



Decrease in the chloride disinfection by-products (DBPs) formation potential in water as a result of coagulation process

Maria Włodarczyk-Makuła*, Anna Nowacka-Klusek

Department of Chemistry, Water and Wastewater Technology, Czestochowa University of Technology, 69 Dąbrowskiego Str, 42-200 Czestochowa, Poland, Tel. 048 34 32 50 919; Fax: 048 32 50 496; email: mwm@is.pcz.czest.pl (M. Włodarczyk-Makuła)

Received 11 April 2019; Accepted 1 July 2019

ABSTRACT

The efficient removal of natural organic matter reduces the potential for by-products that are formed during the process of disinfection. Among the various organic derivatives, the following are listed: halogenoacetonitriles, halogenonitromethanes, halogenoketones and most commonly trihalogenomethanes. The aim of the study was to determine the effect of coagulation process on the change of selected 12 chlorine disinfection by-products (DBPs) formation potential. The coagulation process was carried out with aluminium(VI) sulphate and four pre-hydrolyzed aluminium salts. Among the halogenoacetonitriles (HAN), the following compounds were analyzed: trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN). The trichloronitromethane, otherwise known as chloropicrin (CP) and halogenoketones (HK): 1,1-dichloropropanone (1,1-DCP) and 1,1,1-trichloropropanone (1,1,1-TCP) were also analyzed. Among trihalogenomethanes (THM) trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), tribromomethane (TBM) were analyzed. Furthermore, one compound of trichloroacetaldehyde (chloral hydrate [CH]) was identified, too. Quantitative and qualitative analysis was carried out using gas chromatograph–mass spectrometry (GC-MS). The results of the chlorine potential test indicate that the coagulation efficiency depended on the type of coagulant. The most effective coagulant was one of pre-hydrolyzed salt (FLOKOR 1ASW/B). Addition of FLOKOR 1ASW/B resulted in reduced DBPs formation potential of 60%–82% compared with the raw water.

Keywords: Coagulation; Water treatment; Halogenoacetonitriles; Halogenonitromethanes; Halogenoketones; Trihalogenomethane

1. Introduction

Numerous studies about formation of disinfection by-products (DBPs) processes have been found from 1970s. So far, over 700 compounds of various structure and properties have been identified [1]. The formation of by-products takes place due to the fact that chemical disinfectants that are applied in order to destroy pathogen organisms have strong oxidative properties whereas, in the surface and ground waters the natural organic and inorganic compounds are present. The organic substances classified as natural organic matter (NOM) such as: humic acids (HA) or fulvic acids (FA)

are regarded as main precursors in the formation of DBPs [1,2]. Disinfection process can result in the fates of both organic and inorganic compounds. Inorganic compounds do not have significant negative impact on the water quality, whereas the organic derivatives have toxic properties and type of disinfectant has influence on the quantity and quality of reaction products [3]. As a result of chlorine reaction with compounds of natural organic substances not only chlorine derivatives are formed but also bromine- and chlorine-bromine-organic compounds. Depending on the amount of atoms that are attached to NOM di- and tri-halogen derivatives chemical compounds are formed [4,5]. Considering

* Corresponding author.

the amounts of chlorine DBPs in the water, they are listed as follows: THM, halogenoacetic acids (HAA) and halogenoacetaldehydes (CH). It has also been proved the presence of halogenoketones (HK) bindings. The compounds containing nitrogen in the particle create the special group among DBPs, these are: halogenoacetonitriles (HAN), halogenoacetamides as well as halogenonitromethanes (HNM). In the water, the following compounds are commonly determined: chloromethane (TCM), tribromomethane (TBM) as well as two compounds containing chlorine and bromine: bromodichloromethane (BDCM) and dibromochloromethane (DBCM). Among halogenoacetonitriles two chlorine derivatives such as: trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN) as well as dibromoacetonitrile (DBAN) and bromochloroacetonitrile (BCAN) are mostly determined. Chloropicrin belongs to the nitrogen compounds and nitrogen in the particle occurs on fifth oxidation level (nitrites group $-\text{NO}_2^-$). Among halogenoketones (HK), 1,1-dichloropropane (1,1-DCP) as well as 1,1,1-trichloropropane (1,1,1-TCP) is usually determined. Some of the DBPs have strong toxic effect on indicators and they are probably carcinogenic to humans. IARC makes classification according to toxicological investigations [5–9]. The presence of DBPs should be currently monitored due to their carcinogenic, teratogenic and mutagenic properties. It should also be pointed out that not all compounds mentioned above are listed in the regulations regarding drinking water. In the regulation of Health Ministry in Poland only trihalomethanes are included. The permissible total concentration of four DBPs should not exceed the value of 100 $\mu\text{g/L}$. The permissible concentration of trichloromethane (TCM) in drinking water should not exceed the value of 30 $\mu\text{g/L}$, whereas bromodichloromethane (BDCM) – 15 $\mu\text{g/L}$, respectively. The mentioned regulations are comparable with European Union regulation included in the Directive 98/83/EC of the Council that provided the quality standards of water intended for human consumption [10,11].

At present, the most important problem in the treatment of potable water is to protect from the formation of oxidation by-products (OBPs) as well as DBPs. Thus, in water treatment plants (WTPs) two treatment methods are mainly applied. In the one method, the removal of NOM from the raw waters using physical or chemical processes in the primary step of treatment is applied. In such a way, the precursors of oxidation and DBPs are removed. The ozonation preceded by the biological filtration is regarded as the most efficient system allowing to remove NOM. As a result of decomposition, the organic substances, easily biodegradable compounds are formed. However, the efficiency of ozone preceded by the biological filtration in the removal of NOM is not stable and varies from 10% to 75%. Thus, the primary ozonation is preferred in order to remove of NOM. That allows the removal of precursors that form OBPs as well as DBPs. However, the information of the OBPs is not completed. The following by-products: acetic and oxalic acids as well as keto-acids have been identified, so far [2,12]. In the further unit processes applied in the conventional WTPs, the partial removal of NOM has been achieved [13]. In most circumstances, only the final disinfection process is controlled, whereas others have been omitted. Properly conducted coagulation ensures effective elimination of

