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The use polyaluminium chlorides with various basicity for removing of organic matter from water

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ABSTRACT

Application of coagulation process in surface water treatment allows for decrease in turbidity and colour of water, as well as organic matter content. The aim of this study was to evaluate the effectiveness of the coagulation process using pre-hydrolyzed salts, polyaluminium chlorides (general formula $Al_n(OH)_mCl_{3n-m}$) with different basicity, in reducing the level of pollution of surface water with organic substances. Apart from the typical indicators used to evaluate the content of organic compounds (total organic carbon [TOC], oxidisability [OXI], ultraviolet absorbance [UV_{254}]), the potential for trihalomethanes formation (THM-FP) was also determined. Under the conditions of the coagulation (pH 7.5–7.9, temperature of 20°C–22°C), the best results were obtained using highly alkaline polyaluminium chlorides, decrease in TOC, OXI and UV_{254} by 32%–61% and slightly worse 24%–45% using medium alkaline. Using the low alkaline coagulant, 25%–46% removal of organic matter was obtained. Significant removal of organic compounds in the coagulation process resulted in a decrease in THM-FP value during water chlorination. THM-FP in purified waters was by 41%–65% lower than in untreated surface water subjected to chlorination. The concentration of $CHCl_3$ accounted for 86%–94% of the total THM content in the analyzed waters.

Keywords: Organic matter; Water treatment; Polyaluminium chlorides; Trihalomethanes formation potential

1. Introduction

The natural organic matter (NOM) occurring in surface waters gives them colour, smell and becomes a precursor to the formation of by-products when strong oxidants are used for water treatment. One of the methods used to reduce the organic matter content in water is coagulation [1–3]. An important aspect affecting the effectiveness of coagulation is the type and form of organic pollutants. The degree of removal of organic substances increases with their content in treated water, their molecular weight and the degree of aromaticity. The conventional coagulation process is generally effective in removing high-molecular weight organics, but less so in removing smaller molecular weight fractions [4,5]. Each time there is a necessity to choose the right coagulant, its dose and parameters of the process. The optimum operating conditions to remove turbidity and colour by coagulation are not necessarily the same conditions for NOM removal [4].

Currently, pre-hydrolyzed coagulants based on polymerized aluminium forms are increasingly often applied. Their higher efficiency, compared with aluminium sulphate, is determined by the presence of polycations $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$ and $Al_{13}O_4(OH)_{24}^{7+}$ (is called Al_{13}), as well as the difference in the structure of precipitated flocs of aluminium hydroxide formed during the hydrolysis of these coagulants [6–8]. Al_{13} is claimed to be the most stable aluminium specie in a partially neutralized aluminium solution and the improved coagulation properties of polyaluminium chloride

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are thought to be due to its existence, that is, increased charge neutralization capability, as well as increased molecular size and aggregation ability [9].

The indicator characterizing the pre-hydrolyzed salts is their basicity, described by the formula *B*/0.03, where *B* is the quotient of the number of moles of OH^- to Al^{3+}. The value of molar ratio *B* varies between 0 and 3, which corresponds to changes in the basicity of the coagulant from 0% to 100%. Higher basicity of the coagulant usually indicates its higher efficiency resulting from the greater share of polymerized forms. As stated by Lin et al. [8] the basicity adjusted in the range from 2 to 2.3 during preparation of polyaluminium chloride can produce high content of Al_{13} polycation.

Analysis of the literature data does not allow to explicitly determine the effectiveness of pre-hydrolyzed coagulants in the removal of organic substances from water [1,2,4]. Significant discrepancies in the obtained results can be explained by both the complicated structure of organic compounds and the variety of commercial polyaluminium chloride products, which exact chemical composition is unknown. Polyaluminium chlorides contain significant amounts of polycationic products of preliminary hydrolysis. Aluminium polymer forms are considered stable, while monomeric forms may undergo transformations. This can result, under certain conditions, in the formation of in situ aluminium polymers which neutralize the pollutant load and thus obtain a good water purification efficiency using coagulants containing significant amounts of monomeric forms. Therefore, under certain conditions, the use of coagulants with lower basicity may be more effective [10]. The pH of water plays an important role.

