Removal of trihalomethane (THM) precursors from water during coagulation enhanced by ozonation

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ABSTRACT

The aim of the study was to evaluate the effectiveness of the reduction of surface water pollution level in the coagulation process with polyaluminum chloride and coagulation supported by ozonation process. The effectiveness of these processes was evaluated in relation to the decrease in turbidity and color of water, the content of organic compounds (determined by total organic carbon (TOC) and dissolved organic carbon, oxidizability (OXI), ultraviolet absorbance) and the potential for the formation of THM-FP trihalomethanes. The use of pre-ozonation and coagulation with polyaluminum chloride allowed for a reduction in the content of organic matter determined by TOC, OXI, absorbance UV by 28%–38%, 39%–54%, and 48%–73%, respectively. Compared to the effects obtained using only the coagulation process, this was an increase of 4%–8%, 6%–12%, and 10%–18%, for TOC, OXI, and absorbance UV, respectively. The effectiveness of water purification depended on the quality of raw water, month and location of water collection. The potential for THM formation in treated water in the coagulation process was by 50%–56% lower than in untreated surface water after chlorination. The application of additional pre-ozonation resulted in an additional reduction of THM-FP by 1%–10%.

Keywords: Ozonation; Coagulation; Organic matter; Trihalomethanes (THMs); Water

1. Introduction

The main components of natural organic matter (NOM) present in surface waters are humic substances and compounds with relatively low molecular weights, such as hydrophilic acids, proteins, and amino acids. A particular increase in interest in the composition of humic substances in water is related to the publication of studies on the generation of trihalomethanes (THMs) during water chlorination. The concentration of THM sum, which includes: trichloromethane ($CHCl_3$), tribromomethane ($CHBr_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$) is normalized in drinking water and is equal to 100 µg/L [1]. $CHCl_3$ and $CHCl_2Br$ have been classified as potentially carcinogenic to humans [2]. The prevention of

THM creation in chlorinated water is the effective removal of NOM from water, primarily humic and fulvic acids. The degree of removal of organic substances increases with their content in treated water, as well as with their molecular weight and the degree of aromaticity. The processes used to remove NOM from water include coagulation, adsorption, ion exchange, membrane filtration, chemical oxidation combined with biological filtration [3,4]. Coagulation and flocculation followed by sedimentation/flotation and filtration have been considered as the most common and economically feasible process to remove NOM [3].

The requirement for effective coagulation is the usage of the right coagulant and its optimal dose. The choice of coagulant is determined both by its ability to destabilise the removed impurities, as well as the formation of permanent,

poorly soluble coagulation flocks, susceptible to removal from water. In coagulation, it is more difficult to remove colored substances than those causing turbidity. Both non-hydrolysed and pre-hydrolysed salts are used for the coagulation process. The basic non-hydrolyzed coagulants include $Al_2(SO_4)_3$, $AlCl_3$, $FeSO_4$, $Fe_2(SO_4)_3$, $FeCl_3$. Unlike the abovementioned coagulants, the pre-hydrolysed coagulants contain hydroxyl groups that determine their increased alkalinity. The most studied and applied pre-hydrolysed metal-ion coagulants are polyaluminum chloride, polyferric chloride, polyferric sulfate [5]. These coagulants can be modified with e.g. chitosan [6]. Comparison of the efficiency of organic substance removal using coagulants with different degree of hydrolysis demonstrated a large difference, within the range of 25%–67%, in the reduction in dissolved organic carbon (DOC) content [7]. Significant discrepancies in the results can be explained by both the complex structure of organic compounds and the diversity of commercial coagulants whose accurate chemical composition is unknown. Seasonal changes in water quality also have a great impact on the efficiency of treatment. Zhang et al. [6] argued that polyaluminum chlorides with higher-basicity (with a larger proportion of colloidal and smaller proportion of monomeric Al species in the coagulant) are better for removing water turbidity and NOM.

