

**Lidia DĄBROWSKA**

Częstochowa University of Technology, Faculty of Infrastructure and Environment  
Department of Chemistry, Water and Wastewater Technology  
ul. J.H. Dąbrowskiego 73, 42-201 Częstochowa  
e-mail: [dabrowska@is.pcz.czest.pl](mailto:dabrowska@is.pcz.czest.pl)

## Effect of Variable Content of Organic Matter in Water on the Efficiency of its Removal in the Coagulation Process

Wpływ zmiennej zawartości materii organicznej w wodzie  
na efektywność jej usuwania w procesie koagulacji

The aim of the research was to evaluate the efficiency of the coagulation process using highly alkaline polyaluminium chlorides in reducing the level of surface water pollution with organic substances. In addition to typical indices used to assess the content of organic compounds (total organic carbon TOC, dissolved organic carbon DOC, oxygen consumption, ultraviolet absorbance), the study also evaluated the potential of trihalomethane formation. The SUVA index was calculated as a ratio of  $UV_{254}$  absorbance to the DOC content, allowing for determination of the properties of dissolved organic substances in water and their susceptibility to removal by coagulation. The study examined water collected in July and October 2016, in January, May and November 2017, and in April 2018 from the Warta River in Częstochowa, Poland. Surface water was characterized by colour of  $30\div 40$  mg Pt/dm<sup>3</sup> and turbidity of  $5.4\div 9.6$  NTU. The contents of TOC and DOC were  $7.6\div 18.6$  and  $6.8\div 13.7$  mg C/dm<sup>3</sup>, respectively, oxygen consumption was  $5.2\div 14.0$  mg O<sub>2</sub>/dm<sup>3</sup>, whereas  $UV_{254}$  absorbance was  $0.147\div 0.326$  cm<sup>-1</sup>. The SUVA index was  $1.8\div 2.7$  m<sup>2</sup>/g C. Reduction in the content of TOC in water after coagulation ranged from 26 to 43%, oxygen consumption - in the range of 41÷63%, and  $UV_{254}$  absorbance - from 52÷68%. The SUVA index was  $0.9\div 1.5$  m<sup>2</sup>/g C. This confirms that organic substances which were not susceptible to removal remained to be present in the water after coagulation. CHCl<sub>3</sub>, CHCl<sub>2</sub>Br and CHClBr<sub>2</sub> were present in the water after chlorination, whereas CHBr<sub>3</sub> was not found. Concentrations of CHCl<sub>3</sub> and CHCl<sub>2</sub>Br were  $153\div 430$  and  $19\div 23$  µg/dm<sup>3</sup>, respectively. Concentration of CHCl<sub>3</sub> ranged from 67 to 185 µg/dm<sup>3</sup> in the water after the coagulation process subjected to chlorination. These values were by 51÷61% lower than the CHCl<sub>3</sub> concentrations recorded in untreated surface water subjected to chlorination.

**Keywords:** organic matter, coagulation, polyaluminium chlorides, trihalomethanes, surface water

### Introduction

Various organic compounds present in surface waters are most often referred to as natural organic matter. Among major components are humic substances, such as humic and fulvic acids, and compounds with a relatively low molecular mass,

such as hydrophilic acids, proteins or amino acids [1]. Natural organic matter modifies colour of waters and represents a precursor for formation of by-products if strong oxidants are used for water treatment. A well-known group of by-products that may be formed during the chlorination process is THMs, which include: trichloromethane ( $\text{CHCl}_3$ ), tribromomethane ( $\text{CHBr}_3$ ), bromodichloromethane ( $\text{CHCl}_2\text{Br}$ ), and dibromochloromethane ( $\text{CHClBr}_2$ ). Trihalomethanes can have negative health effects. The International Agency for Research on Cancer classified trichloromethane and bromodichloromethane as compounds from the group of agents that are potentially carcinogenic to humans [2]. The permissible concentration of total THMs in potable water intended for human consumption specified in the Regulation of the Minister of Health in 2017 is  $100 \mu\text{g}/\text{dm}^3$  [3].

Presence of THMs in chlorinated water continues to represent a problem in water treatment plants [4-6]. Various technological approaches have been used to reduce concentrations of these compounds in chlorinated water: removal of THMs formed, removal of THM precursors, and use of disinfectants other than chlorine [1].