water turbidity as well as the colour. Additionally, organic micropollutants, including carcinogenic compounds (polycyclic aromatic hydrocarbons), are removed [14,15]. So far, aluminium(VI)sulphate has been the most frequently applied coagulant in water treatment. However, it is replaced by a pre-hydrolyzed coagulant currently [16–20]. The reason for changing the coagulant is to optimize the process of coagulation and to minimize adverse effects of the process. In accordance with the literature data [17,21–24] confirmed by authors' study [17,18,24], these reagents are more effective in the removal of substances affecting the turbidity of the water and organic impurities. Moreover, they are more resistant to changes of temperature and pH [6]. Pre-hydrolyzed coagulants are classified as polyaluminium chlorides and sulphates. In addition, the presence of many hydrolyzed aluminium hydroxy complexes and polymer " Al_{13} " $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}]^{7+}$ in the polyaluminium chloride solutions, was observed. The mentioned polymer is regarded as the most facilitating stable and effective. Among aluminium polymers, polyaluminium chlorides represented by the general formula: $\text{Al}_n(\text{OH})_m\text{Cl}_{3n-m}$ are primarily used [17,25,26]. These reagents increased the basicity in the range of 15%–85%. Although there are numerous investigations into removal of NOM from water, the studies of determination of potential changes for DBPs formation in the coagulation process have not been carried out so far.

The aim of the study was to determine the effectiveness of selected aluminium coagulants: aluminium(VI)sulphate and five pre-hydrolyzed coagulants of potential changes for selected DBPs (halogenoacetonitriles, trihalomethanes, haloacetones, halogenonitromethanes and haloacetaldehydes) formation.

2. Materials and methods

2.1. Materials

Water samples intended to coagulation process were collected once during a day from a selected WTP in the southern part of Poland. Instantaneous samples were taken during spring season. Analyzed samples were treated as grab samples. Water samples for analysis were collected after pre-ozonation before coagulation process. Samples were stored at the temperature of 4°C. In the studied WTP, there are two production lines running simultaneously. Water for treatment is collected from two independent water supply sources. Raw water entering the first line originates from one surface water intake (dam reservoir). In the second line, water is taken from two independent surface sources. Water samples for analysis were collected after pre-ozonation in the first treatment line. The technological scheme of WTP was presented in the paper published previously [14]. The following three coagulants were applied in the studies:

- Aluminium(VI)sulphate $\text{Al}_2(\text{SO}_4)_3 \times 14\text{H}_2\text{O}$ – ALK, (solid),

IT is the specification of reagents of pre-hydrolyzed coagulants such as:

- polyaluminium chloride – PAX XL19H
- di-aluminium chloride pentahydroxide – FLOKOR 1.2 A
- di-aluminium chloride hydroxide sulphate – FLOKOR 1ASW/B
- di-aluminium chloride hydroxide sulphate – FLOKOR 105V

2.2. Experimental procedure

The coagulation process was carried out using aluminium(VI)sulphate as well as the following aluminium pre-hydrolyzed salts : PAX XL19H; FLOKOR 1,2A; FLOKOR 1ASW/B and FLOKOR 105V made. The coagulation process with the use of aluminium(VI)sulphate is conducted under technical conditions, at present. In Table 1, the characteristics of coagulants are included.

All coagulation experiments were carried out at ambient temperature, without pH correction (results of the former studies have shown that the correction of pH to 5.50 and 7.50 does not improve the efficiency of the process). The coagulation process was carried out in laboratory coagulator set in glass reactors. The capacity of reactor was equal to 2 L; the volume of samples was equal to 1 L. Coagulant (1%) at the optimal dose was added to the water samples. The optimal doses of the coagulants and the optimum process parameters were determined in the previous studies [17]. The optimum doses of used coagulants amounted for:

- aluminium(VI)sulphate – 1.8 mg Al³⁺/L,
- pre-hydrolyzed aluminium coagulants – 1.2 mg Al³⁺/L.

Appropriate doses of coagulants were added to beaker and were shaken rapidly with a mechanical stirrer for 3 min (200 rpm) followed by slow shake for 10 min (30 rpm). Afterwards, the samples were subjected to sedimentation for 60 min. Water samples before and after coagulation process were tested for the potential of by-products formation. The experiment was carried out according to the method including chlorine treatment. The chlorine concentration was in the range of 3–5 mg/L; samples were incubated under the temperature of 25°C for 24 h; pH was adjusted to the value of 7. Afterwards, samples were dechlorinated and the selected DBPs were determined. The incubation time was shorter than that under standard investigations in order to simulate real conditions of water retention time in the purification line. Quality of the water was estimated by determining pH, alkalinity, true colour, turbidity and aluminium content. The concentration of organic compounds in the water was determined by: total organic carbon (TOC), dissolved organic carbon (DOC) and ultraviolet UV absorption (254 nm), respectively.

Table 1
Characteristics of tested coagulants

Parameter	Coagulants				
	Aluminium(VI) sulphate ALK	PAX XL19H	FLOKOR 1.2A	FLOKOR 1ASW/B	FLOKOR 105 V
pH	3.4	3.5	4.2	3.9	3.5
[Al], wt.%*	9.1	12.5	11.0	8.0	6.5
[Al ₂ O ₃], wt.%	17.20	23.60	20.79	15.12	12.28
[Cl ⁻], wt.%	0.0	8.5	7.0	5.2	4.5
[SO ₄ ²⁻], wt.%	0.0	0.0	0.0	0.8	2.8
Basicity, %	0.0	85.0	80.0	70.0	70.0
Density (20°C), g/mL	1.58	1.34	1.28	1.20	1.10
[Al]/[Cl]	0	1.47	1.57	1.54	1.44

*wt. – mass fraction in percentage.

