrochloride was used. Aluminum concentration was determined with the atomic emission spectroscopy (ISP-OES, 5300DV, Perkin Elmer Company, US). Total aluminum and dissolved aluminum concentrations were measured before and after sample filtration through a 0.45 μm membrane, respectively. The temperature and pH of the raw water and the purified water was determined with a WTW Multi-Line P4 with a combination pH electrode with temperature corrections. Turbidity was measured using the Hach 2100N Turbidimeter. Measurement of the electrokinetic potential ζ was made in raw water samples and after the coagulation process using the Zetasizer Nano Analyzer, which calculates the Zeta potential by determining the electrophoretic mobility of the particles using the laser technique of speed measurement based on the Doppler effect. In the water after the coagulation process, the particle size was also measured using the Zetasizer Nano Analyzer. The Zetasizer Nano Analyzer measures particle size using the dynamic light scattering (DLS- Dynamic Light Scattering) process, also known as photon correlation spectroscopy (PCS-Photon Correlation Spectroscopy), which measures Brown's motion and calculates particle size on this basis. The intensity of the fluctuation of the scattered laser light that the particles are illuminated is analyzed.

3. Results and discussion

Based on the obtained test results, the effectiveness of organic substances removed from the water was determined by the volume coagulation method depending on the type and dose of the tested aluminum coagulant. Analysis of the obtained results of the research presented in Fig. 1 showed that the effectiveness of the tested coagulants in removing TOC decreased in accordance with the following series:

PAXXL10 > Aluminium sulphate (VI) > Sodium aluminate

The co-determinant of the effectiveness of coagulants, especially those not pre-hydrolyzed in the removal of organic substances, was the pH value at which coagulation occurred (Fig. 2). The highest efficiency of TOC removal from the water was provided by the pre-hydrolyzed coagulant PAXXL10, and aluminum sulfate (VI) showed a slightly lower efficiency. The differences between the effectiveness of PAXXL10 polyaluminum chloride and aluminum sulfate (VI) in removing TOC were generally greater in the range of smaller doses of these coagulants. The PAXXL10 coagulant was also the most effective in the removal of DOC, but only in the low dose range from 1 to 3 mg Al/L. Aluminum sulfate (VI) which undergoes acid hydrolysis and therefore reduces the pH of the treated water to the greatest extent ((ΔpH = –0.20 ÷ –0.55 (aluminum sulfate (VI); ΔpH = –0.02 ÷ –0.18 (PAXXL10)), ensured greater DOC removal efficiency than PAXXL10 in the high dose range of 4 to 5 mg Al/L. According to literature reports [34] aluminum polymer forms are considered stable, while monomeric forms can be transformed depending on the pH. According to authors [1,9,28,31,41,42], increasing the amount of H^+ ions in the treated water provides the conditions for the formation of cationic hydrolysis products of pre-non-hydrolyzed