One of the methods used to reduce the content of natural organic matter in water intended for human consumption is the use of coagulation process for treatment, mainly by means of aluminium salts. More and more often, pre-hydrolysed salts, e.g. polyaluminium chlorides with the general formula of  $\text{Al}_n(\text{OH})_m\text{Cl}_{3n-m}$  are being used instead of aluminium sulphate(VI). With the controlled initial hydrolysis of aluminium salts occurring during production of polyaluminium chlorides, they contain more polymerized aluminium forms with a high positive charge compared to those generated during typical hydrolysis of aluminium sulphate [7]. In addition to  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_2^+$  monomers (present also in solutions of non pre-hydrolysed aluminium coagulants), presence of aluminium hydroxyl complexes with the general formula of  $\text{Al}_p(\text{OH})_q^{(3p-q)^+}$  e.g.  $\text{Al}_2(\text{OH})_2^{4+}$ ,  $\text{Al}_3(\text{OH})_4^{5+}$ ,  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$  was also identified in polyaluminium chloride solutions. The latter, termed  $\text{Al}_{13}$  polymer, is considered to be the most stable and effective in destabilization of colloids among aluminium polymers. After addition of polyaluminium chloride to the treated water, polycationic products of aluminium pre-hydrolysis are much slower hydrolysed to  $\text{Al}(\text{OH})_3$  compared to aluminium present in the aluminium sulphate solution [8]. Consequently, the use of polyaluminium chloride becomes more effective in destabilizing negative colloids that modify water colour and lead to turbidity compared to the effects achieved using aluminium sulphate. The use of polyaluminium chloride may also be more useful in reducing the concentration of dissolved organic substances and ensuring a lower aluminium concentration after coagulation [7]. It is also important to evaluate the effectiveness of the coagulation process in removing organic compounds that are trihalomethane precursors. The degree of removal of organic substances increases with their content in the treated water and also with their molecular mass and degree of aromaticity. Therefore, UV-absorbing high-molecular hydrophobic compounds, which constitute the main group of trihalomethane precursors, are removed the most effectively [9]. In addition to choosing the right coagulant, it is important for the effective coagula-

tion to use optimal doses and to conduct the process at the appropriate pH value of the treated water.

The aim of the study was to evaluate the efficiency of removing organic natural matter in the coagulation process using pre-hydrolysed polyaluminium chlorides from surface water sampled during different seasons of the year. The extent to which the part of the organic matter that is responsible for the formation of trihalomethanes during water chlorination is removed was also evaluated.

## 1. Material and methods

Water, termed raw water in this study, was collected in July and October 2016, in January, May and November 2017 and in April 2018 from the Warta River in Częstochowa, Poland (Silesian Voivodeship). The water was collected each time from the same place.

Highly basic, pre-hydrolysed polyaluminium chlorides with the trade names PAX-XL19F and PAX-XL1910S (manufactured by KEMIPOL in Police, Poland) were used as coagulants. These coagulants and their dose were adopted based on previous studies [10, 11]. Commercial solutions of the coagulants were characterized by basicity of 85% ( $\text{OH}^-/\text{Al}^{3+} = 2.55$ ) and  $\text{Al}_2\text{O}_3$  content of 16.1 and 19.8% for PAX-XL19F and PAX-XL1910S, respectively. Working solutions of coagulants were prepared by diluting commercial products to contain  $1.0 \text{ g Al/dm}^3$  of solution.

The coagulation process was performed in laboratory settings. Water doses of  $1.5 \text{ dm}^3$  were poured to glass beakers with a capacity of  $2 \text{ dm}^3$  and then  $4.5 \text{ cm}^3$  of coagulant solution was added, corresponding to a dose of  $3.0 \text{ mg Al/dm}^3$ . Using a mechanical stirrer, rapid stirring was continued for 2 minutes (using 250 rpm), followed by slow stirring for 10 minutes (25 rpm). After these operations, the samples were sedimented for 60 minutes. Next,  $0.3 \text{ dm}^3$  of water was decanted and the analyses were performed to determine pH, turbidity, colour, oxygen consumption, total and dissolved organic carbon (TOC and DOC), and ultraviolet absorbance.

The surface water quality indices before and after the coagulation process, were determined using the following methods: pH - potentiometric, turbidity - nephelometric (Eutech Instruments TN-100 turbidity meter), colour - comparison with standards on the platinum-cobalt scale, ultraviolet absorbance at 254 nm wavelength (1 cm cuvette) using the Camspec M501 spectrophotometer, oxygen consumption (OC) - permanganate method, TOC and DOC (after water filtration through  $0.45 \mu\text{m}$  membrane filter) - by infrared spectrophotometry (Analytik Jena's Multi N/C analyzer). The colour was determined twice, whereas other indices were measured in triplicate. SUVA (ratio of  $\text{UV}_{254}$  absorbance to DOC value) was calculated to determine the properties of dissolved organic substances in water and their susceptibility to removal by coagulation.