2.3. Analytical methods

Quantification and qualification analysis of DBPs was carried out using gas chromatograph with mass spectrometry. 12 compounds were determined. Among halogenoacetonitriles (HAN): trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN) were analyzed. Among halogenonitromethanes (THM) group – trichloronitromethane and chloropicrin (CP) were analyzed. Among trihalomethanes: trichloromethane (TCM), tribromomethane (TBM) and two compounds content chloride and bromide: bromodichloromethane (BDCM) and dibromochloromethane (DBCM) were identified. 1,1-dichloropropanone (1,1-DCP) as well as 1,1,1-trichloropropanone (1,1,1-TCP) among halogenoketones (HK) group were chosen. The halogen acetaldehyde (chloral hydrate (CH)) was determined, too. Helium was a carrier gas; the separation of selected compounds was carried out on capillary column RxiTM – 5 ms (Restek). The parameters of column were as follows: thickness of the film 0.5 µm, the external diameter of the column 0.25 mm and the column length – 30 m. The analyzed compounds were extracted from the water using methyl tert-butyl ether (MTBE). The temperature program of chromatographic analysis was as follows: 25°C for 9.5 min, then heating to 200°C, temperature rate was equal to 40°C/min. The detection limit for analyzed compounds was 0.01 µg/L.

pH was measured by potentiometric method. A titrimetric method was used to determine the total alkalinity of water samples. True colour was indicated in accordance with ISO 7887 – Method C, using a spectrophotometer M501 Camspec LTD. Quartz cuvette with path length of light 50 mm was used. It was determined after filtration of the water sample through a membrane filter of pore size 0.45 µm. Colour of the sample was calculated using the following equation:

$$C = \frac{A_{410}}{a \times d} [\text{mg/L}] \quad (1)$$

C – true colour of the sample, A₄₁₀ – absorbance of the sample at λ = 410 nm, a – specific absorption coefficient of the calibration solution of potassium hexachloroplatinate

and cobalt chloride mm^{-1} (mg Pt/L) $^{-1}$, d – optical path length (mm) [27].

Turbidity was designated using turbidity meter (Turbidity Lovibond company – nephelometric method). Determination of UV254 absorbance was performed in accordance with the method given by US EPA [28] using a spectrophotometer Camspec M501 LTD. Quartz cuvette with path length of light 10 mm was used. The sample was filtered through a membrane before DOC analysis. DOC and TOC concentration was analyzed using a carbon analyzer TN/TC model multi NC produced by Analytik Jena (Germany). DOC and UV254 were used in the calculation of the specific UV absorbance (SUVA) (Eq. (2)).

$$\text{SUVA} = \frac{\text{UV}_{254\text{nm}}^{1\text{m}}}{\text{DOC}} \left[\text{m}^3/\text{gC m} \right] \quad (2)$$

SUVA – specific UV absorbance at 254 nm, UV – absorbance at 254 nm (m^{-1}), DOC – dissolved organic carbon (g/m^3) [28].

The determination of DBPs and indicators of water quality was carried out in triplicates. Statistical method including standard deviation was adopted. The significance of changes in DBPs concentration in water was calculated using Excel program and t-student test. The confidence level of 0.95 was adopted. The number determining degree of freedom was 2, The theoretical value of coefficient t_d of t-student test was equal to 4.303.

3. Results and discussion

3.1. Water quality parameters before and after coagulation

Selected indicators of water quality before and after coagulation are included in Table 2. The application of pre-hydrolyzed coagulants was much more efficient in the removal of organic compounds compared with the coagulant added to the water in the water treatment. The concentration of organic compounds in the water after coagulation process was the lowest after adding Flokor 105 V. By using the aforementioned coagulant, the efficiency of removal of organic compounds expressed by TOC ranged 23%. After coagulation using FLOKOR 105 V, the highest decrease of

DOC concentration (17%) was obtained. Addition of the remaining coagulants resulted in the removal of organic substances, expressed as DOC, in the range of 6%–15%.

The highest efficiency in the removal of organic impurities, expressed as UV254 absorbance indicator (filtered samples), was obtained by applying FLOKOR 1ASW/B (51%). The lowest value of SUVA appeared for FLOKOR 1ASW/B when the optimal dose was added to the samples. The results obtained for ALK, FLOKOR 1.2A and FLOKOR 1ASW/B were confirmed in the literature. Hassan et al. [29] demonstrate that the removal of DOC in the coagulation process does not exceed 25% if the SUVA value was less than or equal to $2.0 \text{ m}^3/\text{gC m}$. The use of pre-hydrolyzed coagulants resulted in the decrease of alkalinity. These results were similar to those obtained in the former studies of authors during winter season [14,18] as well as other researchers [30]. In all conducted studies, the same results were obtained in the removal of pollutants affecting the colour (a reduction of 80.0%). The highest efficiency in the removal of compounds that affects the turbidity was found for FLOKOR 1ASW/B (67.2%). Additionally, during autumn season that coagulant has been proven to be effective in the removal of turbidity. The least effective was PAX XL10H (reduction of 53%). The lowest concentration of residual aluminium in the water samples was achieved after the coagulation process using Flokor 1ASW/B. The concentration was about 10.8% and 23.4% lower than in the case of adding ALK and FLOKOR 1.2 A, respectively. However, in all added coagulants, concentration of aluminium after coagulation process increased significantly (statistically) compared with the raw water. Aluminium was determined in non-filtered samples. Concentration after filtration was much lower. Analysis of the results leads to the conclusion that the highest efficiency of the coagulation process appears during autumn season using FLOKOR 1ASW/B.

3.2. Changes of DBPs formation potential during coagulation process

In raw water intended for treatment, the potential of forming selected 12 chlorine products was equal to $492.1 \mu\text{g/L}$. After coagulation process, the decrease of amount of potential of by-products formation occurred.

