

Removal of THM precursors in the coagulation using pre-hydrolyzed salts and enhanced with activated carbon

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ABSTRACT

The aim of this study was to evaluate the effectiveness of the coagulation process in reducing the level of pollution of surface water with organic substances. The coagulants used in the study were aluminium sulphate and pre-hydrolyzed polyaluminium chlorides PAX. Powdered activated carbons with trade names AKPA and CWZ were used for the enhancement of coagulation. Lowering the total organic carbon (TOC) content in water after the coagulation was in the range of 15–45%, and the oxygen consumption in the range of 27–63%, depending on the used coagulant. The largest reduction in values of those indicators were stated using PAX. In the surface water subjected to chlorination, presence of CHCl_3 and CHCl_2Br was demonstrated, and CHBr_3 and CHClBr_2 were not detected. CHCl_3 and CHCl_2Br concentration was equal to 65.3 and 7.4 $\mu\text{g/L}$, respectively. In the water subjected to chlorination after the coagulation process and after the process of coagulation enhanced with powdered activated carbon, CHCl_3 concentration ranged from 55.8 to 39.8 $\mu\text{g/L}$, while CHCl_2Br ranged from 7.8 to 9.0 $\mu\text{g/L}$. These were values by 13–35% lower than trihalomethane (THM) concentration obtained in untreated surface water subjected to chlorination. The lowest CHCl_3 concentration were obtained in chlorinated water after prior purification with PAX-XL19 and powdered activated carbon CWZ.

Key words | coagulation, organic matter, pre-hydrolyzed salts, trihalomethanes

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INTRODUCTION

The application of strong oxidizers such as chlorine, chlorine (IV) oxide or ozone for water disinfection can lead to formation of compounds called disinfection byproducts. A well known group of chlorination byproducts are trihalomethanes (THMs), which include trichloromethane (CHCl_3), tribromomethane (CHBr_3), bromodichloromethane (CHCl_2Br), and dibromochloromethane (CHClBr_2). From among these four compounds, chloroform occurs in the highest concentrations. International Agency for Research on Cancer IARC classified trichloromethane and bromodichloromethane as factors potentially carcinogenic to humans (WHO 2011). The permissible concentration of CHCl_3 , CHCl_2Br and the sum of four THM content in water intended for human consumption in Poland, stated in the Ministry of Health Regulation of the year 2015,

amount to 30, 15 and 100 $\mu\text{g/L}$, respectively (Regulation 2015). The total concentration of trihalomethanes and the formation of individual THM species in chlorinated water strongly depend on the composition of raw water, on the operational parameters and on the occurrence of residual chlorine in the distribution system. Exemplary results of tap water analyses of THM presence are presented in studies (Ristoiu *et al.* 2009; Chang *et al.* 2010; Pardakhti *et al.* 2011; Golea *et al.* 2017).

In order to reduce THM concentrations in drinking water, various technological approaches are applied: removal of produced THMs, removal of THM precursors, and use of disinfectants other than chlorine. In current water purification technology, processes that prevent the formation of trihalomethanes are more important than

the processes that lead to the removal of already formed THMs. The prevention of THM formation is the removal of organic matter from water, primarily humic and fulvic acids.

Different technological processes may be used to reduce the content of organic compounds in water, i.e. coagulation, activated carbon filtration, oxidation, membrane filtration, and ion exchange (Matilainen *et al.* 2010; Zhang *et al.* 2015; Sillanpää *et al.* 2018). The effectiveness of coagulation depends on the physicochemical composition of water, the pH value, the type and dosage of coagulants. The most commonly used coagulant is aluminium sulphate. In recent years, the application of pre-hydrolyzed coagulants, e.g. alkaline polyaluminium chlorides, has become increasingly popular (Yang *et al.* 2011; Hussain *et al.* 2013; Wang *et al.* 2013; Tang *et al.* 2017). Studies on purification of water of various compositions confirm the effectiveness of coagulation in the removal of organic matter with the usage of pre-hydrolyzed salts. Also, a simultaneous application of coagulation and adsorption can be effective in the removal of organic matter (Kweon *et al.* 2009; Kristiana *et al.* 2011). A wide variety of conventional and non-conventional adsorbents have been reviewed for their potential in natural organic matter (NOM) removal from water (Bhatnagar & Sillanpää 2017).

The higher effectiveness of pre-hydrolyzed coagulants, in comparison to aluminium sulphate, is determined by the presence of polycations $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$ and $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, as well as by the difference in structure of precipitated aluminium hydroxide flocs, formed during the hydrolysis of these coagulants (Yan *et al.* 2008; Lin *et al.* 2014).