To determine the potential of formation of THM-PT trihalomethanes,  $50 \text{ cm}^3$  of raw water or water after coagulation was poured into dark bottles. A dose of chlorine water prepared from sodium hypochlorite was such that after 24 hours at a temperature of ca.  $22^\circ\text{C}$ , the concentration of free chlorine ranged from

3 to 5 mg Cl<sub>2</sub>/dm<sup>3</sup>. To determine the concentration of THMs in water samples after 24 hours, 10 cm<sup>3</sup> of water was collected to the test tubes and 1 cm<sup>3</sup> of n-pentane was added, followed by intensive shaking for 2 minutes. 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 (30 m×0.25 mm×0.25 µm) and analysis by means of gas chromatography with an electron capture detector (Agilent 6890N, Agilent Technologies). The analyses were performed in triplicate.

## 2. Results and discussion

Mean values of water quality indices: pH, turbidity, colour, TOC, DOC, oxygen consumption, ultraviolet absorbance UV<sub>254</sub> before and after the coagulation performed using PAX-XL19F and PAX-XL1910S at a dose of 3 mg Al/dm<sup>3</sup> are presented in Tables 1 to 3.

Surface water collected in the period from July 2016 to April 2018 was characterized by turbidity ranging from 5.4 to 9.6 NTU and the colour from 30 to 40 mg Pt/dm<sup>3</sup>. The pH was slightly alkaline (7.39 to 7.91). The content of TOC ranged from 7.6 to 18.6 mg C/dm<sup>3</sup>, whereas oxygen consumption ranged from 5.2 to 14.0 mg O<sub>2</sub>/dm<sup>3</sup>. The UV<sub>254</sub> absorbance was from 0.147 to 0.326 cm<sup>-1</sup>. During the research period, the highest values of analysed water indices were obtained in November 2017, while the lowest - in July 2016 and April 2018.

Table 1. Mean values of indices for water collected in July and October 2016, before and after the coagulation process

Index	Unit	July 2016			October 2016		
		raw	treated PAX		raw	treated PAX	
			19F	1910S		19F	1910S
pH	–	7.84	7.55	7.63	7.39	7.14	7.26
Turbidity	NTU	7.26	0.75	0.84	7.87	1.23	1.17
Colour	mg Pt/dm <sup>3</sup>	30	7	7	35	10	7
Oxygen consumption	mg O <sub>2</sub> /dm <sup>3</sup>	5.8	3.2	3.4	6.5	3.7	3.4
TOC	mg C/dm <sup>3</sup>	7.6	4.4	4.9	10.4	7.5	6.9
DOC	mg C/dm <sup>3</sup>	6.8	4.3	4.7	8.8	7.1	6.6
UV <sub>254</sub> absorbance	l/cm	0.151	0.064	0.067	0.168	0.065	0.060

During surface water treatment in the process of coagulation conducted using polyaluminium chloride PAX-XL19F, water turbidity was reduced by 72÷90%, and by 78÷90% using PAX-XL1910S. The best outcomes were observed in July 2016 and January 2017 (turbidity decreased below 1 NTU) whereas the worst - in May 2017 and April 2018. In the case of water colour, the effectiveness of its reduction ranged from 63 to 83%. The best result was obtained for water collected in January

2017, with the colour decreased from 30 to 5 mg Pt/dm<sup>3</sup>. In the case of water from May and November 2017, the colour was reduced from 40 to 15 mg Pt/dm<sup>3</sup>.

Table 2. Mean values of indices for water collected in January and May 2017, before and after the coagulation process

Index	Unit	January 2017			May 2017		
		raw	treated PAX		raw	treated PAX	
			19F	1910S		19F	1910S
pH	–	7.54	7.30	7.39	7.91	7.64	7.66
Turbidity	NTU	8.03	1.15	0.81	6.46	1.81	1.16
Colour	mg Pt/dm <sup>3</sup>	30	7	5	40	15	10
Oxygen consumption	mg O <sub>2</sub> /dm <sup>3</sup>	7.2	3.4	3.3	8.3	4.0	3.9
TOC	mg C/dm <sup>3</sup>	9.8	7.0	6.5	10.5	6.9	6.4
DOC	mg C/dm <sup>3</sup>	8.6	6.7	6.4	8.4	6.5	6.1
UV <sub>254</sub> absorbance	l/cm	0.174	0.083	0.081	0.228	0.089	0.091