Table 2
Water quality parameters before and after coagulation

Indicator	Raw water	Quality of water after coagulation process with coagulants				
		Al ₂ (SO ₄) ₃ ALK	PAX XL19H	Flokor 1.2A	Flokor 1ASW/B	Flokor 105V
pH	6.4 ± 0.1	7.1 ± 0.1	7.2 ± 0.1	7.2 ± 0.1	7.3 ± 0.1	7.2 ± 0.1
Alkalinity, mval/L	1.8 ± 0.1	1.4 ± 0.1	1.6 ± 0.1	1.5 ± 0.1	1.6 ± 0.1	1.5 ± 0.1
True colour, mg Pt/L	5.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1
Turbidity, NTU	5.9 ± 0.1	2.4 ± 0.1	2.77 ± 0.1	2.6 ± 0.1	1.9 ± 0.1	2.1 ± 0.1
*Absorbance UV254 _{4nm} ^{1m} , m ⁻¹	0.088 ± 0.002	0.048 ± 0.002	0.052 ± 0.002	0.050 ± 0.005	0.043 ± 0.002	0.046 ± 0.002
Dissolved organic carbon (DOC), mgC/L	5.84 ± 0.03	4.41 ± 0.02	4.29 ± 0.02	4.62 ± 0.01	4.19 ± 0.02	4.09 ± 0.01
Total organic carbon (TOC), mgC/L	6.92 ± 0.03	5.47 ± 0.03	5.49 ± 0.02	5.47 ± 0.02	5.46 ± 0.03	5.32 ± 0.02
SUVA, m ³ /gC m	1.51 ± 0.02	1.06 ± 0.02	1.13 ± 0.02	1.19 ± 0.02	1.00 ± 0.02	1.25 ± 0.02
Aluminium, mg Al/L	0.083 ± 0.001	0.379 ± 0.002	0.477 ± 0.002	0.441 ± 0.002	0.338 ± 0.002	0.431 ± 0.002

3.2.1. Changes in the halogenoacetonitriles (HAN) for potential formation

The results of the method describing the potential of nitrogen derivatives formation indicated that the coagulation efficiency depended on the coagulant type. Flokor 1ASW/B was the most efficient coagulant in the decreasing potential of DBPs. After adding Flokor 1ASW/B, the value for DBPs formation decreased of 79% compared with the

raw water. After adding aluminium(VI)sulphate, that is commonly used in practice, 54% decrease of potential for DBPs formation was achieved. The decrease of potential for DBPs formation was in the range of 42%–66% compared with the potential in raw water for the remaining coagulants. The potential of formation of halogenoacetonitriles in raw water amounted to the value of 17.1 µg/L. In Fig. 1 changes in the potential of halogenoacetonitriles are given. The most sufficient coagulant was FLOKOR 1ASW/B, the potential

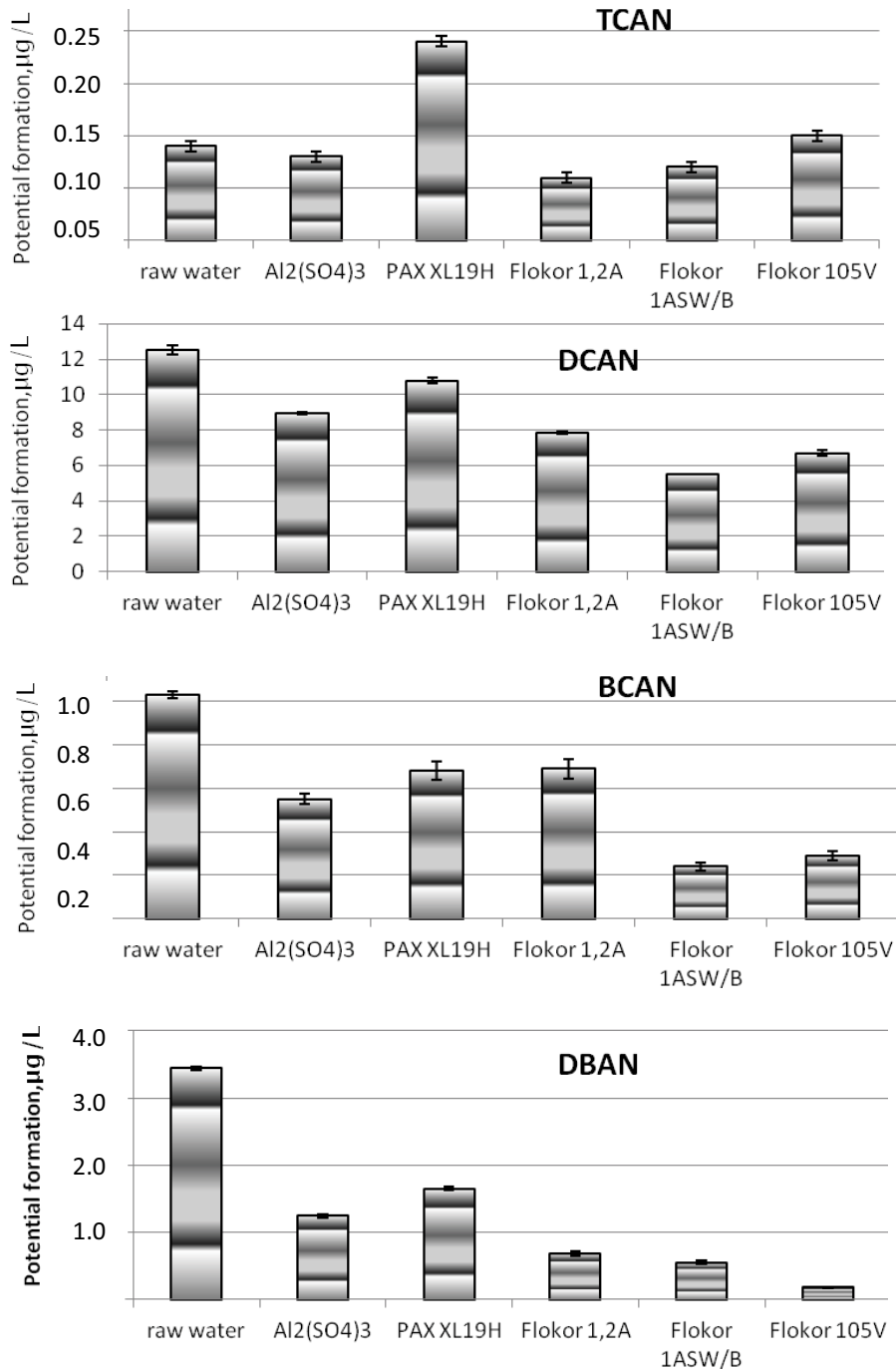


Fig. 1. Changes in the trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN) for potential formation.

of forming halogenoacetonitriles was lower of 63%. The efficiency of the remaining salts resulted in the decrease of potential of organic halogenoacetonitriles by-products formation in the range of 37%–58%. The decrease of potential of halogenoacetonitriles ranged 37% while aluminium sulphate was applied in order to simulate the real conditions.