It is particularly important to evaluate the effectiveness of the coagulation process in the removal of organic compounds which are the precursors of trihalomethanes (THMs). Four derivatives of methane belong to THM group: $CHCl_3$, $CHBr_3$, $CHBrCl_2$, $CHBr_2Cl$. THMs are formed by the reaction between NOM and free chlorine during the disinfection water treatment. The permissible concentration of the sum of their content in drinking water according to Council Directive 98/83/EC [11] equals 100 μg/L. From among these four compounds, chloroform occurs in the highest concentrations. International Agency for Research on Cancer classified trichloromethane and bromodichloromethane as factors which are potentially carcinogenic to humans [12]. The problem of THM presence in water intended for human consumption is still valid [13–16]. Therefore, the removal of THM precursors is one of the most important tasks of a water treatment plant. Now many researchers are focusing on the control of THM formation potential using different coagulants and demonstrated that polyaluminum chlorides could reduce the concentration of disinfection by-products precursors [17].

The aim of the research was to evaluate the effectiveness of the coagulation process using pre-hydrolyzed salts, polyaluminium chlorides of various basicities, in reduction of turbidity and colour of surface water and water pollution with organic substances. The removal of organic matter is not necessarily related to the removal of THM precursors. That is why the THM formation potential of the organic matter remaining in the analyzed waters after their purification in the coagulation process was determined. On this basis, the effectiveness of coagulation as a process decreasing the THM formation potential was evaluated and the best coagulant was indicated.

2. Materials and methods

2.1. Materials

Surface water collected from the Warta river in Częstochowa and from the dam reservoir located in Poraj (Poland) was used for the research. The area of the dam reservoir is 497 ha, length, 4.9 km, and the average depth, 3.9 m. The water was collected in May and June of 2017.

Hydrolyzed salts, polyaluminium chlorides with commercial names PAX18, PAX-XL61, PAX-XL1910, and PAX-XL19F, were used as coagulants, produced by KEMIPOL company in city Police (Poland). The characteristics of the coagulants are shown in Table 1.

Basicity of polyaluminium chlorides varied from 41% to 85%. Commercial solutions of PAX contained from 10.2% to 19.8% of Al_2O_3. For the analyses, coagulant solutions were prepared by diluting commercial products so that they contained 1.0 g-Al/L.

2.2. Jar test procedure

The water after collection was transported to the laboratory and stored until the following day at a temperature of 4°C. The coagulation was carried out at the natural pH of water. For the execution of the coagulation process, a six-station coagulator JLT with mechanical stirrers from company VELP Scientifica, Italy, and glass beakers with a capacity of 2 L were used. A total of 1.5 L of analyzed water was measured into the beakers. The coagulants were introduced at a dose of 3.5 mg-Al/L. The dose of the coagulants was applied based on previously conducted studies. Stirring was carried out applying 250 rpm for 2 min and then 25 rpm for 15 min. After this time the samples were subjected to 1 h of sedimentation. Afterwards 0.5 L of water was decanted and selected physicochemical indicators were determined. An analysis of untreated waters was also conducted.

2.3. Analytical methods

The physicochemical parameters of water were measured with the following methods: pH – potentiometrically, turbidity – nephelometric with TN-100 nephelometer, Eutech Instruments, Singapore, colour – colometrically with platinum–cobalt standard method, dissolved (DOC) and

Table 1
Characteristics of the coagulants

Parameter	Symbols of PAX			
	18	XL61	XL1910	XL19F
Basicity, %	41.0±3	70.0±10	85.0±5	85.0±5
B (OH^-/Al^{3+})	1.23	2.10	2.55	2.55
Al_2O_3, %	17.0±0.6	10.2±0.4	19.8±0.4	16.0±0.9
Chlorides, %	21.0±2.0	11.0±2.0	7.5±1.0	5.5±0.5
pH	1.0±0.2	3.0±0.5	3.5±0.5	4.0±0.5

total organic carbon (TOC) – by infrared spectrophotometry with carbon analyzer Multi N/C, Analytik Jena, Germany (to measure DOC concentration the samples of water were filtered through 0.45 μm filtration membrane), oxidisability (OXI) by potassium permanganate method, aluminium – with Aquaquant 14413 aluminium test. The analyses were performed in duplicate. Absorbance in the ultraviolet UV at wavelength of 254 nm was determined (spectrophotometer M501 by Camspec Ltd., United Kingdom) using 1 cm quartz cells. $SUVA_{254}$ index was calculated as a ratio of absorbance at UV_{254} to the DOC content. Connecting the values of absorbance and DOC into single coefficient $SUVA_{254}$ enables to determine properties of dissolved organic matter in water, and vulnerability to removal in the coagulation process.