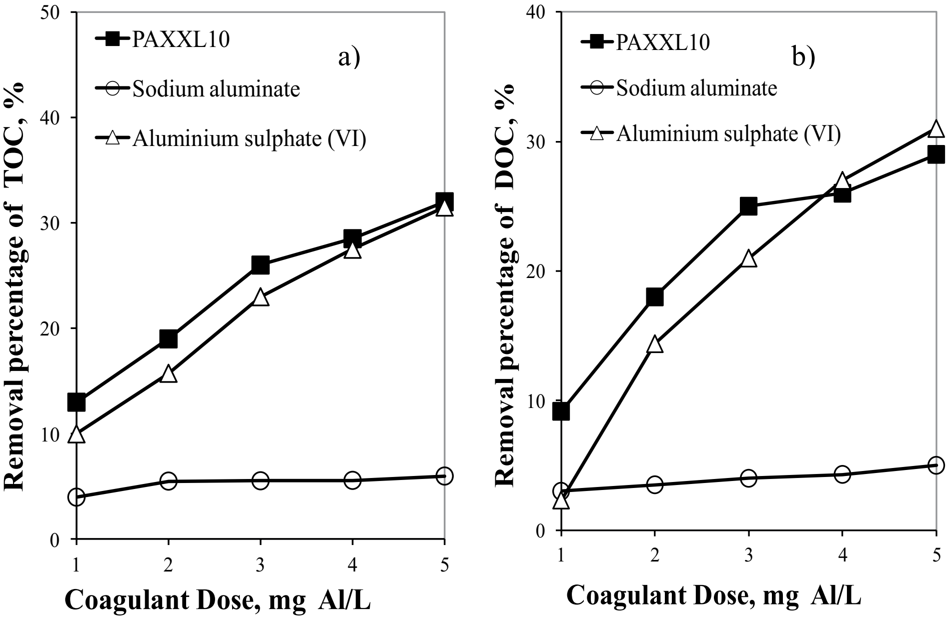

Fig. 1. Effect of the type and dose of a coagulant on the efficiency of removing TOC (a) and DOC (b).

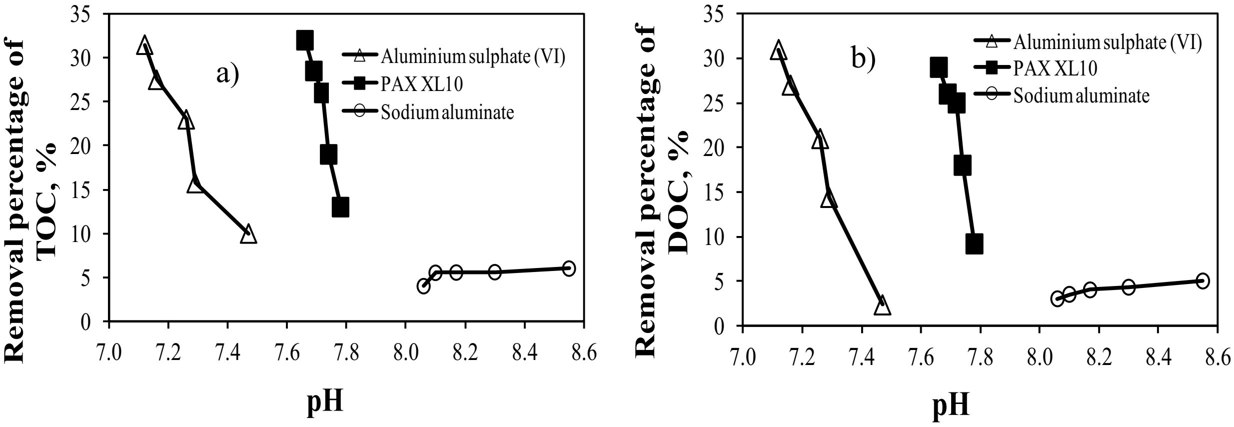

Fig. 2. Influence of the pH value on effectiveness in decreasing TOC (a) and DOC (b) (Coagulant dose = 1–5 mg Al/L).

aluminum sulfate (VI). As a result of lowering the pH value, apart from conditions conducive to the formation of polymeric hydrolysis products of aluminum sulfate (VI), there are also conditions for lower dissociation of organic substances [1,42], which probably improved the TOC and DOC removal efficiency when using aluminum sulfate (VI) and PAXXL10 (Fig. 2).

The least effective coagulant in both TOC and DOC removal was non-hydrolyzed sodium aluminate (Fig. 1) undergoing alkaline hydrolysis during the coagulation [39]. After the coagulation process, this coagulant in purified water showed the highest pH increase in the range from 8.06 to 8.55 (ΔpH = 0.46 ÷ 0.95) for doses from 1 to 5 mg Al/L. The effectiveness of the coagulation process with the tested coagulants was also evaluated by measuring the electrokinetic potential ζ, which determines the stability of the colloidal system. According to literature reports [1,9,40,48] with the increase in the absolute value of the potential ζ, the stability of colloids increases. The implementation of the coagulation process at pH > 8 resulting from the basic hydrolysis of sodium aluminate caused an increase in the absolute value of the electrokinetic potential ζ (Fig. 3). The measured value of the raw water electrokinetic potential was –14 mV, and in water, after coagulation with sodium aluminate, the value of electrokinetic potential was –16.0 to –16.7 mV. According to Alkan et al. [55], the value of electrokinetic potential ζ strongly depends on the pH of the solution. This is related to the fact that the most potent generating ions are the H^+ and OH^- ions. Each colloidal particle found in the aqueous solution acquires a certain density of charge on its surface. At the moment of acidification of the environment, the protons are connected, therefore the particle will show more and more positive (or less negative) values of the potential ζ. In turn, the alkalization of

