

## EFFECTIVENESS OF WATER TREATMENT PROCESSES IN REMOVING PRECURSORS OF CHLORINATED ORGANIC SUBSTANCES FROM MIXTURES OF GROUNDWATER AND SURFACE WATER

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**Abstract.** Due to the correlation of  $UV_{254}$  and  $UV_{272}$  absorbance with the formation of oxidation and disinfection by-products, it is a very important indicator in assessing the effectiveness of water treatment processes. The aim of this study was to determine changes in the value of  $UV_{254}$  and  $UV_{272}$  absorbance in water after successive treatment processes at the Water Treatment Plant in Poland near the city of Zielona Góra, which takes underground and surface water from the Obrzyca River. Mixed water was characterized TOC reached values from 7.80 to 8.23 mgC/dm<sup>3</sup>, DOC from 7.10 to 7.83 mgC/dm<sup>3</sup>, and  $UV_{254}$  and  $UV_{272}$  absorption from 19.34 to 20.38 m<sup>-1</sup> and from 15.65 to 16.16 m<sup>-1</sup>. The treatment processes at the WTP near Zielona Góra include aeration of groundwater, microfiltration of surface water, coagulation of mixed water, sedimentation, filtration on catalytic-oxidative filter bed, filtration on dolomite filter bed and disinfection with chlorine dioxide. During technological studies carried out on a laboratory and technical scale, the following were tested as coagulant polyaluminum chloride with an alkalinity of 70% as well with an alkalinity of 85% which, in its composition, also contained iron. Analysis of the results showed that the highest reduction in  $UV_{254}$  and  $UV_{272}$  absorbance, by about 49 % and 53%, respectively, was obtained after coagulation with the polyaluminum chloride with 70% alkalinity, not containing iron compounds. It was also shown that both dolomite and catalytic-oxidative bed filtration increased the efficiency of removing precursors of oxidation and disinfection by-products. The dolomite bed increased the efficiency by about 7% ( $UV_{254}$ ) and about 9% ( $UV_{272}$ ) and the catalytic-oxidative bed increased the efficiency by about from 3 to 5% ( $UV_{254}$ ) and about from 3 to 4% ( $UV_{272}$ ).

**Keywords:** water treatment, precursors of chlorinated organic substances, polyaluminum chlorides, coagulation, dolomite filter bed.

### 1. Introduction

The need to remove organic substances from water intended for human consumption stems from the risks that these substances may pose to human health (Sillanpää et al., 2018). Some components of natural organic matter are toxic, while others may pose a risk due to the transformations they undergo during water treatment (Marais et al., 2018; Ibrahim & Aziz, 2014). The largest amount of hazardous organic substances is produced during chemical oxidation, especially when chlorine-based oxidants are used. Water abstracted for water supply purposes contains a very wide variety of organic substances that are precursors of oxidation and disinfection by-products, the determination of which requires the use of advanced analytical techniques (Wolska, 2014; Derrien et al., 2019; Jiang et al., 2025). In water supply practice, general indicators of organic substances with simple and rapid analysis are sought, which can be used

to control the operating parameters of individual water treatment processes. The most reliable indicator of the total organic content is total organic carbon (TOC) and dissolved organic carbon (DOC). These indicators directly determine the sum of total and dissolved organic carbon contained in organic compounds (Shetty & Goyal, 2022). Ultraviolet and visible absorption spectroscopy enables to determine the total amount of organic compounds in water by measuring the absorbance at a certain wavelength. The most common wavelengths for natural organic matter (NOM) measurements are from 220 nm to 280 nm. Absorbance at 254 nm is typical for measurements of aromatic compounds (Korshin et al., 1997; Chen et al., 2002; Albrektienė et al., 2012). Absorbance in ultraviolet (UV) light enables the determination of dissolved organic carbon (DOC) fractions and organic compounds characterised by a high content of aromatic rings and unsaturated bonds, which are considered precursors of by-products of oxidation and disinfection