3.2.2. Changes in the trihalogenomethanes (THM) for potential formation

In Fig. 2 changes in the potential of trihalogenomethanes are presented. The value of potential of trihalogenomethanes in raw water was equal to 289.3 $\mu\text{g/L}$. Flokor 1ASW/B appeared to be the most sufficient coagulant in the removal

of trihalogenomethanes. The decrease of potential value of formation of THM was lower in the water of 82% than in the water before the coagulation process. Aluminium(VI) sulphate, used so far, decreased potential value for THM formation of only 56%.

3.2.3. Changes in the chloropicrin (CP) for potential formation

In Fig. 3 changes in the potential of chloropicrin formation are presented. Potential of chloropicrin formation was equal to 3.52 $\mu\text{g/L}$ in raw water. The highest decrease (72%) was obtained during coagulation by adding Flokor 1.2A. The efficiency of the remaining salts in the decrease of potential of forming the nitro organic derivatives was in the range of

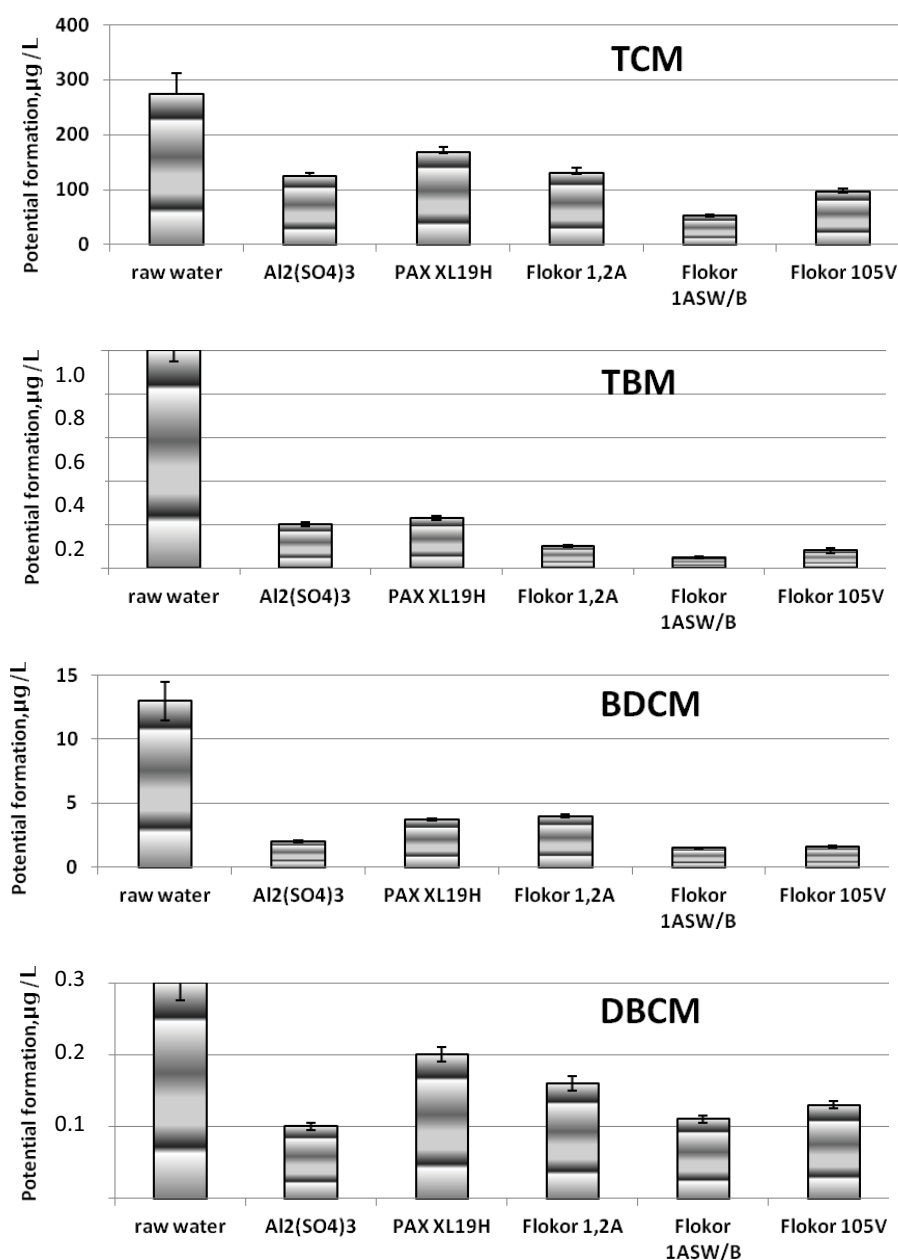


Fig. 2. Changes in the trichloromethane (TCM), tribromomethane (TBM), bromodichloromethane (BDCM) and dibromochloromethane (DBCMB) for potential formation.

45%–70%. While coagulation was carried out by aluminium(VI)sulphate simulating the real conditions applied in practice, 69% decrease of potential of chloropicrin formation was achieved.