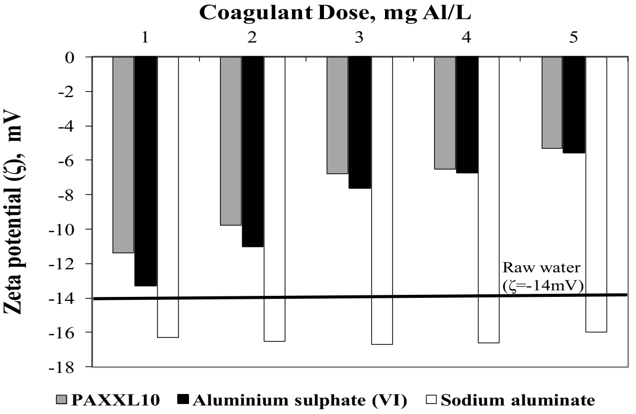

Fig. 3. Effect of the type and dose of a coagulant on the change in Zeta potential.

the environment causes the hydroxyl groups to attach to the surface of the particle, as a result of which the electrokinetic potential reaches increasingly negative values (or smaller positive) of the potential ζ. In the case of organic substances at pH > 8, hydroxyl and acid groups are also dissociated, thereby increasing the negative surface charge value. As the H^+ ion concentration increases, the dissociation process is limited, which in turn reduces the value of the negative surface charge [56]. Analysis of the dependencies presented in Fig. 3 also showed that the highest degree of destabilization of the colloidal system was obtained in samples of water during coagulation with polyaluminum chloride PAXXL10 in the entire range of tested doses from 1 to 5 mg Al/L and samples of water during coagulation of aluminum sulfate (VI) for high doses coagulant 4 and 5 mg Al/L, in which the lowest pH values were found during the coagulation process (pH = 7.16 and pH = 7.12). The zeta potential for post-coagulation (PAXXL10 and aluminum sulfate (VI)) water samples was lower than that found for source water, however, no transition of this potential through the isoelectric point was detected. This may point to the possibility of increasing coagulation effectiveness by a significant increase in coagulant dosage, but this is not economically justifiable.

The concentration of residual aluminum was also determined in the water after the coagulation process. Analysis of the obtained test results showed that after coagulation with sodium aluminate the highest concentrations of residual aluminum were found (Fig. 4) about three times the acceptable concentration in water intended for human consumption (0.2 mg Al/L) and the highest percentage of aluminum dissolved in the remaining aluminum (Fig. 5). At pH ≥ 8 resulting from the basic hydrolysis of sodium aluminate, the transition of $A(OH)_3$ to soluble $Al(OH)_4^-$ aluminate probably occurred, which as a consequence also resulted in the smallest efficiency of organic matter removal (Figs. 1a, b, and Fig. 6). According to Saxen and others [46] the precipitation of $Al(OH)_3$ starts at a pH of about 3, while at a pH of about 8, aluminum hydroxide dissolves into $Al(OH)_4^-$. The lowest concentrations of residual aluminum (from 0.35 to 0.31 mg Al/L) and residual dissolved aluminum (from 0.037 to 0.032 mg Al/L) were found in water samples

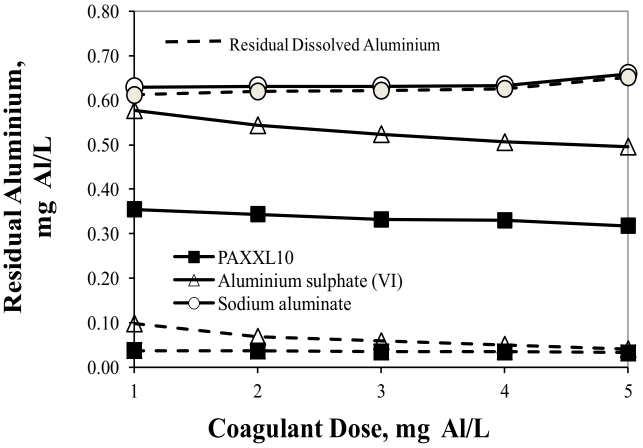

Fig. 4. Effect of the type and dose of coagulant on the residual aluminum content and the residual dissolved aluminum content in the treated water.