In order to determine the formation potential THM-FP, measured into dark bottles surface water samples before treatment and after the coagulation, adjusted to pH 7 with phosphate buffer, were chlorinated using chlorine water prepared with sodium hypochlorite. Such dose was used to achieve, after a period of 24 h at the temperature of 25°C, a concentration of residual free chlorine in the range of 3–5 mg-Cl_2/L [18]. For the determination of THMs in water samples before and after the chlorination process, 10 mL of water was collected into tubes, 1 mL of n-pentane was added, and it was intensively shaken for 2 min. After separation of layers, 2 μL of the extract was collected with a microsyringe and introduced into a chromatography column. Nitrogen was used as a carrier gas. Distribution of the compounds was performed on a capillary column DB-5 (30 m × 0.25 mm × 0.25 μm) and analyzed by means of gas chromatography with microelectron capture detector μECD (chromatograph Agilent 6890N). Temperature program: starting at 40°C, ramp 40°C/min to 120°C, then 15°C/min to 250°C. As a standard, solution by CPAchem Ltd., Bulgaria, was used, containing 4 components ($CHCl_3$, $CHBr_3$, $CHCl_2Br$, $CHClBr_2$) with a concentration of 10 μg/mL each in iso-octane. The THM concentrations were determined in triplicate. The sensitivity of the measurement method was 0.01 μg/L.

The potential for THMs formation was calculated by subtracting from the THM concentration, assayed after 24 h contact of water with chlorine, the concentration of these compounds in water not subjected to chlorination.

3. Results and discussion

The average values of analyzed indicators of water quality from the Warta river and from the Poraj dam reservoir before and after the coagulation process are presented in Tables 2 and 3, respectively. The percentage decrease in turbidity and water colour is shown in Fig. 1, and the content of organic compounds marked as OXI, TOC, DOC, UV in Fig. 2.

Surface water collected from the Warta river was characterized by turbidity of 6.4 NTU and colour of 45 mg-Pt/L. The water pH was alkaline. OXI was equal to 9.3 mg-O_2/L and UV_{254} absorbance 22.8 1/m. The content of TOC and DOC amounted to 11.5 and 9.4 mg/L, respectively.

Table 2
Effect of coagulation with various agents (dose 3.5 mg-Al/L) on selected physicochemical properties of water from the Warta river (the average values)

Parameter	Raw water Warta river	Water purified with PAX			
		18	61	1,910	19F
pH	7.85	7.53	7.62	7.63	7.64
Turbidity, NTU	6.40	3.89	3.33	1.16	2.41
Colour, mg-Pt/L	45	20	18	10	15
Aluminium, mg/L	0	0.35	0.18	0.07	0.15
OXI, mg-O_2/L	9.3	5.2	5.3	3.9	4.0
TOC, mg/L	11.5	8.1	8.7	6.7	6.9
DOC, mg/L	9.4	6.9	7.5	6.4	6.5
UV_{254}, 1/m	22.8	12.2	12.6	9.1	8.9
SUVA, L/mg·m	2.43	1.77	1.68	1.42	1.37

Note: SUVA = UV_{254}/DOC

Table 3
Effect of coagulation with various agents (dose 3.5 mg-Al/L) on selected physicochemical properties of water from the Poraj dam reservoir (the average values)

Parameter	Raw water Poraj dam reservoir	Water purified with PAX			
		18	61	1910	19F
pH	7.94	7.66	7.75	7.86	7.74
Turbidity, NTU	4.76	1.31	1.13	0.48	0.66
Colour, mg-Pt/L	35	10	12	12	15
Aluminium, mg/L	0	0.28	0.12	0	0.03
OXI, mg-O_2/L	7.0	5.2	4.6	3.5	3.4
TOC, mg/L	8.8	6.6	6.7	6.0	5.7
DOC, mg/L	8.2	6.2	6.4	5.6	5.6
UV_{254}, 1/m	20.2	12.3	11.9	8.9	9.8
SUVA, L/mg·m	2.40	1.98	1.86	1.82	1.78

Note: SUVA = UV_{254}/DOC

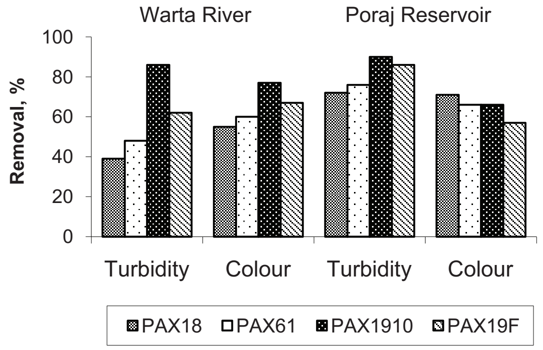

Fig. 1. Percentage of removal of turbidity and colour during coagulation.