3.2.4. Changes in the halogen acetaldehydes (CH) for potential formation

In Fig. 4 changes in the potential of chloral hydrate (halogen acetaldehydes group) are given. The potential for formation of selected compound belonging to the aforementioned group was equal to 136.6 $\mu\text{g/L}$ in the raw water. The potential decreased (75%) most efficiently by adding Flokor 1.2 A. The efficiency of the remaining salts in the reduction of potential for the nitro organic derivative formation was in the range of 41%–61%. 44% decrease of potential for chloropicrin formation occurred, carrying coagulation process by aluminium(VI) sulphate simulating the real conditions applied in practice.

3.2.5. Changes in the halogenoketones (HK) for potential formation

In Fig. 5 changes in the potential of halogenoketones (1,1-dichloropropanone (1,1-DCP), 1,1,1-trichloropropanone (1,1,1-TCP)) are presented. The potential of formation of the aforementioned compounds was equal to 136.6 $\mu\text{g/L}$ in raw water. In the water after coagulation, the potential of forming determined halogenoketones was equal to 6.3 $\mu\text{g/L}$. The obtained decrease of potential value of aforementioned

compounds formation was lower of 86%, whereas during coagulation process with aluminium(VI)sulphate (used so far in water treatment plant), the decrease of value of this parameter does not exceed 70%.

4. Conclusion

Analysis of the water quality indicators showed that the highest efficiency of the coagulation process was achieved using FLOKOR 105 V coagulant. The application of FLOKOR 105V resulted in the lowest concentration of alkalinity, turbidity, the lowest content of organic compounds expressed in indicator UV254 absorbance, DOC and TOC, respectively.

FLOKOR 1ASW/B appeared to be the most efficient coagulant in the reducing potential for selected disinfection organic by-products formation from the water during the spring season. In Table 3 the percentage of reducing potential for selected DBPs formation is given.

Statistically, FLOKOR 1ASW/B appeared to be the most effective in the decrease of potential of trihalomethanes (82%) and halogenoketones (81%) formation. The presence of selected organic by-products of disinfection may also be related to the structure and properties of the resulting flocs after coagulation using this coagulant. The highest efficiency in decrease of tribromomethane (95%) and 1,1,1-tribromopropanone (90%) was found when FLOKOR 1ASW/B was applied. This phenomenon might be related to the high molecular weight, that indicates a strong capacity to adsorb the aforementioned hydrocarbons to the surface of the flocs and their molecular structure. Changes in concentration of

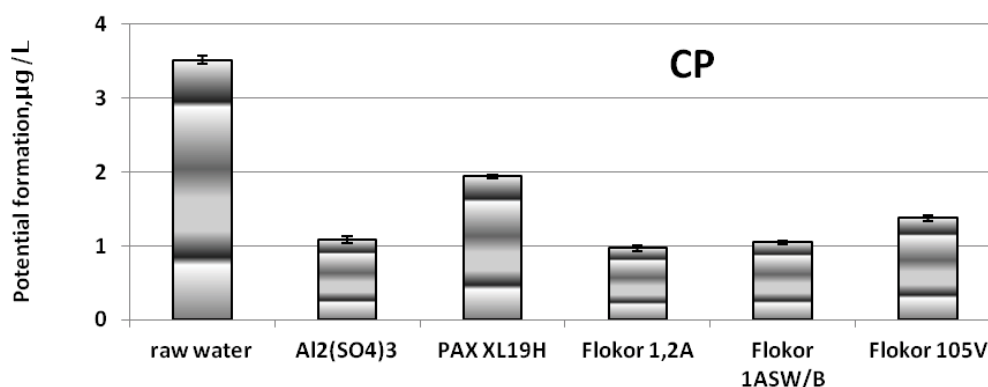


Fig. 3. Changes in the chloropicrin (CP) for potential formation.

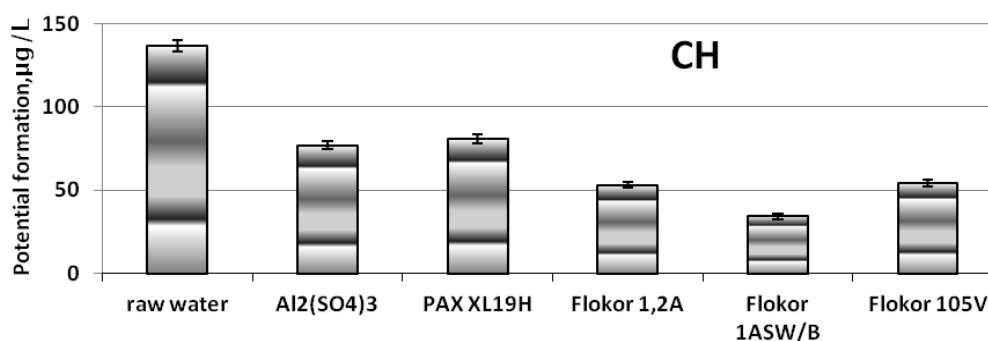


Fig. 4. Changes in the chloral hydrate CH for potential formation.