Coagulation can be enhanced by the oxidation process, that is, with ozone or adsorption using powdered activated carbon [8–10]. Ozonation is an effective oxidation technology for the removal of recalcitrant organic compounds. Two major oxidants involved are molecular ozone O_3 and hydroxyl radical $OH^\bullet$ [11]. Ozone can react with substances dissolved in water in two ways: in the direct reaction of molecular ozone and indirectly through the reactions of free radicals formed during the breakdown of the ozone molecule in water [12]. Pre-ozonation can cause an increase in the average size of colloidal particles, the formation of colloidal particles from dissolved organic matter, improvement of removal of organic matter or turbidity in sedimentation and filtration processes. Studies demonstrated that ozonation can oxidize and transform large-molecular and highly hydrophobic NOM to smaller-size and more hydrophilic substances [11]. Ozonation generally increases the biodegradability of NOM in water through the transformation of larger organic molecules that are more easily biodegraded [13]. Pre-ozonation is not recommended for waters with high algae concentrations due to the concerns about the formation of disinfection by-products DBPs [14].

Enhancing the removal of organic matter with ozone can take place in two ways: ozonation with low doses of ozone (0.1–0.5 mg-O_3/mg-C) and then solid-phase removal processes or removal of organic matter by ozonation with doses > 1 mg-O_3/mg-C and filtration through biologically active carbon. Almost complete color removal is achieved for ozone doses of 1–3 mg-O_3/mg-C. Although ozonation does not lead to mineralization of organic carbon, but rather only a slight decrease in its content is observed, in neutral pH conditions a significant reduction in the molecular weight of humic substances occurs.

In previous studies, the assessment of the effectiveness of these processes was most often conducted in relation to the reduction of the overall NOM content. In the presented research, the applied processes were also evaluated in terms of reducing this organic matter, which may be a precursor of trihalomethane formation during chlorination of water. This approach to the assessment of the coagulation process and coagulation preceded by water ozonation was to indicate the need to optimize processes not only in terms of reducing water turbidity and color and the content of organic compounds but also in terms of the effectiveness of removing precursors of water disinfection by-products in these processes. The authors of other publications point to the constant need for research in this area [8,11–13].

2. Materials and methods

2.1. Materials

Surface water collected in May and July 2018 in the city of Częstochowa from the Rivers Warta and Stradomka, hereinafter referred to as raw waters, were used for the research.

The coagulant was chosen based on earlier studies (Table 1 [15]) during which the best effects of purification of water from the Warta River were obtained using highly basicity, pre-hydrolyzed polyaluminum chloride with a trading name PAX-1910 produced by the company KEMIPOL in city Police (Poland). The basicity of the commercial coagulant solution was 85% (OH^-/Al^{3+} = 2.55) and the Al_2O_3 content was 19.8%. The remaining coagulants PAX-18, PAX-61, and PAX-19F were characterized by the basicity of 41%, 70%, and 85%, respectively, and an Al_2O_3 content of 17%, 10%, and 16%, respectively. A working solution of coagulant PAX-1910 was prepared by diluting commercial product to contain 1.0 g-Al/L of solution.

2.2. Ozonation water and jar test procedure

The process of water ozonation was carried out under laboratory conditions. For this purpose, 1.5 L of water was measured into a 2 L reactor. Ozonation with a dose of 5 mg-O_3/L was carried out for 5 min. The dose was selected based on literature data [9–12,16]. High purity oxygen (99%) was supplied with a flow rate of 1.2 L/min to an ozone generator (Model L20 SPALAB, Korona, Poland). A spherical stone diffuser was used to disperse the air enriched with ozone directly into a 1.5 L sample at the bottom of a reactor. Applied and transferred ozone dosage was determined by the iodometric titration of trapped ozone in potassium iodide solution. The unreacted ozone in the off-gas was also trapped in iodide solution and quantified by iodometric titration.

After the ozonation process, the water was poured into the first 2 L glass beaker, and 1.5 L of non-ozonated water was measured into second. 4.5 mL of coagulant solution was introduced into the water in both beakers, corresponding to a dose of 3.0 mg-Al/L. Using a mechanical stirrer, rapid stirring was continued for 2 min (using 250 rpm), followed by slow stirring for 15 min (25 rpm). After this time, the samples were subjected to 60 min sedimentation. Next, 0.4 L of water was decanted and the analysis were performed to determine: color, turbidity, pH, oxygen consumption, total organic carbon (TOC), dissolved organic carbon (DOC), and ultraviolet absorbance.