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(Ates et al., 2007; Hua & Reckhow, 2007; Chowdhury et al., 2009; Machi & Molczan, 2016; Pan et al., 2016; Ding et al., 2019). UV absorption method is fast, simple, and requires neither complicated equipment nor chemical reagents for quantification of natural organic matter. Thus, UV absorption can be applied in practice as an alternative for the standard methods that have been used so far (Albrektienė et al., 2012; Pan et al., 2016). Absorbance measurements at wavelengths of 254 and 272 nm, which are not regulated by Polish law, are typically used for this purpose (Regulation of the Minister of Health, 2017). Sugars, ethers, alcohols and saturated carboxylic acids do not show absorbance at  $UV_{254}$  and  $UV_{272}$ , unlike humic acids, phenols, lignins and other compounds containing aromatic rings. Humic acids are the richest fraction of natural organic compounds in terms of chromophore content (Matilainen et al., 2011; Machi & Molczan, 2016; Rodríguez et al., 2016; Li & Hur, 2017; Jiang et al., 2025). The change in absorbance at  $UV_{254}$  during chlorination allows for monitoring of this process and assessment of the potential for the formation of chlorinated organic compounds, including trihalomethanes (THMs) (Gallard & Von Gunten, 2002; Beauchamp et al., 2018). However, it should be noted that absorbance measurement at  $UV_{254}$  is not completely selective either in relation to organic substances or their reactive forms. Nitrates, bromides and non-reactive organic compounds with conjugated double bonds also exhibit the ability to absorb radiation at this wavelength. It is suggested that the proportion of trihalomethanes (THMs) precursors can be measured more accurately at a wavelength of 272 nm, but this may be hindered by the rapidly decreasing absorbance of organic compounds present in water as the wavelength increases, which at low concentrations may make measurement difficult. The amount of precursors of chlorinated organic substances is proportional to the dissolved organic carbon (DOC) content in the water undergoing treatment, but above all to the absorbance of UV radiation at wavelengths of 272 nm and 254 nm. According to literature reports, organic substances that absorb UV radiation are mainly removed during adsorption and coagulation processes (Matilainen et al., 2011; Xu et al., 2011; Nowacka et al., 2014). Therefore, it is important to maximise the removal of organic substances containing aromatic rings in processes preceding disinfection with chlorine oxidants.

The aim of the study was to determine changes in absorbance values in the ultraviolet range ( $UV_{254}$  and  $UV_{272}$ ) as an indicator of organic matter content considered to be precursors of chlorinated organic compounds after successive stages of the water treatment process. The aim of this study was also to determine whether the presence of iron ions in high-basic polyaluminum chlorides and increasing the pH of the water during the coagulation process influences the final efficiency of purifying water obtained in the entire technological process. It was assumed that under such conditions, iron-organic complexes, difficult to remove from water, may be

formed between the DOC fraction containing aromatic rings present in water and iron ions introduced with the coagulant or present in the purified water.

## 2. Materials and methods

Scientific research was conducted to determine the effectiveness of removing organic substances containing aromatic rings at a Water Treatment Plant (WTP) in Poland, near Zielona Góra, which takes surface and groundwater. The subject of the study, conducted on a technical and laboratory scale, was a mixture of surface water from the Obrzyca River and groundwater from Quaternary formations. The groundwater, after aeration, was mixed with surface water after microfiltration on drum microfilters in a volume ratio of 1:2. Mixed water was characterized TOC reached values from 7.80 to  $8.23 \pm 0.05$  mgC/dm<sup>3</sup>, DOC from 7.10 to  $7.83 \pm 0.05$  mgC/dm<sup>3</sup>,  $UV_{254}$  and  $UV_{272}$  absorption from 19.34 to  $20.38 \pm 0.01$  m<sup>-1</sup> and from 15.65 to  $16.16 \pm 0.01$  m<sup>-1</sup>. This indicates that among the dissolved substances in the purified water were also organic substances containing aromatic rings, which have a high potential to form oxidation or disinfection by-products. Mixed water was characterized also by an increased total iron content from 1.00 to  $1.10 \pm 0.10$  mgFe/dm<sup>3</sup>, increased turbidity from 11 to  $15 \pm 0.10$  NTU, with the intensity of colour from 35 to  $40 \pm 1$  mgPt/dm<sup>3</sup> and pH from 8.10 to  $8.20 \pm 0.10$ .