The aim of the research was to evaluate the effectiveness of coagulation, with the usage of aluminium sulphate, polyaluminium chlorides and enhanced with powdered activated carbon, in reducing the level of surface water contamination with organic matter. For the evaluation of organic compounds content following indicators were used: oxidizability, total and dissolved organic carbon, ultraviolet UV_{254} absorbance. It was also assessed how high trihalomethanes formation potential had the organic matter remaining in water after the coagulation process and after the process of coagulation was enhanced with powdered activated carbon.

MATERIALS AND METHODS

Water, coagulants, activated carbons

Water collected from the Stradomka river in Częstochowa in May and June 2016 was used for the research. Water analyses and research on water purification in the process of coagulation and adsorption were carried out in the laboratories of the Department of Chemistry, Water and Wastewater Technology at the Częstochowa University of Technology.

Aluminium sulphate and pre-hydrolyzed polyaluminium chlorides with trade names PAX-XL1910 and PAX-XL19, with 85% alkalinity, were used as coagulants. The alkalinity of polyaluminium chlorides is defined by the ratio of OH^- moles to Al^{3+} moles in the coagulant. The ratio is defined as coefficient $r = [\text{OH}^-]/[\text{Al}^{3+}]$ and it is used as a measure of polymerization degree. There is a following correlation between 'r' and alkalinity of a coagulant: alkalinity (%) = $r/0.03$. The PAX-XL1910 solution contained 19.8% Al_2O_3 , while PAX-XL19 16.0% Al_2O_3 . The coagulant solutions were prepared for the studies by diluting the commercial products to contain 1.0 gAl/L.

Powdered activated carbons with trade names CWZ-30 and AKPA-22 were used for the enhancement of coagulation. The carbons were characterized by the specific surface area of 1,134 and 914 m^2/g , iodine number 1,190 and 940 mg/g, and methylene number 30 and 28 cm^3 , respectively.

Jar test procedure

The process of coagulation and adsorption was conducted in laboratory conditions (temp. $20 \pm 2^\circ\text{C}$). In the first stage of the study, the coagulation process was conducted in glass beakers with 2 L volume, to which 1.5 L of analysed water was measured. The coagulants were introduced at a dose of 1.5; 2.5; 3.5 mgAl/L, and with the use of a mechanical stirrer fast stirring was performed for 2 min (applying 250 rpm), followed by slow stirring (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 pH, colour, turbidity, oxidizability and total organic carbon (TOC) were assayed.

In the second stage of the study, the coagulation process was repeated using a coagulant dose equal to 3.0 mgAl/L and the analysis was extended by further determining: dissolved organic carbon, ultraviolet absorbance and THM formation potential.

In the third stage, for chosen pre-hydrolyzed polyaluminium chloride, coagulation enhanced with powdered activated carbon was performed. The research was conducted as in the first stage, introducing the carbon during fast stirring, 2 min after the coagulant. Thus, fast stirring was carried out for 4 min. The carbon dose amounted to 30 mg/L of water and it was proposed based on previously conducted research (Sperczyńska *et al.* 2016).

Analytical methods

The physicochemical parameters of water were measured with the following methods: pH – potentiometrically; turbidity – with Eutech Instruments TN-100 nephelometer (expressed in NTU – Nephelometric Turbidity Unit); colour – colorometrically with platinum-cobalt standard method; dissolved (DOC) and TOC – by infrared spectrophotometry (with carbon analyser Multi N/C Analytic Jena) – to measure DOC concentration the water samples were filtered through 0.45 µm filter; oxidizability (OXI) – by potassium permanganate method; aluminium – with Aquaquant 14413 aluminium test (by visual comparison of the colour of the analysed solution with colour fields of a colour card; in weakly acidic acetate buffered solution aluminium forms blue-violet colour lacquer with chromazurol S). The analyses were carried out before and after coagulation as well as adsorption.

Absorbance in the ultraviolet UV at wavelength of 254 nm was determined (spectrophotometer M501 by Cam-spec). $SUVA_{254}$ 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, surface water samples, measured into dark bottles, before treatment and after the coagulation 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 to 5 mgCl₂/L. The concentration of chlorine in the chlorine water was determined iodometrically, and the chlorine remaining after 24 h in water samples by means of spectrophotometric method using orthotolidine as a factor in the colour reaction. 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 electron capture detector ECD (chromatograph Agilent 6890N). As a standard, solution by CPAchem Ltd was used, containing four THMs (CHCl₃, CHBr₃, CHBrCl₂, CHBr₂Cl) with a concentration of 100 ng/µL each in iso-octane.