Table 3. Mean values of indices for water collected in November 2017 and April 2018, before and after the coagulation process

Index	Unit	November 2017			April 2018		
		raw	treated PAX		raw	treated PAX	
			19F	1910S		19F	1910S
pH	–	7.50	7.18	7.26	7.68	7.54	7.58
Turbidity	NTU	9.60	1.45	1.32	5.41	1.28	1.19
Colour	mg Pt/dm <sup>3</sup>	40	12	15	35	10	7
Oxygen consumption	mg O <sub>2</sub> /dm <sup>3</sup>	14.0	5.4	5.9	5.2	2.6	2.8
TOC	mg C/dm <sup>3</sup>	18.6	10.7	11.4	8.7	6.2	6.4
DOC	mg C/dm <sup>3</sup>	13.7	9.8	10.2	8.1	6.0	6.1
UV <sub>254</sub> absorbance	l/cm	0.326	0.103	0.116	0.147	0.057	0.059

The percentage decrease in the content of TOC and DOC and the value of oxygen consumption OC and UV<sub>254</sub> absorbance during coagulation of the surface water collected in 2016-2018 is illustrated in Figures 1 and 2. The content of organic compounds, designated as TOC, in waters after the coagulation process using PAX-XL9F and PAX-XL1910S, decreased by 28÷43% and 26÷39%, respectively. Oxygen consumption decreased by 41÷63%. The greatest reduction in these ratios was found for treatment of water collected in November 2017.

The SUVA index for untreated water was 1.8÷2.7 m<sup>2</sup>/g C. As demonstrated in [12], this value in the range of 2÷4 m<sup>2</sup>/g C 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 coagula-

tion ranging from 25 to 50% if aluminium salts are used. However, the authors of publications [13] argue that the reduction of DOC content during coagulation may range from 25 to 67%.

In the studies presented in this paper, the DOC content in water after coagulation decreased from 19 to 37% (the best effect was recorded in July 2016). These values were lower than the percentage reduction of  $UV_{254}$  absorbance (52÷68%). It is believed [13] that a higher reduction in absorbance with respect to the reduction of DOC means that aromatic substances are removed more effectively during coagulation compared to other fractions of natural organic matter. The SUVA value after coagulation was  $0.9\div 1.5\text{ m}^2/\text{g C}$ , which indicates the presence of non-humic, hydrophilic, and low molecular weight substances in treated water [12]. Tubić et al. [14] obtained a ca. 50% reduction in DOC content using polyaluminium chloride and a ca. 60% decrease in  $UV_{254}$  absorbance.

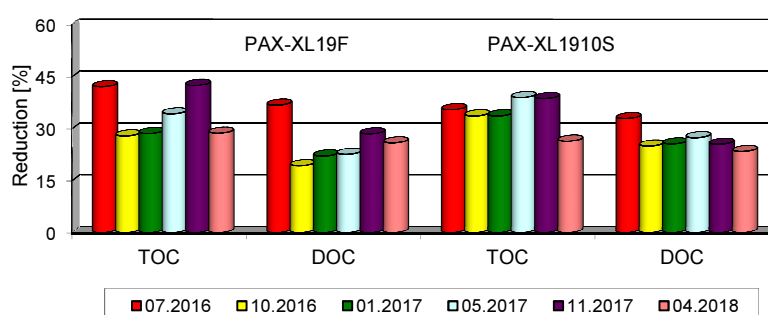


Fig. 1. Percentage of removal of TOC and DOC contents after the coagulation process

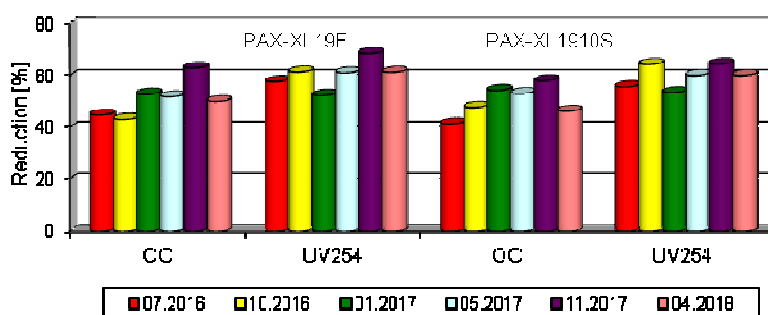


Fig. 2. Percentage of removal of oxygen consumption and  $UV_{254}$  after the coagulation process

Analysis of the literature data does not allow for an unequivocal determination of the efficiency of coagulants in the removal of organic substances from water intended for human consumption [13, 15]. 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.