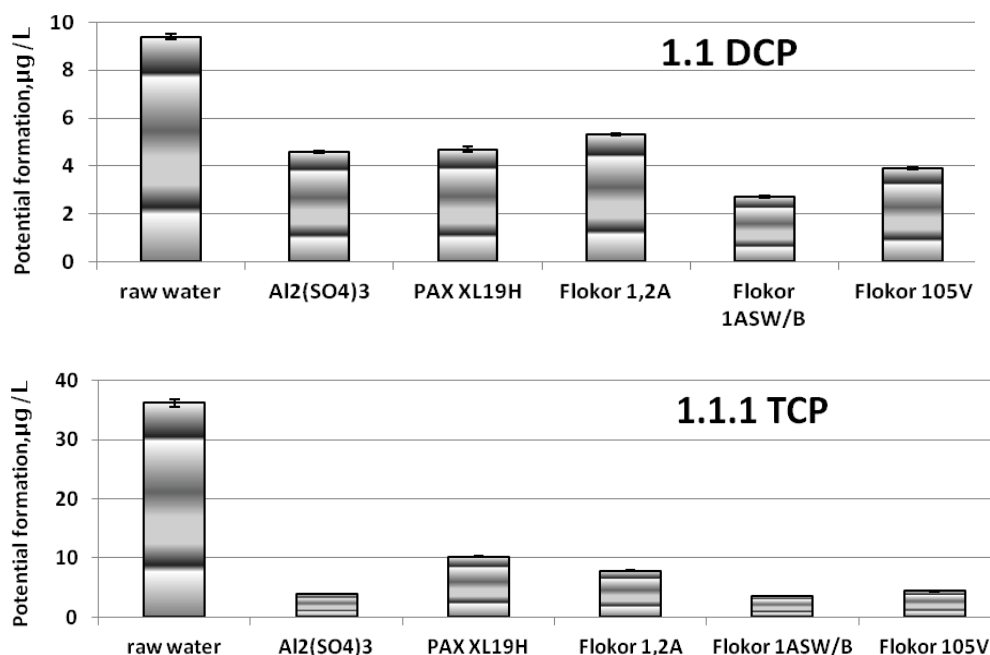


Fig. 5. Changes in the 1,1-dichloropropanone (1,1-DCP) and 1,1,1-trichloropropanone (1,1,1-TCP) for potential formation.

Table 3
Percentage of reducing potential for selected DBPs formation

Group of compounds	By-products	Al ₂ (SO ₄) ₃ ALK	PAX XL19H	Flokor 1.2A	Flokor 1ASW/B	Flokor 105V
Halogenoacetonitriles	TCAN	11 ± 2	–	33 ± 2	22 ± 1	–
	DCAN	28 ± 1	14 ± 1	37 ± 2	56 ± 3	47 ± 2
	BCAN	47 ± 3	34 ± 2	33 ± 2	77 ± 3	72 ± 3
	DBAN	64 ± 3	52 ± 3	80 ± 3	84 ± 2	95 ± 4
Trihalomethanes	TCM	55 ± 2	39 ± 2	53 ± 4	81 ± 2	65 ± 3
	BDCM	85 ± 4	72 ± 4	69 ± 3	88 ± 4	88 ± 2
	DBCM	67 ± 3	33 ± 2	47 ± 2	63 ± 4	57 ± 1
	TBM	80 ± 4	77 ± 4	90 ± 4	95 ± 3	92 ± 3
Halogenonitromethanes	CP	69 ± 4	45 ± 3	72 ± 4	70 ± 4	61 ± 4
Halooacetaldehydes	CH	44 ± 3	41 ± 2	61 ± 3	75 ± 3	60 ± 3
Halogenoketones	1.1 DCP	51 ± 2	50 ± 4	44 ± 4	71 ± 4	59 ± 2
	1.1.1 TCP	89 ± 3	72 ± 3	78 ± 2	90 ± 2	88 ± 2

analyzed compounds may result in the physicochemical transformations of these compounds in the water, mainly sorption onto solid particles. Comparison of the obtained results with the literature data is difficult because studies on the NOM removal from water have been carried out in the process of coagulation or oxidation and membrane processes [13,16,26–31]. Most literary sources aim conditions of forming trihalomethanes or halogenoacetic acids in primary oxidation and photo-oxidation processes with respect to DBPs [4,12,32]. The effectiveness of these compounds were different and depended on NOM characteristics, technological parameters of oxidation process and did not exceed 50% [31,32]. However, the impact of coagulation process using various coagulants (simultaneously) on the potential of forming other DBPs (seven group of compounds) has not

been described so far. In the available studies, five formulations have been investigated, among these only one replaced the aluminium(VI) sulphate. That will allow to reduce the potential for DBPs formation. Additionally, the higher efficiency in the removal of NOM, compared with the basic coagulant, will be achieved.

The studies conducted on the effectiveness of non-hydrolyzed aluminium(VI)sulphate and pre-hydrolyzed aluminium coagulants: PAX XL19H; FLOKOR 1,2A; FLOKOR 1ASW/B and FLOKOR 105V allowed to state that during coagulation process the DBPs formation potential may be effectively reduced. The efficiency of coagulants primarily hydrolyzed with respect to some compounds in the decrease of formation of potential was similar. However, statistically the highest efficiency in reducing the DBPs formation

potential was obtained by adding FLOKOR 1 ASW/B in most cases. The aforementioned coagulant contains sulphate ions, the percentage of aluminium oxide is about 15% and pH value does not exceed 4 (Table 1). It is successfully used in other WTP for removal of turbidity and true colour. The results of this research have confirmed it is effective for decrease of DBPs formation potential. Decrease in the sum of selected DBPs formation potential was in the range of 60%–82%. The most efficient removal of individual compounds was obtained after adding pre-hydrolyzed aluminium coagulants (using lower coagulant dose than in case of ALK). In this case, the reducing potential for formation of DBPs was for:

- halogenoacetonitriles: 14%–95%,
- trihalomethanes: 33%–95%,
- halogenonitromethanes such as chloropicrin: 45%–72%,
- halogenoketones: 50%–90%
- halogenacetaldehyde such as chloral hydrate: 41%–75%.

Taking into considerations the reduction the by-products formation potential (contain chlorine), the most favorable would be to replace the coagulant – aluminium(VI) sulphate to Flokor 1ASW/B.