The most effective in removal of turbidity from water collected from the Warta river was high-basicity polyaluminium chloride PAX1910, which reduced turbidity from 6.4 to 1.16 NTU (by 82%). It was also effective to use this coagulant to reduce the colour of water from 45 to 10 mg-Pt/L (by 78%). Whereas, using the remaining coagulants: high-basicity PAX19F, medium-basicity PAX61 and low-basicity PAX18,

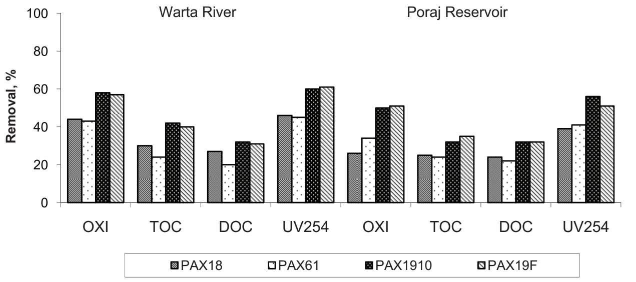

Fig. 2. Percentage of removal of organic matter determined as OXI, TOC, DOC, UV_{254} during coagulation.

the turbidity decreases by 62%, 48% and 39%, and colour by 67%, 60% and 55%, respectively, was obtained (Fig. 1).

Surface water collected from the Poraj dam reservoir was characterized by lower indicator values than water from the Warta river. Turbidity amounted to 4.76 NTU, colour 35 mg-Pt/L, OXI 7.0 mg-O_2/L and UV_{254} absorbance 20.2 1/m. The TOC content was equal to 8.8 and DOC 8.2 mg/L.

In the case of purification of water collected from the Poraj reservoir, the best effects of turbidity removal were obtained both with high-basicity coagulant PAX1910 and PAX19F, by 90% and 86%, respectively. Using a medium-basicity PAX61, a turbidity reduction of 76% was achieved. In contrast, in decreasing the water colour, the most effective was the usage of low-basicity PAX18 (Fig. 1).

A research on removal of turbidity from surface water using coagulants of various basicities was conducted by Yang et al. [19]. They obtained an efficiency amounted to approx. 80% with the usage, with a dose of 12 mg/L, of coagulants with basicity 67% and 77% and efficiency approximately 60% with the usage of a coagulant with 50% basicity. Also Yang et al. [10] using the same coagulants obtained the efficiency of turbidity removal from model water equal to 85%, 80% and 55%, respectively.

After the coagulation process conducted with the usage of the low-basicity PAX18, the content of organic compounds in water collected from the Warta river, assayed as OXI and TOC, decreased respectively from 9.3 mg-O_2/L and 11.5 mg/L to 5.2 mg-O_2/L and 8.1 mg/L. With the usage of the medium-basicity polyaluminium chloride PAX61, OXI reduction down to 5.3 mg-O_2/L and TOC content down to 8.7 mg/L were obtained. The best effects of reducing the content of organic compounds were obtained using high-basicity coagulants: PAX1910 and PAX19F. The TOC content in water after the coagulation amounted to 6.7 and 6.9 mg/L, and OXI 3.9 and 4.0 mg-O_2/L. This means a decrease in the value of these indicators by 40%–42% and 57%–58%, respectively. Also in the case of purifying water from the Poraj reservoir, the best results were obtained after applying high-basicity coagulants. The TOC content decreased from 8.8 to 5.7–6.0 mg/L, and OXI from 7.0 to 3.43.5 mg-O_2/L, which indicates a decrease by 32%–35% and 50%–51%, respectively (Fig. 2).

The $SUVA_{254}$ value for collected water amounted to 2.4 L/mg·m. In the case of water with a value of this indicator in the range of 2–4 L/mg·m, it is believed that in that water occurs a mixture of hydrophilic and hydrophobic humic substances and other natural organic compounds, of both low and high molecular weight, and DOC removal is equal to 25%–50%. The hydrophobic fraction of NOM is generally removed in coagulation more efficiently than the hydrophilic fraction [1].