The use of polyaluminium chlorides for the removal of organic substances was also examined by Yang et al. [16]. The authors conducted the tests in the water

pH range of 4 to 9. They used polyaluminium chlorides with basicity of 50, 67, and 77%. At pH 7, the researchers achieved the effects of reducing  $UV_{254}$  absorbance by 37, 45, and 38%, respectively, whereas at pH = 8, by 34, 42, and 33%, respectively. Furthermore, the DOC contents decreased by 24, 29, 12% and by 23, 26, 12%, respectively. Better results were obtained for a coagulant with basicity of 67% compared to that with basicity of 77%. Polyaluminium chlorides contain significant amounts of polycationic pre-hydrolysis products. Polymer forms of aluminium are considered stable, while monomeric forms may be transformed. This can lead to the formation of in-situ aluminium polymers that neutralize the pollutant load under certain conditions. Therefore, good water treatment efficiency can be obtained using coagulants with lower basicity, containing significant amounts of monomeric forms.

No trihalomethanes were found in the surface water and in the water after the coagulation process. However, their presence was demonstrated in the waters after the chlorination process. Mean THM concentrations in the surface water sampled in different months and in the water treated with coagulation, after 24 hours of contact with chlorine, and the potential of formation of THM-PT trihalomethanes are shown in Tables 4 to 6.

Table 4. THM concentrations in the surface water collected in July and October 2016 and in chlorinated water treated in the coagulation process

THM	Unit	July 2016			October 2016		
		raw	treated PAX		raw	treated PAX	
			19F	1910S		19F	1910S
$CHCl_3$	$\mu\text{g}/\text{dm}^3$	187.3	72.5	75.3	162.3	72.0	67.3
$CHCl_2Br$	$\mu\text{g}/\text{dm}^3$	19.4	13.5	11.9	19.4	13.5	11.9
$CHClBr_2$	$\mu\text{g}/\text{dm}^3$	1.0	1.4	1.4	1.2	1.5	1.4
$CHBr_3$	$\mu\text{g}/\text{dm}^3$	nd	nd	nd	nd	nd	nd
THM-PT	$\mu\text{g } CHCl_3/\text{dm}^3$	202.0	83.1	84.8	177.1	82.7	76.8

nd - below the threshold of determination

Table 5. THM concentrations in the surface water collected in January and May 2017 and in chlorinated water treated in the coagulation process

THM	Unit	January 2017			May 2017		
		raw	treated PAX		raw	treated PAX	
			19F	1910S		19F	1910S
$CHCl_3$	$\mu\text{g}/\text{dm}^3$	153.4	71.5	68.2	327.0	129.7	136.5
$CHCl_2Br$	$\mu\text{g}/\text{dm}^3$	19.3	15.4	15.6	22.3	17.4	18.2
$CHClBr_2$	$\mu\text{g}/\text{dm}^3$	1.1	1.5	1.4	0.7	0.9	1.1
$CHBr_3$	$\mu\text{g}/\text{dm}^3$	nd	nd	nd	nd	nd	nd
THM-PT	$\mu\text{g } CHCl_3/\text{dm}^3$	168.1	83.6	80.4	343.6	142.9	150.4

nd - below the threshold of determination

Table 6. THM concentrations in the surface water collected in November 2017 and April 2018 and in chlorinated water treated in the coagulation process

THM	Unit	November 2017			April 2018		
		raw	treated PAX		raw	treated PAX	
			19F	1910S		19F	1910S
CHCl <sub>3</sub>	µg/dm <sup>3</sup>	430.0	185.2	177.0	252.0	116.8	124.2
CHCl <sub>2</sub> Br	µg/dm <sup>3</sup>	23.2	22.4	22.1	22.9	17.1	17.5
CHClBr <sub>2</sub>	µg/dm <sup>3</sup>	0.6	1.1	0.9	1.6	2.3	1.9
CHBr <sub>3</sub>	µg/dm <sup>3</sup>	nd	nd	nd	nd	nd	nd
THM-PT	µg CHCl <sub>3</sub> /dm <sup>3</sup>	447.2	202.1	193.9	269.6	130.6	138.0

nd - below the threshold of determination

CHCl<sub>3</sub>, CHCl<sub>2</sub>Br and CHClBr<sub>2</sub> were present in the surface water subjected to 24 h chlorination, whereas CHBr<sub>3</sub> was not found. The highest concentration was found for CHCl<sub>3</sub>. In the case of the water collected and chlorinated in July and October 2016, the concentrations were 187 and 162 µg/dm<sup>3</sup>, respectively, while in the water collected in January, May and November 2017 and in April 2018, these values were 153, 327, 430 and 252 µg/dm<sup>3</sup>, respectively. The values accounted for 90, 89, 88, 93, 95 and 91%, respectively, of the total contents of the four analysed THMs in the water samples from the Warta River after the chlorination process.