The potential for trihalomethanes 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.

RESULTS AND DISCUSSION

Surface water, hereinafter referred to as raw water, was characterized by turbidity amounting to 6.35–6.95 NTU and colour equal to 30–40 mgPt/L. The TOC content amounted to 9.3–10.9 mgC/L, oxidizability OXI 6.67–8.43 mgO₂/L. The water reaction was slightly alkaline.

The values of turbidity and water colour, the organic compound content assayed as TOC and OXI, depending on the type of the used coagulant and the coagulant dose, were obtained in the first stage of the research are presented in Table 1.

The pre-hydrolyzed polyaluminium chloride PAX-XL19 was the most effective for removal of turbidity from water, with the application of which, with a dose of 3.5 mgAl/L, turbidity was reduced from 6.35 to 0.66 NTU (by 90%). PAX-XL1910 has shown to be effective also, the application of which resulted in an 86% turbidity reduction. Colour

Table 1 | Effect of coagulation with various agents on selected physicochemical properties of water

Coagulant	Dose mgAl/L	pH –	Turbidity (NTU)	Colour (mgPt/L)	OXI (mgO ₂ /L)	TOC (mg/L)
Raw water	–	7.30	6.35	40	8.43	10.9
Al ₂ (SO ₄) ₃	1.5	6.91	5.86	35	7.54	9.8
	2.5	6.87	6.57	30	7.27	9.5
	3.5	6.75	7.03	20	6.75	9.0
PAX-XL1910	1.5	7.11	2.86	30	6.56	8.6
	2.5	7.08	1.63	20	5.29	7.7
	3.5	7.02	0.91	10	4.11	6.9
PAX-XL19	1.5	7.07	1.94	20	6.14	8.2
	2.5	7.03	1.08	10	4.31	6.8
	3.5	7.01	0.66	5	3.62	6.1

reduction amounted to 50–88%. Better effectiveness of PAX products was probably connected to the fact that in solutions of these compounds polymerized products of preliminary hydrolysis are present. During water purification by means of the coagulation process, often over 90% and 50% reduction is obtained, respectively, for turbidity and colour (Sperczyńska *et al.* 2016).

The organic matter content after the coagulation process using PAX-XL19, determined as OXI and TOC, decreased from 8.43 mgO₂/L and 10.9 mg/L to 3.62 mgO₂/L and 6.1 mg/L, by 57% and 44%, respectively. With the usage of PAX-XL1910, OXI decreased by 51% and TOC by 37%, while with the application of Al₂(SO₄)₃ OXI reduction by 20% was obtained and TOC by 17%. Therefore, better effects of organic compounds removal were obtained using pre-hydrolyzed salts.

Water quality indicators: pH, turbidity, colour, TOC, DOC, OXI, residual aluminium Al and ultraviolet absorbance UV₂₅₄, obtained during the second stage of the research, with the coagulant dose of 3.0 mgAl/L, are presented in Table 2.

The research results for the coagulant dose of 3.0 mgAl/L confirmed obtaining higher effectiveness in removal of turbidity, colour and organic compounds with the usage of pre-hydrolyzed polyaluminium chlorides PAX-XL1910 and PAX-XL19; 81% and 87% turbidity removal, 71% and 86% colour reduction, and 41% and 45% reduction in TOC content were obtained. The efficiency of reduction of organic compound content, assayed as OXI, amounted to 56% and 63% using PAX, whereas with the application of Al₂(SO₄)₃ was 27% (Figure 1).

With regard to the concentration of aluminium remaining after the coagulation process, it was preferable to use pre-hydrolyzed coagulants.