During research conducted on a technical scale water samples were taken after successive treatment stages at a WTP near Zielona Góra in Poland. The samples were taken during the summer season. The treatment processes at the WTP near Zielona Góra include: aeration of groundwater in four cascades, with forced airflow, microfiltration of surface water using microscreen drum filters with 10 µm pores, coagulation and sedimentation of mixed water, filtration on sand filter bed covered by manganese (IV) and iron (III) oxides i.e. the so-called catalytic-oxidative filtration bed, filtration on dolomite filter bed where the filter bed is activated dolomite (CaCO<sub>3</sub>·MgO) and disinfection with chlorine (IV) oxide. Scheme of the water treatment process train applied in the WTP near Zielona Góra is shown in Figure 1. During technological studies carried out on a technical scale, the following were tested as coagulant polyaluminum chloride with an alkalinity of 70% (PAC-70) as well polyaluminum chloride with an alkalinity of 85% (PAC-85) which,

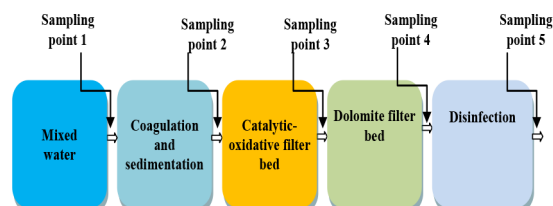


Figure 1. Water treatment process train applied in the Zielona Góra WTP

in its composition, also contained iron (0.7%). The doses of tested coagulants were 4 mgAl/dm<sup>3</sup>. The same coagulants were also tested on a laboratory scale.

Water samples were taken on intake (mixed water), after coagulation and sedimentation, after filtration on catalytic-oxidative filter bed, after filtration on dolomite filter bed and on plant outlet after disinfection. Table 1 shows the water sampling locations. On a laboratory scale a coagulation process was carried out with the use of the jar test. The jar tests were carried out by a 1 dm<sup>3</sup> six-place paddle stirrer (FlocculatorKemira 2000, Sweden). Coagulation was carried out in water samples of 1 dm<sup>3</sup> 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, PAC-70 as well as PAC-85 were tested. The doses of coagulants were expressed in mgAl/dm<sup>3</sup> and varying from 1 to 5 mg Al/dm<sup>3</sup>. After coagulation, the samples were subject to the sedimentation process for 1 h.

Table 1. Water sampling points

Sample number	Water sample collection points
1	Mixed water
2	After coagulation and sedimentation
3	After the filtration process on catalytic-oxidative filter bed
4	After the filtration process on a dolomite filter bed
5	After disinfection with chlorine (IV) oxide

For all water samples the following were determined: pH, turbidity, colour, total iron, UV absorbance at wavelengths of 254 nm and 272 nm, total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations. The physical-chemical composition of the raw water as well as treated water was determined according to the International Standard methods. The organic substances concentration was monitored by measuring the TOC, DOC, and UV absorbance at 254 and 272 nm. The TOC and DOC were measured using the thermal method and a multi N/C 3100 DUO Analytik Jena TOC Analyzer (Jena, Thuringia, Germany). DOC was analyzed by the TOC Analyzer after filtration through 0.45 µm pore diameter membranes. UV absorbance at 254 nm (UV<sub>254</sub>) and at 272 nm (UV<sub>272</sub>) were measured by a UV-Vis spectrophotometer Cary 3500 (Santa Clara, California, USA) using a quartz cell with 1 cm path length after filtration through 0.45µm membrane. The colour (according to Pt scale) and total iron were determined with the Agilent Cary 60 spectrophotometer (Santa Clara, California, USA). Turbidity was measured using the Hach 2100N Turbidimeter (Düsseldorf, Germany). The pH of the raw water and the purified water was determined with an WTW 3620 IDS SETC (Troisdorf, Germany) with a combination pH electrode with temperature corrections.

### 3. Results

Changes in the effectiveness of reducing UV<sub>254</sub> and UV<sub>272</sub> absorbance values and the effectiveness of TOC and DOC removal at subsequent stages of water treatment are shown in Figures 2–5.