Table 1
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) [15]

Parameter	Raw water Warta River	Water purified with PAX			
		18	61	1910	19F
Turbidity, NTU	6.40	3.89	3.33	1.16	2.41
Color, mg-Pt/L	45	20	18	10	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

2.3. Analytical methods

The surface water quality indices before and after the treated process were determined using the following methods: color–comparison with standards on the platinum-cobalt scale, turbidity–nephelometric (HI 98703 Hanna Instruments turbidity meter), pH–potentiometric (CX-505 multifunction laboratory meter Elmetron), oxygen consumption – oxidisability (OXI)–permanganate method, TOC and DOC (after water filtration through 0.45 μm membrane filter)–by infrared spectrophotometry (Analytik Jena's Multi N/C analyzer), ultraviolet absorbance at 254 nm wavelength UV$_{254}$ (UV 5600 Shanghai, China Metash Instruments spectrophotometer). The color was determined twice, whereas other indices were measured in triplicate. SUVA (ratio of UV$_{254}$ absorbance to DOC value) was calculated to determine the properties of dissolved organic substances in water and their susceptibility to removal by coagulation.

2.4. THM formation potential

To determine the potential of the formation of THM-FP trihalomethanes, 50 mL of raw water or treated was poured into dark bottles [17]. A dose of chlorine water prepared from sodium hypochlorite was such that after 24 h at a temperature of ca. 22°C, the concentration of free chlorine ranged from 3 to 5 mg-Cl$_2$/L. To determine the concentration of THMs in water samples after 24 h, 10 mL of water was collected to the test tubes and 1 mL of *n*-pentane was added, followed by intensive shaking for 3 min. After separation of the layers, a 2 μL extract was sampled with a microsyringe, followed by the separation of the compounds on a DB-5 capillary column and analysis by means of gas chromatography with an electron capture detector (a model Agilent 6890N, Agilent Technologies, USA). The analysis were performed in triplicate. The equation was used to report THM-FP in unit of μg-CHCl$_3$/L: $A + 0.728B + 0.574C + 0.427D$ (where A = μg-CHCl$_3$/L; B = μg-CHCl$_2$Br/L; C = μg-CHClBr$_2$/L; D = μg-CHBr$_3$/L) [17]. The potential for THM formation in chlorinated raw water after 15, 30, 60, 120, 180, and 360 min was also determined in a way described above.

3. Results and discussion

The values of quality indicators for raw water and water after the coagulation process or coagulation enhanced by the ozonation process, such as pH, turbidity, color, oxidisability (OXI), TOC, DOC, absorbance in ultraviolet UV$_{254}$, are presented in Tables 2–5.

Surface waters collected in May and July 2018 were characterised by varied turbidity and color. The turbidity of water from the Warta River amounted to 29 and 6 NTU and from the Stradomka River 7 and 14 NTU. The color water was estimated at the level of 30–45 mg-Pt/L. The water reaction was alkaline (pH 7.45–7.91), with the exception of water from the Stradomka River collected in May (pH 6.8). The TOC content varied from 8 to 13 mg/L and the oxidisability varied from 7 to 9 mg-O$_2$/L. DOC represented 77%–86% of TOC. The UV$_{254}$ absorbance was equal to from 19 to 25 m^{-1}. The values of these indicators were comparable to the values obtained for waters collected from the Warta River in the period of July 2016–April 2018, which respectively amounted for TOC from 8 to 19 mgC/L, DOC from 7 to 14 mgC/L, UV absorbance from 15 to 33 m^{-1} [18].

UV absorbance is commonly used as an indicator of the content of aromatic groups, considered to be components very reactive during water disinfection. The highest values of the analyzed indicators such as TOC, DOC and UV absorbance, were obtained for water from the Stradomka River collected in May 2018.