The specific UV absorbance (SUVA) value for raw water was equal to 3.4 m²/gC. As stated in (Matilainen *et al.* 2010), this value in the range of 2–4 m²/gC indicates that, in surface water, there is a mixture of hydrophilic and hydrophobic humic substances and other natural organic compounds, of both small and large molecular weights. During the conducted studies with the usage of PAX, over 40% effectiveness in removal of organic matter, determined as TOC, was obtained. The reduction of DOC content in water after the coagulation amounted to 38% and 43%, UV₂₅₄ absorbance value 51% and 53%, OXI absorbance value 56% and 63% (Figure 1). As it is stated by the authors of the publication (Matilainen *et al.* 2010), the DOC content reduction in the coagulation process can range from 25% to 67% and UV₂₅₄ value from 44% to 77%. Tubić *et al.* (2016) 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 (Matilainen *et al.* 2010) that the hydrophobic fraction of NOM is generally removed in coagulation more efficiently than the hydrophilic fraction. Compared to DOC,

Table 2 | Effect of coagulation with various agents (dose 3.0 mgAl/L) on selected physicochemical properties of water

Coagulant	pH (–)	Turbidity (NTU)	Colour (mgPt/L)	OXI (mgO ₂ /L)	TOC (mg/L)	DOC (mg/L)	UV ₂₅₄ (cm ⁻¹)	Al (mg/L)
Raw water	7.28	6.85	35	6.67	9.3	8.4	0.288	0.0
Al ₂ (SO ₄) ₃	6.83	4.22	20	4.88	7.9	7.6	0.223	0.30
PAX-XL1910	7.09	1.30	10	2.92	5.5	5.2	0.142	0.07
PAX-XL19	7.12	0.88	5	2.48	5.1	4.8	0.136	0.04

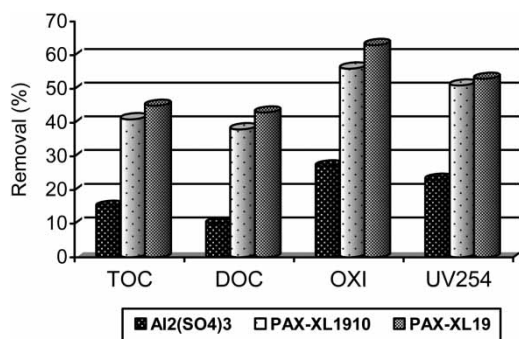


Figure 1 | Percentage of removal of organic matter OM determined as TOC, DOC, OXI, UV₂₅₄ during coagulation. The characteristics of the OM in raw water were: TOC = 9.3 mg/L; DOC = 8.4 mg/L; OXI = 6.67 mgO₂/L; UV₂₅₄ = 0.288 cm⁻¹ (coagulant dose: 3 mgAl/L).

UV₂₅₄ has been noted to reduce more, suggesting that aromatic materials are removed more effectively than other organic matter fractions. Hydrophobic NOM has been noted to carry high levels of negative charge due to the presence of ionized groups such as carboxylic and phenolic groups. Thus, the hydrophobic fraction is noted to dominate the specific colloidal charge character of water, and fractions with higher charge are observed to be more amenable to removal (Matilainen *et al.* 2010). The SUVA value in purified water was equal to 2.7–2.9. This confirms that in water after the coagulation, organic substances remained, which are unsuitable to the removal in this process.

The values of water quality indicators after the coagulation process with PAX-XL19 and enhanced with powdered activated carbon CWZ or AKPA (third stage of the research) are presented in Table 3.

The application of activated carbon did not significantly influence the reduction of organic compound content. The efficiency of reduction of OXI and UV₂₅₄ value and TOC and DOC content in water purified in the coagulation process enhanced by adsorption was higher only by 4–8% in comparison to water purified without the use of powdered activated

carbon. This was low efficiency (44–48%) compared to the results obtained by Uyak *et al.* (2007) who during the enhancement of the coagulation process with powdered activated carbon obtained an increase in DOC removal from 45% to 76%. Both applied activated carbon (Kemisorb) and water composition, had an effect on such high efficiency obtained. As emphasized in the work (Uyak *et al.* 2007), the types of NOM most likely to be removed by coagulation are those possessing high molecular weight and negatively charged functional groups able to engage in charge neutralization and adsorption onto floc particles. On the other hand, powdered activated carbon is more effective for the adsorption of low molecular weight and uncharged NOM.

Studies conducted by Yang *et al.* (2011) have shown that an increase in the efficiency of organic matter removal in the coagulation process can be achieved by lowering water pH. Also, the application of ozonation prior to the coagulation process can be effective in removal of organic matter and can contribute to reducing the THM formation potential during water chlorination. Application of pre-ozonation enhanced total coagulation efficiency (up to 61% and 80% for DOC and UV₂₅₄, respectively), probably due to its microfloculation effect (Tubić *et al.* 2016). The pre-treatment resulted in NOM oxidation to lower molecular weight hydrophilic organic substances.