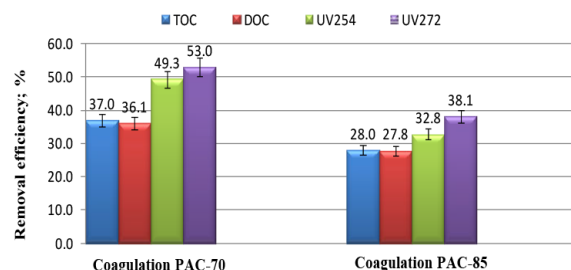


Figure 2. Efficiency of organic pollutant removal from water by coagulation

Analysis of the relationships shown in Figures 2–5 showed that the highest effectiveness of removing all fractions of organic substances was achieved during the coagulation process. Analysis of the results obtained showed that, of all the organic substance fractions in the coagulation process, UV<sub>272</sub> absorbance was reduced to the greatest extent, which, according to literature reports, can be used to measure THMs precursors. UV<sub>272</sub> absorbance was reduced by 53.0% and 38.1%, while UV<sub>254</sub> absorbance was reduced by 49.3% and 32.8%, respectively, after coagulation using PAC-70 and PAC-85 and also containing iron – Figure 2. The measurement of absorbance at a wavelength of 254 nm allowed the identification of the DOC fraction containing aromatic rings, which is also characterised by a high potential for the formation of oxidation and disinfection by-products. According to literature reports, the effectiveness of removing organic contaminants in the coagulation process increases with their degree of aromaticity and molecular weight. Among natural organic substances, low-molecular-weight, non-ionic and basic hydrophilic fractions are the most difficult to remove in the coagulation process, while large-molecular-weight aromatic compounds are best removed (Gray et al., 2002). The effectiveness of TOC and DOC removal in the PAC-70 coagulation process was 37.0% and 36.1%, respectively, and after the use of PAC-85 containing iron compounds, 28.0% and 27.8%, respectively. The pH in water after coagulation with PAC-85 was 7.90, and after coagulation with PAC-70 it was 7.50. As the pH of water increases, the degree of dissociation of organic compounds increases, and larger doses of coagulants are then required to remove them (Gray et al., 2002). The effectiveness of water purification in the coagulation process depended on the type of polyaluminium chloride tested. PAC-85, which was characterised by higher alkalinity and contained iron ions, resulted in significantly lower efficiency in removing all fractions of organic substances, as well as

lower efficiency in removing iron compounds and reducing turbidity. The effectiveness of iron removal from water and turbidity reduction was 67% and 77% during coagulation with PAC-85 and 88% and 93% during coagulation with PAC-70. The reason for the lower effectiveness of water purification in the coagulation process after the use of PAC-85 was probably the formation of iron-organic compounds, most likely in the form of protective colloids. The iron concentration, colour and turbidity in water after coagulation with PAC-85 were 0.40 mgFe/dm<sup>3</sup>, 18 mgPt/dm<sup>3</sup> and 4 NTU while in water after coagulation with PAC-70 were 0.12 mgFe/dm<sup>3</sup>, 11 mgPt/dm<sup>3</sup> and 1 NTU. In water after coagulation with PAC-85 the pH was 7.90, and in water after coagulation with PAC-70 the pH was 7.50.

The analysis of the relationship shown in Figure 3 showed that filtration through a catalytic-oxidative bed slightly increased the efficiency of removing all fractions of organic substances, in the range of 3 to 5%. A slightly higher efficiency in removing UV<sub>254</sub> and UV<sub>272</sub> absorbance, as well as TOC and DOC, as a result of filtration through a catalytic-oxidative bed was obtained for water after coagulation with PAC-70 (Figure 3).

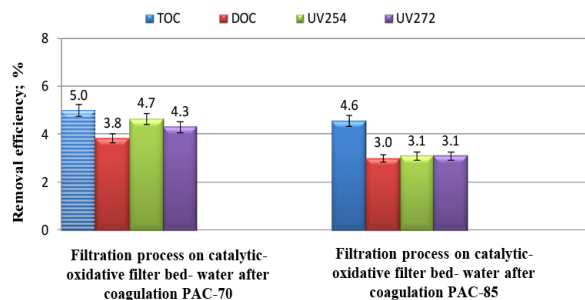


Figure 3. Efficiency of organic pollutant removal from water by filtration on a catalytic-oxidative filter bed

The iron concentration in water after filtration through a catalytic-oxidative bed for water after coagulation with PAC-85 was 0.3 mg Fe/dm<sup>3</sup>, while in water after coagulation with PAC-70 it was below 0.1 mgFe/dm<sup>3</sup>.

The analysis of the relationship presented in Figure 4 showed that the filtration process through the dolomite bed increased the efficiency of removing all fractions of organic substances by 3.3 to 9.3%. Among all fractions of organic substances, the removal efficiency of dissolved organic substances containing aromatic rings increased the most. The removal efficiency of UV<sub>272</sub> and UV<sub>254</sub> as a result of filtration through the dolomite bed increased by 9.3% and 6.2% for water after coagulation with PAC-85 and by 9.1% and 7.3% for water after coagulation with PAC-70 (Figure 4).