During surface water purification in the coagulation process conducted using polyaluminum chloride PAX-1910, a 69%–86% reduction in water turbidity was obtained. The color of the analyzed waters was reduced by 55%–67%. Better results were obtained in the case of purification of water from the Warta River. Coagulation enhancement by the ozonation process mainly improved the effect of water-color removal. The decrease in the value of this indicator increased by 16%–29%. In the case of turbidity, the increase in efficiency was equal to 7%–12%.

The percentage reduction in the TOC content, as well as the values of oxidation and UV$_{254}$ absorbance during the coagulation process and coagulation enhanced by the ozonation process of the analyzed surface waters are presented in Figs. 1 and 2, respectively. The effectiveness of water purification depended on the quality of raw water, month and location of water collection.

The content of organic compounds, determined as TOC and DOC, in waters after the coagulation process using polyaluminum chloride PAX-1910 decreased by 28%–34% and 18%–24%, respectively. DOC in treated waters accounted for 90%–97% of TOC. Oxidisability decreased by 39%–47% and the value of UV$_{254}$ absorbance by 48%–62%. A greater reduction in the value of indicators was obtained in the case of purification of water collected from the Stradomka River.

Both these and previously conducted studies indicate that the effectiveness of water purification is affected by seasonal variations in water quality. The presented results were obtained for water collected in the spring and summer of 2018. In previous research on the purification of water collected in the various months of 2016 and 2017 from the Warta River, the effectiveness of the coagulation process with the usage of PAX-1910 in case of reducing TOC, DOC and UV absorbance amounted to 26%–39%; 23%–33%; 53%–64%, respectively [18]. Therefore, it was slightly higher than obtained in the presented research.

Brookes and others [19] also emphasized the impact of seasonal variability of raw water quality on the effectiveness

Table 2
Selected physicochemical properties of water from the Warta River collected in May and water treated

Parameter	Raw water Warta River	Water treated in May using	
		PAX	O_3 + PAX
pH	7.45 ± 0.02	7.18 ± 0.03	7.30 ± 0.02
Turbidity, NTU	28.7 ± 0.3	4.3 ± 0.2	2.3 ± 0.1
Color, mg-Pt/L	35.0 ± 0.0	15.0 ± 0.0	5.0 ± 0.0
OXI, mg-O_2/L	9.0 ± 0.1	5.5 ± 0.1	4.7 ± 0.1
TOC, mg/L	10.2 ± 0.2	6.7 ± 0.1	6.3 ± 0.1
DOC, mg/L	7.9 ± 0.1	6.5 ± 0.1	6.2 ± 0.1
UV_{254}, 1/m	20.5 ± 0.2	10.6 ± 0.1	6.9 ± 0.0
SUVA, L/mg-C·m	2.59 ± 0.04	1.63 ± 0.02	1.11 ± 0.01

SUVA = UV_{254}/DOC

Table 3
Selected physicochemical properties of water from the Warta River collected in July and water treated

Parameter	Raw water Warta River	Water treated in July using	
		PAX	O_3 + PAX
pH	7.91 ± 0.03	7.61 ± 0.01	7.73 ± 0.02
Turbidity, NTU	6.3 ± 0.2	1.0 ± 0.1	0.4 ± 0.1
Color, mg-Pt/L	30 ± 0.0	10 ± 0.0	5 ± 0.0
OXI, mg-O_2/L	6.8 ± 0.1	4.0 ± 0.1	3.6 ± 0.0
TOC, mg/L	7.5 ± 0.2	5.2 ± 0.1	5.0 ± 0.1
DOC, mg/L	6.6 ± 0.1	5.0 ± 0.1	4.7 ± 0.1
UV_{254}, 1/m	18.9 ± 0.1	8.1 ± 0.1	5.1 ± 0.1
SUVA, L/mg-C·m	2.86 ± 0.06	1.62 ± 0.06	1.09 ± 0.04

SUVA = UV_{254}/DOC

Table 4
Selected physicochemical properties of water from the Stradomka River collected in May and water treated