In the conducted research (at pH 7.5–7.9), a reduction in DOC content in water after the coagulation by 20%–32% and UV_{254} absorbance by 39%–61% was obtained, depending on the coagulant used. A significant reduction in the value of these indicators was reported both with the usage of high-basicity polyaluminium chlorides PAX1910 and PAX19F, as well as low-basicity chloride PAX18. Compared with DOC, UV_{254} has been noted to reduce more, suggesting that aromatic materials are removed more effectively than other NOM fractions [1]. It has been shown that the DOC removal rate depends on the content of Al_{13}, and the efficiency of UV reduction depends both on the presence of Al_{13} as well as the precipitated forms of aluminium [19,20]. Tubić et al. [21] obtained, with the use of polyaluminium chloride sulphate and polyaluminium chloride, approximately 50% reduction in DOC content and approximately 60% reduction in UV absorbance. It is believed [22] that UV_{254} is a good indicator of the potential formation of THMs.

The $SUVA_{254}$ value of water after the coagulation was equal to 1.4–2.0 L/mg·m. This indicates that in water after the coagulation, organic substances that are difficult to remove in this process remained. The $SUVA_{254}$ value <2 L/mg·m suggests the presence of mostly non-humics, low hydrophobicity, low molar mass compounds [1].

The effect of basicity of aluminium coagulants and pH of water on the removal of organic substances was studied by Yang et al. [10]. They used polyaluminium chlorides with basicity of 50%, 67% and 77% and conducted research with pH changes in the range of 4–9. They obtained, along with the increasing basicity of coagulants at pH 7 and 8, the effects of reducing the UV_{254} value by 37%, 45% and 38%, and 34%, 42% and 33%. While the DOC content was reduced by 24%, 29% and 12%, and 23%, 26% and 12%. Thus, along with the increasing basicity of the coagulants, their effectiveness in removal of organic substances has not always increased. The best was a coagulant with a basicity of 67% ($OH^-/Al^{3+} = 2$). When initial pH was between 6.0 and 8.0 the colloids were easily adsorbed and co-precipitated by formed high-polymeric positive hydrolyzates and $Al(OH)_3$, which had low solubility and large surface area [10].

The lowest concentration of residual aluminium occurred in water after the coagulation when high-basicity PAXs were used. It amounted to from 0.03 to 0.15 mg-Al/L and it was lower than the limit value for drinking water equal to 0.2 mg-Al/L [11]. Also with the application of medium-basicity PAX61, the concentration of remaining aluminium below 0.2 mg-Al/L was obtained, while with the usage of low-basicity PAX18 it was higher than this value.

In collected surface water as well as in water after the coagulation process, the presence of THMs was not discovered. However, their presence was demonstrated in these waters after the chlorination process. THM concentrations in water from the Warta river and from the Poraj dam reservoir subjected to chlorination for 24 h and in those waters previously treated in the coagulation process and then subjected to chlorination for 24 h are presented in Tables 4 and 5.

The presence of $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ was found in analyzed water after the chlorination process, $CHBr_3$ was not detected. The concentration of $CHCl_3$ and $CHCl_2Br$ was equal

Table 4
THM concentrations in surface water from Warta river and in water purified in the coagulation subjected to chlorination for 24 h (the average values)

THM	Raw water Warta river	Water purified with PAX			
		18	61	XL1910	XL19F
$CHCl_3$, µg/L	341.0	131.2	148.4	119.3	126.6
$CHCl_2Br$, µg/L	25.3	15.5	17.1	16.4	17.2
$CHClBr_2$, µg/L	0.6	0.8	0.7	0.9	1.1
$CHBr_3$, µg/L	nd	nd	nd	nd	nd
THM-FP, µg-$CHCl_3$/L	359.8	142.9	161.3	131.8	139.8

nd, not detected.