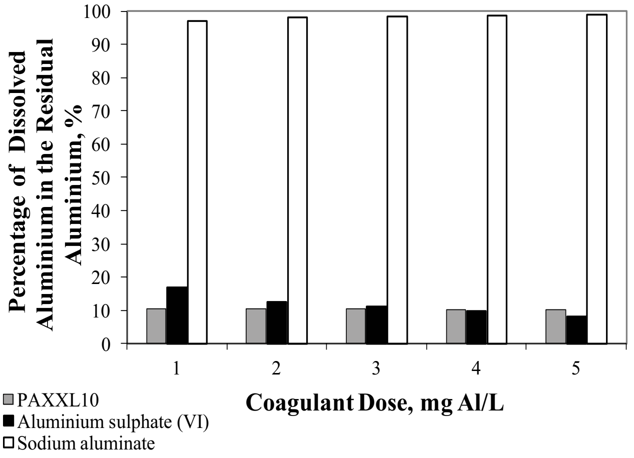

Fig. 5. Effect of the type and dose of coagulant on the percentage of dissolved aluminum in the residual aluminum in the treated water.

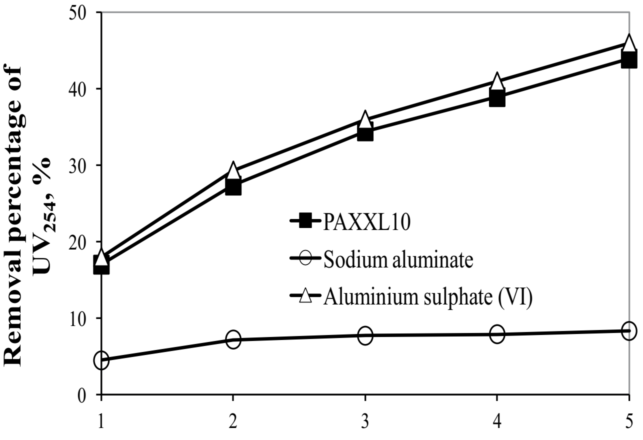

Fig. 6. Effect of the type and dose of a coagulant on the efficiency of removing UV_{254}.

after coagulation with polyaluminum chloride PAXXL10. According to Pernitsky and Edzwald [36,37], pre-hydrolyzed coagulants, such as polyaluminum chlorides, form readily sedimentary post-coagulation sediments with chain structures, and in the water after the coagulation process, low concentrations of residual aluminum are found. It is very important due to the fact, that increased aluminum concentration may pose a potential risk to human health, causing brain lesions characteristic for Alzheimer's disease [57]. The suggested negative effect of the aluminum presence in water on human health as well as its allowable concentration in water intended for human consumption of ≤0.2 mg Al/L in Poland [58] as well as the recommendations of WHO and EU impose and obligation to guarantee the minimum aluminum content in water intended for human consumption [47].

The analysis of the obtained test results also showed that in the range of applied doses of tested coagulants DOC fractions characterized by a high content of aromatic rings (UV_{254} – Fig. 6) were effectively eliminated, and thus a large potential for creating by-products of disinfection. It is believed that a higher reduction in the UV absorbance value of 254 with respect to the reduction of DOC means that aromatic substances are removed more effectively during coagulation than other organic matter fractions [34].

The efficacy of the tested coagulants in the reduction of UV_{254} decreased in accordance with the following series: Aluminium sulfate (VI) > PAXXL10 > Sodium aluminate. The greatest efficiency in removing DOC fraction characterized by a high content of aromatic rings from 18% to 44% was provided by aluminum sulfate (VI) undergoing acid hydrolysis during coagulation, and the efficiency of removing these impurities increased with increasing coagulant dose and thus lowering the pH in purified water in the range from 7.47 to 7.12.

The reduction in DOC was accompanied by a decrease in ultraviolet absorbance (UV_{254}), and therefore by a decrease in chlorinated organic substance precursors. The reduction in ultraviolet absorbance (UV_{254}) was also accompanied by a decrease in color (Table 2). In the water after the coagulation process, showed linear correlations between the remaining total iron and other TOC, DOC and UV_{254} (Table 3), which may indicate that in the purified water there were connections of iron with organic substances. According to numerous researchers [59,60], one of the reasons for iron stabilization by organic substances in the formation of chelate complexes and the formation of the so-called protective colloids of hydrophilic character.