In the water collected in July and October 2016 and in January 2017, treated by coagulation and subjected to chlorination for 24 hours, the concentration of CHCl<sub>3</sub> was 68÷75 µg/dm<sup>3</sup> and by 53÷61% lower than that obtained in chlorinated non-coagulated water (see Fig. 3). Furthermore, in the water collected in May and November 2017 and in April 2018, treated by coagulation and chlorinated, the concentration of CHCl<sub>3</sub> was 130÷137, 177÷185 and 117÷124 µg/dm<sup>3</sup>, and was by 51÷60% lower than the values obtained in untreated chlorinated surface water (Fig. 3). This demonstrates the high efficiency of removal of organic water components that are precursors of trichloromethane as a by-product of chlorination.

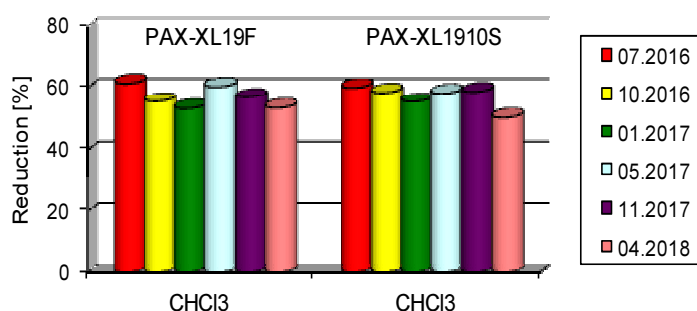


Fig. 3. Percentage of reduction in CHCl<sub>3</sub> concentration in chlorinated water treated by coagulation using PAX-XL19F and PAX-XL1019S as coagulants



The concentration of  $\text{CHCl}_2\text{Br}$  in the untreated water subjected to chlorination was from 19.3 to 23.2  $\mu\text{g}/\text{dm}^3$ , whereas in the water treated by coagulation and chlorinated, this value ranged from 11.9 to 22.4  $\mu\text{g}/\text{dm}^3$ . The  $\text{CHClBr}_2$  content was from 0.9 to 2.3  $\mu\text{g}/\text{dm}^3$ . The concentration of trichloromethane accounted for 80–95% of the total THM content in the chlorinated waters.

The potential for formation of THM-PT trihalomethanes in the untreated water ranged from 177 to 447  $\mu\text{g CHCl}_3/\text{dm}^3$ , whereas in the water after coagulation and chlorination, it ranged from 77 to 202  $\mu\text{g CHCl}_3/\text{dm}^3$ . The highest potential was found for the water collected and treated in November 2017, with the highest values of the analysed indices (oxygen consumption OC, TOC, DOC,  $\text{UV}_{254}$  absorbance). A reduction in THM-PT was 49–59% (the highest values were found for water from July 2016). These values were comparable to previous results (52–61%) presented in studies on treatment of the water from the Stradomka River [17].

The percentage of the isolated groups of organic compounds in the formation of trihalomethanes was discussed in [18]. Hydrophilic bases, hydrophobic acids, hydrophobic and hydrophilic neutral compounds were indicated as the most reactive fractions of organic substances in the formation of THMs. Organic carbon content is merely one of the factors determining the formation of THMs. Other factors include chlorine dose, time, pH, temperature and presence of bromides.

Matilainen et al. [13] argues that in waters treated by coagulation, a reduction in the potential of THM formation can reach from 25 to 66%. Furthermore, the use of ozonation before coagulation and additional process support with activated carbon can be effective in removing organic matter and contribute to the reduction of the potential of THMs formation during water chlorination [19]. Studies have also examined the removal of organic matter from water using other processes, e.g. ion exchange, biodegradation, advanced oxidation processes, adsorption on nanomaterials, and membrane processes [20, 21]. However, coagulation and adsorption on activated carbon supported by ozonation are prevalent in the systems for treatment of water intended for human consumption. Therefore, the research is expected to be continued in order to evaluate the effectiveness of combined ozonation, coagulation and adsorption processes in removing natural organic matter that is a precursor to the formation of THMs during water chlorination.