Parameter	Raw water Stradomka River	Water treated in May using	
		PAX	O_3 + PAX
pH	6.80 ± 0.01	6.83 ± 0.02	6.93 ± 0.03
Turbidity, NTU	7.4 ± 0.2	2.3 ± 0.1	1.7 ± 0.1
Color, mg-Pt/L	45 ± 0.0	20 ± 0.0	10 ± 0.0
OXI, mg-O_2/L	8.8 ± 0.1	4.5 ± 0.1	4.0 ± 0.1
TOC, mg/L	12.9 ± 0.2	8.7 ± 0.1	8.1 ± 0.1
DOC, mg/L	10.5 ± 0.1	8.2 ± 0.1	7.9 ± 0.1
UV_{254}, 1/m	24.6 ± 0.1	11.2 ± 0.1	7.8 ± 0.1
SUVA, L/mg-C·m	2.34 ± 0.03	1.37 ± 0.03	0.99 ± 0.02

SUVA = UV_{254}/DOC

Table 5
Selected physicochemical properties of water from the Stradomka River collected in July and water treated

Parameter	Raw water Stradomka River	Water treated in July using	
		PAX	O_3 + PAX
pH	7.87 ± 0.04	7.77 ± 0.02	7.84 ± 0.02
Turbidity, NTU	13.6 ± 0.3	3.5 ± 0.2	1.9 ± 0.1
Color, mg-Pt/L	40 ± 0.0	15 ± 0.0	5 ± 0.0
OXI, mg-O_2/L	8.5 ± 0.1	4.9 ± 0.0	3.9 ± 0.1
TOC, mg/L	9.8 ± 0.2	7.1 ± 0.1	6.3 ± 0.1
DOC, mg/L	8.4 ± 0.1	6.4 ± 0.1	5.8 ± 0.1
UV_{254}, 1/m	22.5 ± 0.1	8.6 ± 0.1	6.2 ± 0.1
SUVA, L/mg-C·m	2.68 ± 0.03	1.34 ± 0.03	1.07 ± 0.02

SUVA = UV_{254}/DOC

of water purification, pointing out the importance of favorable conditions for algae development and short-term weather events (downpours).

It is believed [7] that a higher reduction in UV absorbance with respect to the reduction in DOC content means that aromatic substances are removed more effectively during coagulation compared to other fractions of organic matter. According to Marais et al. [20], aromatic fractions of NOM are the main precursors of THMs formation in some but not all seasons of the year (especially in warmer summer months). The calculated SUVA index (UV_{254}/DOC) for raw waters amounted to 2.3–2.9 L/mg-C·m. As demonstrated in [7], this value in the range of 2.0–4.0 L/mg-C·m indicates a mixture of humic and non-humic, hydrophilic and hydrophobic substances (high and low molecular) in surface water, with the effectiveness of DOC removal in the process of coagulation ranging from 25% to 50% if aluminum salts are used. Whereas, SUVA <2.0 L/mg-C·m indicates the presence of non-humic, hydrophilic, low molecular weight substances in the purified water.

Coagulation enhancement by the ozonation process resulted in greater efficiency in the removal of organic compounds. The removal efficiency of organic compounds determined as TOC and OXI increased by 4%–8% and 6%–12%, respectively, and determined as the UV absorbance by 10%–18% (Figs. 1 and 2). Tubić et al. [21] obtained a ca. 50% reduction in DOC content using polyaluminum chloride and a ca. 60% decrease in UV_{254} absorbance. Application of pre-ozonation enhanced total coagulation efficiency (up to 61% and 80% for DOC and UV_{254}, respectively), probably due to its micro-flocculation effect.

According to Bose and Reckhow [8] in a water-containing both humic and non-humic NOM, the beneficial effects of ozonation on NOM removal may only be obtained if ozone is allowed to react exclusively with the non-humic components of the NOM. This is possible if the humic substances are removed by an initial coagulation step. Subsequent ozonation of the pre-coagulated water, followed by a second coagulation step, will achieve superior DOC [8].

THM concentrations in water from the Warta and Stradomka Rivers subjected to chlorination for 24 h and in waters treated in the process of coagulation or coagulation enhanced by ozonation and then subjected to chlorination for 24 h are presented in Tables 6–9.