According to literature reports (Krupińska, 2019), the processes of removing organic substances containing aromatic rings, such as humic substances, as a result of filtration through a dolomite filter bed are related to the ability of these substances to form complexes with

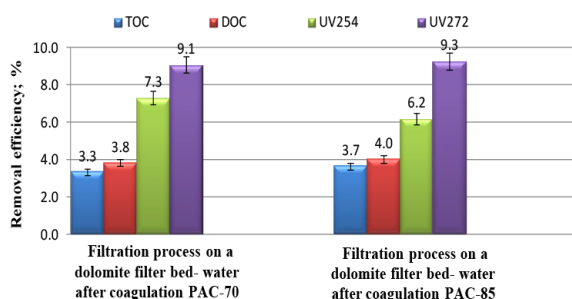


Figure 4. Efficiency of organic pollutant removal from water by filtration on a dolomite filter bed

calcium and magnesium ions. The complexes formed by calcium and magnesium ions with organic substances formed as a result of the ion exchange of the H<sup>+</sup> cation to a metal ion or as a result of the formation of coordinate bonds by -COOH and -OH functional groups containing oxygen, which play the role of a ligand as well as partially by ionic bonding (Krupińska, 2019, 2021).

During the chlorine (IV) oxide disinfection process, the greatest reduction in absorbance measured at a wavelength of 272 nm was observed, by 7.9% and 7.5% for water after coagulation with PAC-70 and PAC-85, respectively. The disinfection process also resulted in a reduction in absorbance measured at a wavelength of 254 nm by 5.8% and 4.2% for water after coagulation with PAC-70 and PAC-85, respectively (Figure 5).

Chlorine (IV) oxide, thanks to its radical structure is, above all, an acceptor of electrons and thus an oxidizer; in contrast to chlorine, it does not stimulate bonding or substitution reactions, and thus the chlorination reaction (Deborde & Von Gunten, 2008; Swietlik et al., 2009; Huang et al., 2020).

The by-products of the oxidation of organic substances in this case are mainly aldehydes, ketones and carboxylic acids. Although the disinfection process with chlorine (IV) oxide may result in the formation of by-products of organic compound oxidation, final disinfection with this reagent is necessary to maintain the appropriate bacteriological quality of water supplied to the water supply network.

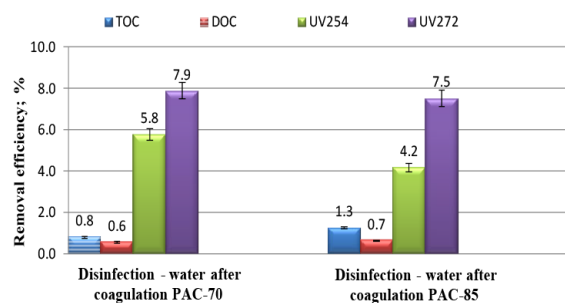


Figure 5. Efficiency of organic pollutant removal from water by disinfection

Analysis of the test results showed that after the use of PAC-85 containing iron compounds in the water

treatment process train at the WTP near Zielona Góra, the treated water did not meet the water quality requirements due to the concentration of TOC, iron and turbidity, which were 5.14 mgC/dm<sup>3</sup>, 0.22 mgFe/dm<sup>3</sup> and 1.10 NTU, respectively (Regulation of the Minister of Health, 2017). However, after using PAC-70 as a coagulant, the treated water met al. the parameters for water intended for human consumption. Analysis of the test results also showed that the absorbance values in treated water measured at wavelengths of 254 and 272 nm were 10.39 m<sup>-1</sup> and 7.38 m<sup>-1</sup>, and 6.90 m<sup>-1</sup> and 4.15 m<sup>-1</sup>, respectively, for water purified with PAC-85 and PAC-70.

Laboratory studies of the coagulation process using the jar test were also carried out, applying the same coagulants PAC-70 and PAC-85 in doses from 1 to 5 mgAl/dm<sup>3</sup>. The subject of the studies was also the same mixture of the surface water from the Obrzyca River after microfiltration, as well as groundwater subjected to the aeration process collected in the summer season at the Zawada Water Treatment Plant.