## Conclusions

During the research period of July 2016 to April 2018, surface water was characterized by a variable content of organic matter. The content of organic compounds that reflected oxygen consumption ranged from 5.2 to 14.0  $\text{mg O}_2/\text{dm}^3$ , whereas the contents of those that reflected TOC and DOC, were 7.6–18.6 and 6.8–13.7  $\text{mg C}/\text{dm}^3$ , respectively.

The effect of the variable content of organic matter on the efficiency of its removal in the coagulation process was also found. In the laboratory conditions of the process using pre-hydrolysed coagulants (PAX-XL19F, PAX-XL1910S),

reductions in oxygen consumption, TOC and DOC contents depending on the month when water was collected were 41÷63%, 26÷43% and 19÷37%, respectively, whereas reduction in UV<sub>254</sub> absorbance ranged from 52 to 68%.

The study confirmed the usefulness of the coagulation process in the removal of organic matter, which represents a precursor for formation of trihalomethanes. The potential for THMs formation in treated water was by 49÷59% lower than in untreated surface water after chlorination. The concentration of trichloromethanes was 80÷89% of the total THM content in the chlorinated treated waters.

### Acknowledgements

*The study was financed from funds allocated for statutory research BS-402-301/2011 (the task implemented in 2016-2018).*

### References

- [1] Nawrocki J. (red.), Uzdatnianie wody. Procesy fizyczne, chemiczne i biologiczne, Wydawnictwo Naukowe PWN, Warszawa 2010.
- [2] Guidelines for Drinking-water Quality, 4th ed., World Health Organization, Geneva, Switzerland, 2011.
- [3] Rozporządzenie Ministra Zdrowia z dnia 7 grudnia 2017 r. w sprawie jakości wody przeznaczonej do spożycia przez ludzi, poz. 2294.
- [4] Font-Ribera L., Colomer Cotta J., Gómez-Gutiérrez A., Villanueva C.M., Trihalomethane concentrations in tap water as determinant of bottled water use in the city of Barcelona, *Journal of Environmental Sciences* 2017, 58, 77-82.
- [5] Golea D.M., Upton A., Jarvis P., Moore G., Sutherland S., Parsons S.A., Judd S.J., THM and HAA formation from NOM in raw and treated surface waters, *Water Research* 2017, 112, 226-235.
- [6] Niu Z.-G., Hu X.-P., Zhang Y., Sun Y.-Y., Effect of chlorine dose in prechlorination on trihalomethanes and haloacetic acids during water treatment process, *Environmental Science and Pollution Research* 2017, 24, 5068-5077.
- [7] Kowal A.L., Świdorska-Bróz M., *Oczyszczanie wody. Podstawy teoretyczne i technologiczne, procesy i urządzenia*, Wydawnictwo Naukowe PWN, Warszawa 2009.
- [8] Gumińska J., Kłos M., Analiza stabilności form glinu w koagulantach wstępnie zhydrolizowanych, *Przemysł Chemiczny* 2013, 92(8), 1444-1448.
- [9] Świdorska-Bróz M., Wolska M., Usuwanie frakcji ogólnego węgla organicznego z wody powierzchniowej w procesie koagulacji, *Ochrona Środowiska* 2011, 33(1), 9-12.
- [10] Dąbrowska L., Removal of organic matter from surface water using coagulants with various basicity, *Journal of Ecological Engineering* 2016, 17(3), 66-72.
- [11] Dąbrowska L., Ogrodnik A., Rosińska A., Wpływ skuteczności usuwania materii organicznej w procesie koagulacji na stężenie THM w chlorowanej wodzie, *Rocznik Ochrona Środowiska* 2016, 18, 455-467.
- [12] Machi J., Mołczan M., Metody charakterystyki naturalnych organicznych składników wód ujmowanych z przeznaczeniem do spożycia przez ludzi, *Ochrona Środowiska* 2016, 38(4), 25-32.
- [13] Matilainen A., Vepsäläinen M., Sillanpää M., Natural organic matter removal by coagulation during water treatment. A review, *Advances in Colloid and Interface Science* 2010, 159, 189-197.