In collected surface water, as well as in water after the coagulation and adsorption process, presence of trihalomethanes was not discovered. Their presence, however, was demonstrated in these waters after the chlorination process. THM concentrations and values of trihalomethanes formation potential THM-FP in surface water and in water purified in the coagulation process, after a 24-h contact with chlorine, are presented in Table 4.

In water after the coagulation subjected to chlorination for 24 h, the concentration of CHCl₃ amounted to from 55.8 to 39.8 µg/L and the concentration of CHCl₂Br from

Table 3 | Effect of powdered activated carbon addition on selected physicochemical properties of water during coagulation with PAX-XL19

Coagulant, activated carbon	pH (-)	Turbidity (NTU)	Colour (mgPt/L)	OXI (mgO ₂ /L)	TOC (mg/L)	DOC (mg/L)	UV ₂₅₄ (cm ⁻¹)	Al (mg/L)
Raw water	7.22	6.95	35	7.52	10.2	8.6	0.275	0.0
PAX-XL19	7.07	1.08	5	2.77	5.8	5.2	0.149	0.04
PAX-XL19 + CWZ	7.12	1.23	<5	2.44	5.3	4.5	0.131	0.0
PAX-XL19 + AKPA	7.10	1.42	<5	2.51	5.5	4.8	0.138	0.0

Table 4 | THM concentrations in surface water and in water purified in the coagulation and adsorption process

Coagulant/activated carbon	CHCl ₃ (µg/L)	CHCl ₂ Br (µg/L)	CHClBr ₂ (µg/L)	CHBr ₃ (µg/L)	THM-FP (µgCHCl ₃ /L)
Raw water	65.3	7.4	nd	nd	70.7
Al ₂ (SO ₄) ₃	55.8	7.8	nd	nd	61.5
PAX-XL1910	49.6	9.0	nd	nd	56.2
PAX-XL19	45.7	8.8	nd	nd	52.1
PAX-XL19 + CWZ	39.8	8.3	nd	nd	45.9
PAX-XL19 + AKPA	43.0	8.2	nd	nd	49.0

nd – not detected.

9.0 to 7.8 µg/L. The lowest concentrations of these compounds were obtained in water subjected to chlorination after prior purification using PAX and after enhancement of the coagulation with activated carbon. This was related to better removal efficiency of organic compounds. The potential for THM formation in purified water subjected to chlorination amounted to 61.5; 56.2; 52.1 µgCHCl₃/L if Al₂(SO₄)₃, PAX-XL1910, PAX-XL19, respectively, were used for the coagulation. In the case of the use of PAX, it was lower by 21% and 26% than in raw water subjected to chlorination. These were lower values in comparison with the previous results (29–32%) obtained during research with the use of these coagulants for purification of water from the Pilica river (Dąbrowska *et al.* 2016). The lowest potential for THM formation was obtained in the case of the coagulation conducted with PAX-XL19 and powdered activated carbon CWZ and it amounted to 45.9 µgCHCl₃/L. It was a value lower by 35% than that obtained for chlorinated surface water which was not purified. The share of separated groups of organic compounds in the formation of trihalomethanes was discussed in (Włodyga-Bergier & Bergier 2011). Hydrophilic and hydrophobic neutral compounds, and hydrophilic and hydrophobic acids were indicated as the most reactive fractions of organic substances in the formation of THMs. The organic carbon content is only one of the factors determining the formation of THMs. Other factors include chlorine dose, time, pH, temperature, and the presence of bromides. Exemplary results of studies focused on determining the relationship between these factors and THM concentration in chlorinated water are presented in research (Hong *et al.* 2007; Platikanov *et al.* 2012; Dominquez-Tello *et al.* 2017).

CONCLUSIONS

The application of pre-hydrolyzed coagulants allowed to reduce the content of TOC and DOC by 38–45% and the UV₂₅₄ value by 51–53%, while with the application of Al₂(SO₄)₃ TOC and DOC reduction by 10–15% was obtained and UV₂₅₄ by 23%. Therefore, better effects of organic compounds removal were obtained using pre-hydrolyzed salts.

Depending on the coagulant used for water purification, the potential for trihalomethanes formation after 24-h contact with chlorine amounted to 52–61 µgCHCl₃/L. The lowest value (46 µgCHCl₃/L) was obtained in chlorinated water after prior purification with PAX-XL19 and powdered activated carbon CWZ. THM-FP in water purified in the coagulation process with the usage of PAX and CWZ was 35% lower than in untreated surface water subjected to chlorination. Although a significant portion of organic matter was removed during the coagulation process, however, the remaining portion was still characterized by high THM formation potential.

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