The analysis of the obtained results showed that, similarly to the studies carried out on a technical scale, a higher effectiveness of water purification was obtained when applying the coagulant PAC-70 rather than PAC-85. The pH of water after coagulation with the PAC-85 ranged from 7.85 to 7.96, and in water following PAC-70, from 7.50 to 7.80 for doses from 1 to 5 mgAl/dm<sup>3</sup>. In water samples following PAC-85 coagulation, a higher concentrations of organic substances measured as TOC, DOC as well as UV<sub>254</sub> and UV<sub>272</sub> were noted. The concentration of TOC changed from 7.22 to 5.79 mgC/dm<sup>3</sup>, DOC from 6.92 to 5.59 mgC/dm<sup>3</sup>, UV<sub>254</sub> from 17.73 to 13.20 m<sup>-1</sup>, and UV<sub>272</sub> from 14 to 10.32 m<sup>-1</sup> for doses from 1 to 5 mgAl/m<sup>3</sup>. The colour after coagulation with PAC-85 changed in the range from 24 to 16 mgPt/dm<sup>3</sup>. In water samples following PAC-85 coagulation, the concentration of iron as well as turbidity for doses from 1 to 5 mgAl/m<sup>3</sup> ranged from 0.31 to 0.22 mgFe/dm<sup>3</sup> and from 3.20 to 2.34 NTU, and were significantly greater than after PAC-70 coagulation. The concentration of iron and turbidity of the water after coagulation with the PAC-70 coagulant took on respective values ranging from 0.14 to 0.08 mgFe/dm<sup>3</sup> and from 2.11 to 0.91NTU.

The analysis of relationships presented in Table 2 showed that, in water following coagulation with PAC-85, linear correlations were confirmed between iron, turbidity, color and UV<sub>254</sub>.

This confirms that chromatic iron-organic complexes were created in the water following coagulation. After the coagulation process with PAC-85 containing iron additives in its composition, the high values of the Pearson coefficient were confirmed between iron and dissolved organic substances containing aromatic rings, as well as between turbidity and iron and also between the colour and UV<sub>254</sub>.

The reason behind the formation of chromatic iron-organic complexes over the course of coagulation with

the highly-alkaline PAC-85 coagulant may have been the high pH, falling into the range of 7.96 to 7.85, in which the functional groups of -COOH and -OH organic substances are more reactive in relation to iron ions (Krupińska, 2021).

Table 2. Parameters of linear correlations between the iron, turbidity and the organic matter indices of the water samples after PAC-85 coagulation

Linear correlation equation	Coefficient of the Pearson correlation (R)
Fe = 0.0206 UV <sub>254</sub> - 0.1334	0.9389
Turbidity = 9.9331Fe + 1.2595	0.9489
Turbidity = 0.2431UV <sub>254</sub> - 0.8480	0.8526
Colour = 74.105 Fe + 34.041	0.8834
Colour = 1.7273 UV <sub>254</sub> - 3.3383	0.9802

The second reason may have been the introduction of additional iron ions along with the coagulant, which may have reacted with the organic substance present in the treated water. The chromatic iron-organic complexes formed during PAC-85 coagulation most likely exhibited the character of protective colloids, hence leading to the significantly higher turbidity that followed PAC-85 coagulation as compared to the turbidity after PAXXL10 coagulation. During the research conducted by Albrektiene (Albrektiene et al., 2011) with the use of groundwater containing iron-organic complexes, it was shown that water pH has the greatest impact on the removal of iron-organic complexes from drinking water during coagulation. Iron-organic complexes are best eliminated from drinking water when its pH is from 6.8 to 6.5 a rise in pH reduces the effectiveness of their removal.

#### 4. Conclusions

The analysis of the effectiveness of removing organic fractions at individual stages of the water treatment process in the summer showed that precursors of chlorinated organic substances, assessed as the content of substances exhibiting absorption of ultraviolet radiation with wavelengths of 254 and 272 nm, were most effectively removed in the coagulation process. The effectiveness of their removal depended on the alkalinity and iron content of the tested polyaluminium chlorides. The reason for the lower effectiveness of removing organic substances showing absorbance at wavelengths of 254 and 272 nm in the coagulation process after the use of polyaluminium chloride with a higher alkalinity of 85% and containing iron in its composition was the formation of iron-organic compounds, most likely in the form of protective colloids. This was also confirmed by laboratory tests using the jar test for the same coagulants that were tested on a technical scale but at variable doses.

Analysis of the test results also showed that both the filtration stage on the catalytic-oxidative bed and on the

dolomite bed increased the effectiveness of removing precursors of chlorinated organic substances, and the processes of their removal from water were probably

the result of co-precipitation with iron and manganese compounds as well as calcium and magnesium.

Further research is planned using highly alkalinity polyaluminium chlorides to determine the impact of seasonal changes in the physical and chemical composition of treated water, with particular emphasis on organic fractions, on the possibility of forming iron-organic complexes and, consequently, on the quality of treated water.

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