In the case of water collected from the Warta River and subjected to chlorination, the concentration of $CHCl_3$ amounted to 402 and 327 μg/L, while for the water from the
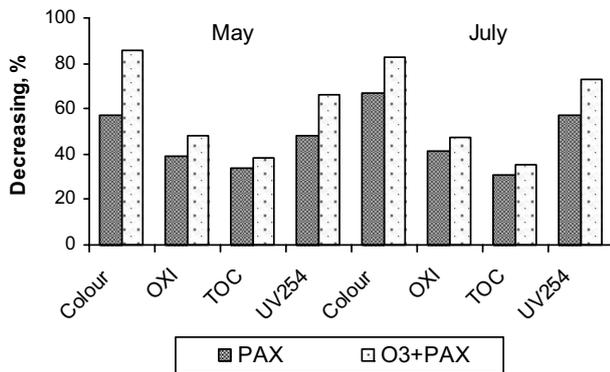
Fig. 1. Decreasing of color, OXI, TOC and UV absorbance after the coagulation using PAX, and coagulation enhancement by ozonation process (water from the Warta River).
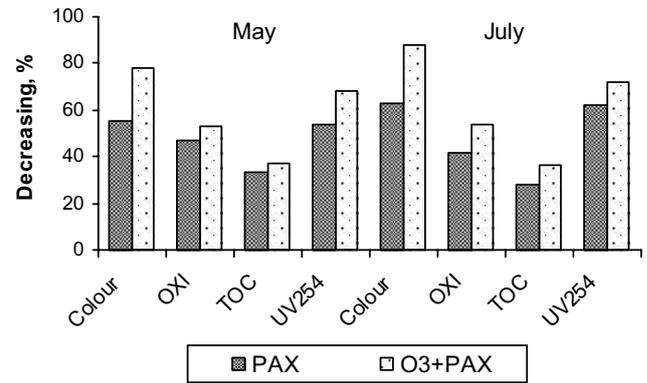
Fig. 2. Decreasing of color, OXI, TOC and UV absorbance after the coagulation process using PAX, and coagulation enhancement by the ozonation process (water from the Stradomka River).

Table 6
THM concentrations in raw water collected in May and water treated subjected to chlorination for 24 h

Parameter	Raw water Warta River	Water treated in May using	
		PAX	O_3 + PAX
$CHCl_3$, µg/L	402.0 ± 5.0	188.7 ± 3.2	182.1 ± 2.5
$CHCl_2Br$, µg/L	33.4 ± 2.1	24.4 ± 1.9	27.8 ± 1.4
$CHClBr_2$, µg/L	1.5 ± 0.1	2.1 ± 0.2	2.5 ± 0.2
$CHBr_3$, µg/L	<0.1	<0.1	<0.1
THM-FP, µg-$CHCl_3$/L	427.2 ± 6.6	207.7 ± 4.7	203.8 ± 3.6

Table 7
THM concentrations in raw water collected in July and water treated subjected to chlorination for 24 h

Parameter	Raw water Warta River	Water treated in July using	
		PAX	O_3 + PAX
$CHCl_3$, µg/L	327.0 ± 3.8	148.5 ± 2.8	140.2 ± 2.6
$CHCl_2Br$, µg/L	20.2 ± 1.8	20.8 ± 1.1	18.2 ± 0.7
$CHClBr_2$, µg/L	0.9 ± 0.1	1.5 ± 0.2	2.1 ± 0.2
$CHBr_3$, µg/L	<0.1	<0.1	<0.1
THM-FP, µg-$CHCl_3$/L	342.2 ± 5.2	164.5 ± 3.7	154.7 ± 3.2

Table 8
THM concentrations in surface water collected in May and water treated subjected to chlorination for 24 h