References

- [1] Water Pollution, Drinking Water and Drinking Water Treatment, J. Hrubec, Ed., Springer-Verlag, Berlin, Heidelberg, 1995.
- [2] X. Zhang, C. Cui, S. Yu, Identifying oxidation intermediates formed during ozone-UV of fulvic acid, *Desal. Wat. Treat.* 74 (2017) 258–268.
- [3] Drinking Water Treatment, C. Ray, R Jain, Eds., Springer, Dordrecht, 2011.
- [4] M. Kowalska, The Effectiveness of Removal of Haloacetic Acids from Water using Bioreactor with Native Enzymes, (Membranes and Membrane Processes in Environmental Protection), Monographs of Environmental Engineering Comitee, 2014, pp. 49–59.
- [5] A. Włodyka-Bergier, T. Bergier, W. Zając, Assessment of applicability of UV irradiation in swimming pool water treatment – a case study, *Environ. Prot.*, 37 (2011) 25–35.
- [6] J. Gregory, V. Duan, Properties of flocs produced by water treatment coagulants, *Water Sci. Technol.*, 44 (2014) 231–236.
- [7] C. Jung, H. Son, The relationship between disinfection by-products formation and characteristics of natural organic matter in raw water, *Korean J. Chem. Eng.*, 25 (2008) 714–720.
- [8] A. Włodyka-Bergier, T. Bergier, W. Zając, Assessment of applicability of UV irradiation in swimming pool water treatment – a case study, *Environ. Prot.*, 39 (2017) 53–56.
- [9] IARC - International Agency of Research on Cancer, 1991, 1999, 2002, 2004.
- [10] Council Directive 98/83/EC on the Quality of Water Intended for Human Consumption, Official Journal of the European Union L 330, 3 November 1998, pp. 90–112.
- [11] Directive 2008/105/EC of European Parliament and of the Council on Environmental Quality Standards in the Field of Water Policy, Amending and Subsequently Repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and Amending Directive 2000/60/EC of the European Parliament and of the Council, Official Journal of the European Union L 348, 24 December 2008, pp. 84–97.
- [12] M. Sadrnourmohammadi, B. Gorczyca, Effects of ozone as a stand-alone and coagulation-aid treatment on the reduction of trihalomethanes precursors from water with high DOC and low calcium hardness, *Desal. Wat. Treat.*, 78 (2017) 117–126.
- [13] M. Kabsch-Korbutowicz, A. Urbanowska, K. Majewska-Nowak, J. Kawiecka-Skowron, Removal of organic substances from aqueous solutions with the use of ceramic membrane, *ROZ OCHR SROD*, 12 (2010) 467–478.
- [14] A. Nowacka, M. Włodarczyk-Makuła, Effectiveness of priority PAH removal in a water coagulation process, *Water Sci. Technol. Water Supply*, 15 (2015) 683–692.
- [15] M. Włodarczyk-Makuła, Physical and Chemical Fates of Organic Micropollutants, Scholar's Press, OmniScriptum GmbH & Co., Saarbrücken, 2015.
- [16] J. Duan, J. Gregory, Coagulation by hydrolysing metal salts, *Adv. Colloid Interface Sci.*, 100–102 (2003) 475–502.
- [17] A. Nowacka, M. Włodarczyk-Makuła, B. Macherzyński, Comparison of effectiveness of coagulation with aluminum sulfate and pre-hydrolyzed aluminum coagulants, *Desal. Wat. Treat.*, 52 (2014) 3843–3851.
- [18] A. Nowacka, M. Włodarczyk-Makuła, Impact of selected pre-hydrolyzed aluminum coagulants on improving of treated water quality, *ROZ OCHR SROD*, 16 (2014b) 226–350.
- [19] D. Pernitsky, J. Edzwald, Selection of alum and polyaluminum coagulants: principles and applications, *J. Water Supply Res. Technol. AQUA*, 55 (2006) 121–141.
- [20] M. Rak, M. Świdorska-Bróz, On the advantages of using prehydrolysed aluminum coagulants, *Environ. Prot. Eng.*, 27 (2001) 5–17.
- [21] J. Gumińska, M. Kłos, Analysis of post-coagulation properties of flocs in terms of coagulant choice, *Environ. Prot. Eng.*, 38 (2012) 103–113.
- [22] S. Sinha, Y. Yoon, G. Amy, J. Yoon, Determining the effectiveness of conventional and alternative coagulants through effective characterization schemes, *Chemosphere*, 57 (2004) 1115–1122.
- [23] L. Zhanmeng, L. Simin, Z. Haixia, N. Fahui, W. Qunhui, Preparation, characterisation and coagulation behavior of a novel inorganic coagulant – polyferric(III)-magnesium(II)-sulfate, *Environ. Prot. Eng.*, 39 (2013) 57–71.
- [24] A. Nowacka, M. Włodarczyk-Makuła, Removal of oxidation and disinfection by-products of water, *Ecol. Technol.*, 1 (2014a) 11–17. (in Polish).
- [25] J. Edzwald, D. Pernitsky, W.L. Parmenter, Polyaluminum Coagulants for Drinking Water Treatment: Chemistry and Selection, *Chemical Water and Wastewater Treatment*, VI, Springer, 2000, pp. 3–14.
- [26] D. Ghernaout, B. Ghernaout, A. Kellil, Natural organic matter removal and enhanced coagulation, *Desal. Wat. Treat.*, 2 (2009) 203–222.
- [27] International Standard, Water Quality – Examination and Determination of Colour, ISO 7887, 2011.
- [28] B.B. Poter, Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm in Source Water and Drinking Water, USEPA, 2005.
- [29] A. Hasan, N.P. Thacker, J. Bassin, Trihalomethane formation potential in treated water supplies in urban metro city, *Environ. Monit. Assess.*, 168 (2010) 489–497.
- [30] I. Krupińska, Effect of the Type of Aluminium Coagulant on Effectiveness at Removing Pollutants from Groundwater in the Process of Coagulation, Section: Water Engineering 9th International Conference “Environmental Engineering”, Vilnius, Lithuania, May 22–23, 2014. VGTUPress. Available at: http://leidykla.vgtu.lt/conferences/ENVIRO_2014/Articles/2/082_Krupinska.pdf.
- [31] O. Tsydenova, V. Batoev, A. Batoeva, Solar-enhanced advanced oxidation processes for water treatment: simultaneous removal of pathogens and chemical pollutants, *Int. J. Environ. Res. Public Health*, 12 (2015) 9542–9561.
- [32] Q. Han, Y. Wang, H. Yan, B. Gao, D. Ma, S. Sun, J. Lin, Y. Chu, Photocatalysis of THM precursors in reclaimed water: the application of TiO₂ in UV irradiation, *Desal. Wat. Treat.*, 57 (2016) 9136–9147.