After the coagulation process with PAXXL10 polyaluminum chloride and after aluminum sulfate (VI) coagulation, the highest Pearson coefficient values were obtained for linear correlations between total iron and DOC and between total iron and UV_{254} (Table 3), which may indicate that the remaining total iron in water formed connections with dissolved organic substances containing aromatic rings in their composition. Based on the SUVA value calculated for raw water of 2.66 m^2/gC, it can be concluded that it contained both hydrophilic and hydrophobic as well as small and large-molecule organic compounds [21,22]. According to the literature [25,27] for waters characterized by $SUVA_{254} \le 3$ m^2/gC, the decrease in DOC content using aluminum coagulants

Table 2
Parameters of linear correlations between the of ultraviolet absorbance (UV_{254}) removed and the of DOC and between the of ultraviolet absorbance (UV_{254}) and the of color removed in the coagulation process

Type of coagulant	Linear correlation equation	Coefficient of the Pearson correlation (*R*)
PAXXL10	ηUV_{254} = 0.9628 DOC+15.636	0.9990
	ηUV_{254} = 0.6262 Colour+12.302	0.9806
Aluminum sulfate (VI)	ηUV_{254} = 1.3078 DOC+4.3095	0.9879
	ηUV_{254} = 0.4924 Colour+11.569	0.9806
Sodium aluminate	ηUV_{254} = 1.734 DOC+0.2515	0.8630
	ηUV_{254} = 0.18 Colour+4.4255	0.9840

Table 3
Parameters of linear correlations between the iron and the indices of the organic matters of the water samples after coagulation

Type of coagulant	Linear correlation equation	Coefficient of the Pearson correlation (*R*)
PAXXL10	Fe_{tot} = 9.8961 UV_{254}+8.8955	0.9679
	Fe_{tot} = 3.0948 DOC+4.4970	0.9939
	Fe_{tot} = 4.0261 TOC+4.7347	0.8850
Aluminum sulfate (VI)	Fe_{tot} = 7.0731 UV_{254}+8.6417	0.9369
	Fe_{tot} = 2.4163 DOC+4.7820	0.9806
	Fe_{tot} = 4.0261 TOC+4.7347	0.8949
Sodium aluminate	Fe_{tot} = 2.8214 UV_{254}+11.113	0.7000
	Fe_{tot} = 0.7287 DOC+5.5329	0.6416
	Fe_{tot} = 0.7802 TOC+6.1769	0.8623

usually does not exceed 30%, which was also confirmed by the results obtained by the author (Fig. 1b). Lowering the $SUVA_{254}$ value is associated with a decrease in the share of reactive DOC forms, which results in a lower risk of creating by-products of oxidation [23,24].

Fig. 7 shows changes in the $SUVA_{254}$ value in water during the coagulation process depending on the type and dose of the coagulant tested. The lowest $SUVA_{254}$ values from 2.07 to 1.80 m^2/gC respectively for doses of 1 to 5 mg Al/L were found in the water after coagulation with aluminum sulfate (VI), which undergoes acid hydrolysis. According to the technical guidelines regarding the risk of creating by-products of oxidation and disinfection, there is no need for coagulation for $SUVA_{254} \leq 2$, and it is assumed that the criterion of safe water production has been met [1]. The $SUVA_{254}$ values in water after coagulation with polyaluminum chloride PAXXL10 ranged from 2.25 to 1.95 m^2/gC and only the criterion of safe water production was met after the highest dose of 5 mg Al/L. In the water after coagulation with sodium aluminate, which is basic hydrolysis, found $SUVA_{254}$ highest values in the range of 2.31–2.28 m^2/gC and for any of the doses tested was not fulfilled the production of safe water. Based on the calculated values of $SUVA_{254}$ and literature [23,24], it can be concluded that in water after coagulation with sodium aluminate both hydrophilic and hydrophobic as well as small and large organic compounds were present, and in water, after coagulation with aluminum sulfate (VI) for doses from 2 to 5 mg Al/L and after coagulation of PAXXL10 only for the dose of 5 mg Al/L there were hydrophilic, low molecular weight non-humus substances ($SUVA_{254} \leq 2$ m^2/gC). In the water samples after the coagulation process, the particle size was also measured using the dynamic light scattering process. Analysis of the obtained test results showed that in the water after the coagulation of sodium aluminate, there were particles whose diameter ranged from 164 to 1990 nm. The most 85% were particles with a diameter of 1000–1484 nm, 9% were particles with a diameter between 1700–1990 nm, while the least about 6% were particles with a diameter of 164 to 255 nm. In water after coagulation with aluminum (VI) sulfate, the particle diameter was in the range of 58 to 105 nm, and after coagulation with polyaluminum chloride PAXXL10 from 32 to 68 nm. In water after coagulation with aluminum sulfate (VI), as many as 86% were particles with a diameter between 58–75 nm and 14% were particles with a diameter between 92–105 nm. In contrast, in water after coagulation of PAXXL10, the highest percentage was 96% of particles with a diameter between 32–51 nm and 4% were particles with a diameter between 60–68 nm.