Parameter	Raw water Stradomka River	Water treated in May using	
		PAX	O_3 + PAX
$CHCl_3$, µg/L	394.0 ± 4.8	190.4 ± 2.9	150.7 ± 3.3
$CHCl_2Br$, µg/L	28.4 ± 1.3	23.9 ± 0.9	21.4 ± 0.6
$CHClBr_2$, µg/L	1.3 ± 0.2	1.9 ± 0.1	2.3 ± 0.2
$CHBr_3$, µg/L	<0.1	<0.1	<0.1
THM-FP, µg-$CHCl_3$/L	415.4 ± 5.9	208.9 ± 3.6	167.6 ± 3.9

Table 9
THM concentrations in raw water collected in July and water treated subjected to chlorination for 24 h

Parameter	Raw water Stradomka River	Water treated in July using	
		PAX	O_3 + PAX
$CHCl_3$, µg/L	484.0 ± 4.2	205.8 ± 4.4	176.0 ± 3.2
$CHCl_2Br$, µg/L	25.7 ± 1.7	19.1 ± 1.1	22.5 ± 0.5
$CHClBr_2$, µg/L	1.1 ± 0.2	1.3 ± 0.2	0.8 ± 0.1
$CHBr_3$, µg/L	<0.1	<0.1	<0.1
THM-FP, µg-$CHCl_3$/L	503.3 ± 5.6	220.5 ± 5.3	192.8 ± 3.6

Stradomka River – 394 and 484 µg/L. These values constituted respectively 92%, 94%, 93%, and 95% of the sum of the contents of four analyzed THM. The high relative formation of $CHCl_3$ in accordance with previous findings regarding THM formation within drinking water [22].

It has been shown that already during 2 and 6 h of water chlorination, 38%–48%, and 52%–60% of $CHCl_3$ are formed, respectively, in relation to the value obtained after 24 h of chlorination–Table 10.

According to Marais et al. [20], most of the THMs are formed during the first 6 h after the introduction of chlorine into the water. Other factors include the pH of the

water, composition of raw water, chlorine dose, temperature and the presence of bromides [23–25]. Typically, compounds containing active structures (e.g., unsaturated bonds, amines, aromatic bonds) are highly reactive with chlorine [11]. Hydrophobic acids HoA were indicated as the most reactive fractions of organic substances in the formation of THMs [26]. However, as demonstrated in [27], the mixture of hydrophobic base and neutral HoS fraction, containing lower lever of DOC and UV_{254} than the HoA fraction, exhibited higher chloroform yields than the HoA fraction.

In the water from the Warta River treated in the coagulation process and subjected to chlorination for 24 h, the

Table 10
Trichloromethane concentration (µg/L) in surface waters
subjected to chlorination for 24 h

Time, (h)	Raw water from the Warta River		Raw water from the Stradomka River	
	May	July	May	July
0.25	88.4 ± 2.6	78.2 ± 2.3	115.6 ± 2.7	142.2 ± 3.2
0.5	120.1 ± 3.1	117.3 ± 2.8	167.2 ± 4.1	181.4 ± 4.3
1.0	136.7 ± 2.9	129.4 ± 4.0	182.4 ± 2.9	203.1 ± 3.7
2.0	153.4 ± 3.4	138.1 ± 3.5	191.3 ± 3.9	214.0 ± 3.3
3.0	162.3 ± 3.6	145.2 ± 3.8	202.6 ± 3.7	221.3 ± 3.6
6.0	209.0 ± 2.8	180.3 ± 4.1	237.0 ± 3.5	269.0 ± 4.4
24.0	402.0 ± 5.0	327.0 ± 3.8	394.0 ± 4.8	484.0 ± 4.2

Fig. 3. Decreasing of $CHCl_3$ concentration and of THM-FP value in chlorinated waters treated by coagulation and coagulation enhancement by ozonation (V – May, VII – July).

concentration of $CHCl_3$ was equal to 189 and 149 µg/L and was by 53% and 55%, respectively, lower than the values obtained in chlorinated water not subjected to coagulation. These values were comparable with previously obtained results–65% [15] and prove the high efficiency of removal of organic water components in the coagulation process, which are precursors of the by-product of chlorination – trichloromethane. Coagulation enhancement by the ozonation process did not result in a significant further reduction of $CHCl_3$ concentration in treated chlorinated water.