Table 5
THM concentrations in surface water from Poraj reservoir and in water purified in the coagulation subjected to chlorination for 24 h (the average values)

THM	Raw water Poraj dam reservoir	Water purified with PAX			
		18	61	1910	19F
$CHCl_3$, µg/L	315.0	162.2	178.1	110.3	102.7
$CHCl_2Br$, µg/L	17.9	18.7	19.3	16.2	15.8
$CHClBr_2$, µg/L	0.6	0.7	0.8	0.8	1.0
$CHBr_3$, µg/L	nd	nd	nd	nd	nd
THM-FP, µg-$CHCl_3$/L	328.4	176.2	192.6	122.6	114.8

nd, not detected.

to 341 and 25 µg/L, respectively, in water from the Warta river subjected to chlorination, and 315 and 18 µg/L in water from the Poraj dam reservoir subjected to chlorination. Whereas, in waters chlorinated after their previous purification in the coagulation process, the concentration of $CHCl_3$ ranged from 103 to 162 µg/L, and $CHCl_2Br$ from 16 to 19 µg/L. The lowest concentration of these compounds was obtained when high-basicity polyaluminium chlorides were used for the coagulation process: PAX1910 for water from the Warta river, PAX19F for water from the Poraj reservoir. The concentration of $CHCl_3$ was lower by 65% and 67%, respectively, than in the untreated surface water subjected to chlorination. The highest concentration of $CHCl_3$ was obtained in chlorinated waters, which were purified in the coagulation process using a medium-basicity coagulant PAX61.

The potential of THMs formation THM-FP in water purified in the coagulation process and subjected to chlorination ranged from 165 to 292 µg-$CHCl_3$/L. These values obtained after purification of water from the Warta river using high-basicity, medium and low-basicity coagulant were respectively by 61%–63%, 55% and 60% lower, and in the case of water from the Poraj reservoir by 63%–65%, 41% and 46% lower than in unpurified waters subjected to chlorination (Fig. 3). The concentration of trichloromethane accounted for 86%–94% of the total THM content in the analyzed waters. Matilainen et al. [1] state that in water purified in the coagulation process, THM-FP reduction by 25%–66% can be obtained.

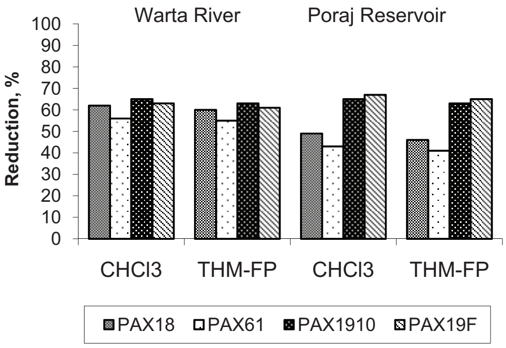

Fig. 3. Percentage decrease in $CHCl_3$ and THM-FP in purified and chlorinated water.

As known, the coagulation process mainly removes high molecular weight organic matter. Although a significant part of the organic matter was removed during the coagulation process, the remaining part was still characterized by a high THM-FP. Hydrophobic acids were indicated as the most reactive fractions of organic substances in the formation of THMs [23,24]. However, it is believed [25] that not all aromatic compounds in the hydrophobic acid fraction reacted effectively with chlorine to produce chloroform. For example, the structure rich in aromatic carbon but with no activated functions (such as OH^- or nitrogen-substituted aromatics) also have high UV absorption, but had poor chlorine reactivity and formed low level of THMs [26]. The organic carbon content is only one of the factors determining the formation of THMs. Other factors include chlorine dose, water temperature and pH, bromide ion concentration, and reaction time [13,22].

4. Conclusions

- An influence of the type of coagulant (low, medium, high basicity) on the effectiveness of removal of turbidity and colour of water and the content of organic compounds has been confirmed. The best results of TOC reduction by 32%–42% were obtained using high-basicity polyaluminium chlorides PAX1910 and PAX19F, slightly worse 25%–30% with the usage of low-basicity PAX18.
- Also the composition of water collected from the river and the dam reservoir influenced the obtained purification efficiency. A greater reduction in the amount of organic matter responsible for the formation of THM was obtained in the case of treatment of water from the Warta river.
- The effectiveness of the coagulation process in the removal of THM precursors has been confirmed. Significant removal of organic compounds in the coagulation process resulted in a decrease in THM-FP value during water chlorination. THM-FP in purified waters was by 41%–65% lower than in untreated surface water subjected to chlorination.
- The highly alkaline coagulant PAX1910 was indicated as the best in the purification of the studied waters (practical aspect). The efficiency of coagulation as a process decreasing the OXI and UV_{254} value amounted to 50%–60%, and the THM formation potential 63%.

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