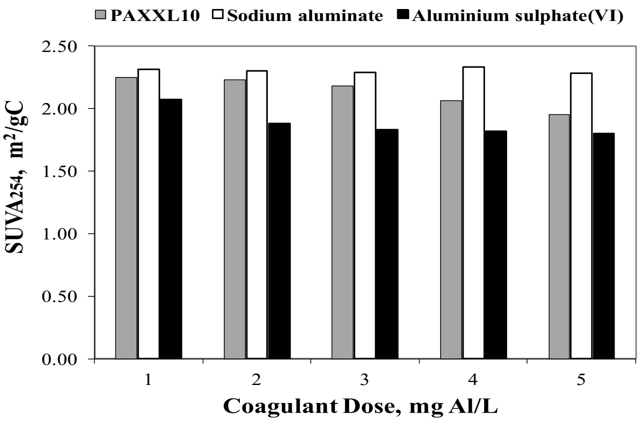

Fig. 7. Effect of the type and dose of a coagulant on the change in $SUVA_{254}$.

4. Conclusions

The test results analysis leads to the following conclusions:

- The effectiveness of removing organic substances depended on the type and dose of coagulant and pH during the coagulation process. In terms of the doses of test coagulants used, DOC fractions with a high content of aromatic rings and thus a large potential to create by-products of disinfection were more effectively eliminated.
- Among the tested coagulants, the highest efficiency of TOC removal from the water was provided by the pre-hydrolyzed coagulant PAXXL10, which was also the most effective in removing DOC, but only in the low dose range from 1 to 3 mg Al/L.
- Aluminium sulfate (VI) undergoing acid hydrolysis and therefore the highest pH-lowering of the water to be treated provided greater DOC removal efficiency than PAXXL10 in the high dose range of 4 to 5 mg Al/L and the highest efficiency of removing dissolved organic aromatic substances in the entire range of doses tested.
- The least useful coagulant for removing all organic matter fractions was sodium aluminate undergoing basic hydrolysis in water. The realization of the coagulation process at pH ≥ 8 resulting from the alkaline hydrolysis of sodium aluminate caused an increase in the absolute value of the electrokinetic potential ζ and the transition of $A(OH)_3$ to soluble $Al(OH)_4^-$ which resulted in the lowest reduction of UV_{254}, TOC, and DOC.
- After the sodium aluminate coagulation, the value of $SUVA_{254}$ ranged from 2.28 to 2.31 m^2/gC, which means that in water purified with this coagulant there were both hydrophilic and hydrophobic, as well as low and high molecular organic compounds and the criterion of safe water production was not met ($SUVA_{254} \leq 2$ m^2/gC).
- Due to the fulfillment of the safe water production criterion, the most useful coagulant turned out to be aluminum sulfate (VI) in an amount of 2 to 5 mg Al/L and polyaluminum chloride PAXXL10 in the amount of 5 mg Al/L. Based on the SUVA value ($SUVA_{254} \leq 2$ m^2/gC), it can be concluded that in the water purified with these coagulants there were hydrophilic, low molecular weight non-humus substances.

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