- [14] Tubić A., Agbaba J., Molnar Jazić J., Watson M., Dalmacija B., Pilot scale investigation of coagulation combined with ozonation and pH adjustment in treatment of NOM rich water, *Water Science Technology: Water Supply* 2016, 16(3), 837-844.
- [15] Sillanpää M., Ncibi M.Ch., Matilainen A., Vepsäläinen M., Removal of natural organic matter in drinking water treatment by coagulation: A comprehensive review, *Chemosphere* 2018, 190, 54-71.
- [16] Yang Z., Gao B., Wang Y., Wang Q., Yue Q., Aluminum fractions in surface water from reservoirs by coagulation treatment with polyaluminum chloride (PAC): Influence of initial pH and  $\text{OH}^-/\text{Al}^{3+}$  ratio, *Chemical Engineering Journal* 2011, 170, 107-113.
- [17] Dąbrowska L., Skuteczność usuwania materii organicznej z wody powierzchniowej z zastosowaniem chlorku poliglinu (Effectiveness of removing organic matter from surface water using polyaluminium chloride), *Proceedings of ECOpole* 2017, 11(2), 489-496.
- [18] Włodyga-Bergier A., Bergier T., Charakterystyka prekursorów lotnych ubocznych produktów chlorowania wody w sieci wodociągowej Krakowa, *Ochrona Środowiska* 2011, 33(3), 29-33.
- [19] Wang F., Gao B., Yue Q., Bu F., Shen X., Effects of ozonation, powdered activated carbon adsorption, and coagulation on the removal of disinfection by-product precursors in reservoir water, *Environmental Science and Pollution Research* 2017, 24, 17945-17954.
- [20] Zainudin F.M., Hasan H.A., Abdullah S.R.S., An overview of the technology used to remove trihalomethane (THM), trihalomethane precursors, and trihalomethane formation potential (THMFP) from water and wastewater, *Journal of Industrial and Engineering Chemistry* 2018, 57, 1-14.
- [21] Bhatnagar A., Sillanpää M., Removal of natural organic matter (NOM) and its constituents from water by adsorption. A review, *Chemosphere* 2017, 166, 497-510.

## Streszczenie

Celem badań była ocena efektywności procesu koagulacji z wykorzystaniem wysoko zasadowych chlorków poliglinu w obniżeniu poziomu zanieczyszczenia wody powierzchniowej substancjami organicznymi. Oprócz typowych wskaźników stosowanych do oceny zawartości związków organicznych (całkowity i rozpuszczony węgiel organiczny - OWO i RWO, utlenialność, absorbancja w nadfiolecie UV) oznaczono również potencjal tworzenia trihalometanów THM. Obliczono wskaźnik SUVA jako stosunek wartości absorbancji w  $\text{UV}_{254}$  do zawartości RWO, który umożliwia określenie właściwości rozpuszczonych substancji organicznych w wodzie i ich podatności na usuwanie w procesie koagulacji. Do badań wykorzystano wodę pobraną w lipcu i październiku 2016 roku, w styczniu, maju i listopadzie 2017 roku oraz w kwietniu 2018 roku z rzeki Warty w Częstochowie. Woda powierzchniowa charakteryzowała się barwą równą  $30 \div 40 \text{ mg Pt/dm}^3$  i mętnością  $5,4 \div 9,6 \text{ NTU}$ . Zawartość OWO i RWO wynosiła odpowiednio  $7,6 \div 18,6$  i  $6,8 \div 13,7 \text{ mg C/dm}^3$ , utlenialność -  $5,2 \div 14,0 \text{ mg O}_2/\text{dm}^3$ , a absorbancja w  $\text{UV}_{254}$  -  $0,147 \div 0,326 \text{ cm}^{-1}$ . Wartość SUVA była równa  $1,8 \div 2,7 \text{ m}^2/\text{g C}$ . Obniżenie zawartości OWO w wodzie po koagulacji było w granicach  $26 \div 43\%$ , utlenialności w zakresie  $41 \div 63\%$ , a wartości absorbancji  $\text{UV}_{254}$  -  $52 \div 68\%$ . Wartość SUVA była równa  $0,9 \div 1,5 \text{ m}^2/\text{g C}$ . Potwierdza to, że w wodzie po koagulacji pozostały substancje organiczne niepodatne na usuwanie w tym procesie. W badanych wodach po procesie chlorowania stwierdzono obecność  $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$ , nie wykryto  $\text{CHBr}_3$ . Stężenie  $\text{CHCl}_3$  i  $\text{CHCl}_2\text{Br}$  było równe odpowiednio  $153 \div 430$  i  $19 \div 23 \text{ } \mu\text{g/dm}^3$ . W wodach po procesie koagulacji poddanych chlorowaniu stężenie  $\text{CHCl}_3$  wynosiło od 67 do  $185 \text{ } \mu\text{g/dm}^3$ . Były to wartości o  $51 \div 61\%$  niższe od uzyskanych stężeń  $\text{CHCl}_3$  w nieoczyszczonych wodach powierzchniowych poddanych chlorowaniu.

**Słowa kluczowe:** materia organiczna, koagulacja, chlorki poliglinu, trihalometany, woda powierzchniowa