In the case of water from the Stradomka River treated in the coagulation process and subjected to chlorination, the concentration of $CHCl_3$ was equal to 190 and 206 µg/L and was respectively by 52% and 57% lower than the values obtained in chlorinated raw surface water. The application of the ozonation process before the coagulation resulted in a further reduction of $CHCl_3$ concentration in water by 10% and 7%.

The concentration of $CHCl_2Br$ in untreated waters subjected to chlorination amounted to from 20 to 33 µg/L, and in chlorinated waters previously treated in the coagulation process from 19 to 24 µg/L. Ozone enhancement of the coagulation did not significantly influence the concentration of $CHCl_2Br$ during the chlorination of purified water. The presence of $CHClBr_2$ was at the level of 0.8–2.5 µg/L.

Percentage decreases of $CHCl_3$ concentration and THM-FP value in chlorinated waters treated in the coagulation process using the coagulant PAX-1910 and in the coagulation process preceded by water ozonation are shown in Fig. 3.

THM-FP was 50%–56% lower in water treated in the coagulation process and subjected to chlorination for 24 h than the values obtained in chlorinated raw water. Matilainen et al. [7] argue that in waters treated by coagulation, a reduction in the potential of THM formation can reach from 25% to 66%. The application of an additional ozonation process resulted in a further reduction in the THM-FP value by 1%–10%. The possibility to reduce the THM-FP value during water treatment with ozonation and coagulation has been confirmed by other studies [16,21].

Agababa et al. [28] studied waters with different DOC contents (5–10 mg/L) and a hydrophobic fraction of NOM ranging from 42% to 79%. It was determined that increasing
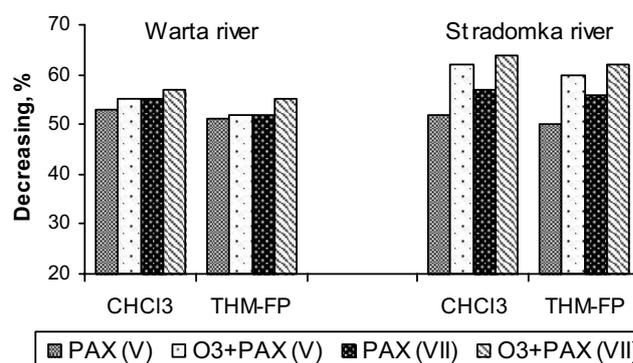
the ozone dose (0.2–0.8 mg-O_3/mg-C) led to reductions in DOC (2%–26%) and THM-FP values (4%–58%).

According to Deeudomwongsa et al. [11], water pre-treatment by ozonation leads to NOM oxidation to lower molecular weight hydrophilic organic substances. In the samples ozonated with 1–5 mg/L of ozone, the aromatic compounds, as measured by the absorbance of UV_{254}, were removed in the range of 23%–60%, but the reduction of THM-FP was only 10%. An increase in the dose of ozone to 15 mg/L did not significantly improve the reduction of THM-FP and influenced mainly the decrease in the concentration of $CHClBr_2$ [11].

4. Conclusions

The study confirmed the usefulness of the coagulation process in the removal of organic matter, which represents a precursor for the formation of trihalomethanes. In the laboratory conditions conducting the coagulation process using pre-hydrolyzed polyaluminum chloride PAX-1910, the decrease in the content of organic compounds determined with the indicators: oxidisability and TOC, depending on the place and month of water collection, amounted to 28%–47%. The application of ozonation before the coagulation process did not significantly reduce the values of these indicators. The decrease increased by 4%–12%. On the other hand, the usage of ozonation before the coagulation process significantly improved the effect of color removal and reduction of UV absorbance by 16%–29% and 10%–18%, respectively.

An important aspect of the conducted research was to demonstrate the effectiveness of ozone and coagulation process application to remove this part of organic matter that is a precursor to the formation of trihalomethanes during chlorination of water. The concentration of trichloromethane in water treated in the coagulation process was by 52%–57% lower than in untreated surface water subjected to chlorination. A further reduction of $CHCl_3$ concentration (by 2%–10%) was obtained in chlorinated water purified in coagulation preceded by the ozonation process.

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