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CIVIL AND ENVIRONMENTAL ENGINEERING REPORTS

E-ISSN 2450-8594

CEER 2019; 29 (4): 236-247
DOI: 10.2478/ceer-2019-0057
Original Research Article

HALOGENATED ORGANIC COMPOUNDS IN WATER AND IN WASTEWATER

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Abstract

Currently, organic halogen compounds (halogen derivatives) are often identified in water. The paper presents the problem of the presence of these newly formed compounds during water treatment processes and their occurrence in sewage. The general indicator determining the content of these compounds in aqueous solutions is the concentration of halogen derivatives of organic compounds adsorbed on activated carbon AOX, which is converted to the concentration of chlorides. The groups of derivatives of halogenated organic compounds containing chlorine and/or bromine in a molecule were characterized, and the precursors and potential for the formation of these compounds in water were described. Moreover, technological methods to prevent and remove them were described.

Keywords: water, wastewater, NOM, DBPs, OBPs, AOX, THM, HAN, HK, CP, CH

1. INTRODUCTION

The formation of halogen organic compounds takes place as a result of the attaching of the atoms of elements from the group of halogens, i.e. fluorine, chlorine, bromine, and iodine to hydrocarbons. The source of these compounds in the environment is natural and anthropogenic processes. Natural processes include the formation of these compounds during combustion, fires, and volcanic eruptions but also from synthesis carried out by fungi, algae, sponges, and lichens. The share of naturally occurring organic halogen derivatives in the environment

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is much smaller than those occurring from anthropogenic sources. These include chemical oxidation, disinfection, and coagulation with chlorine-containing compounds (e.g. iron chloride III, iron chloride II). For the determination of the total content of these compounds in the environmental matrices, the following indicators are used:

1. AOX/NAOX – *adsorbable/non-adsorbable organic halogens,*
2. VOX/NVOX – *volatile/non-volatile organic halogens,*
3. POX/NPOX – *purgeable/non-purgeable organic halogens,*
4. EOX – *extractable organic halogens.*

The AOX indicator was defined in 1976 in Germany and is a measure of the content of organic compounds containing chlorine, bromine, and iodine derivatives converted into chlorides. This was consistent with the identification of chloroform, which was detected in surface water treated with chlorine. Toxicological studies have shown that this compound is carcinogenic, and this was an indication for detailed analysis and identification of other toxic compounds as products of oxidation. So far, more than 700 compounds of different structures and properties have been identified, all of which belong to the so-called *oxidation/disinfection by-products* (OBPs/DBPs) [1,2]. It is remarkable that these compounds are identified in water which is in the process of being prepared for consumption and are formed during processes commonly used in water treatment. This mainly concerns the disinfection process, i.e. chlorination and ozonation, in which organochlorinated and not fully oxidised organic compounds are formed, respectively. Due to their properties, these compounds can be divided into volatile and non-volatile compounds which include halogenoacetonitrile trihalomethanes, halogen derivatives of carboxylic acids, halogenated phenols, phthalates, amines, ketones, aldehydes, and aromatic compounds. The above-mentioned compounds are formed because the surface-water intakes contain precursors of these by-products of oxidation. These are natural organic compounds, which include, among others, humic acids, chlorophyll a, metabolites of organisms living in water, aromatic carboxylic acids, aliphatic hydroxy acids, aldehydes, fulvic acids, nitro organic compounds or algae [3,4]. Therefore, OBPs and DBPs can be formed in any water treatment plant and their type depends on the composition of the natural organic matrix and the type of disinfectant and oxidant used in the unit processes [3,5]. The presence of halogen organic compounds has also been confirmed in municipal and industrial wastewater. The sources of these compounds in municipal wastewater are mainly surfactants, plant protection products, other chemical products, hospital outflows, and outflows from the pulp and paper industry [6-9]. Due to the constantly increasing level of contamination of organic fluorinated waters, it is necessary to take measures aimed at limiting their occurrence and/or removing them from waters and sewage. The aim of the study was to outline the problem of the occurrence of halogen (fluorinated) organic compounds in water and sewage and to present methods of preventing their formation and/or disposal.

2. GENERAL CHARACTERISTICS OF HALOGENATED ORGANIC COMPOUNDS

As already mentioned, the formation of by-products results from the fact that the chemical disinfectants used to inactivate pathogenic microorganisms have strong oxidative properties, while surface water and groundwater contain naturally organic and (*natural organic matter* NOM) inorganic compounds. The NOM content of waters depends on hydrogeological conditions, climate and other environmental indicators. There are both hydrophobic and hydrophilic compounds. Hydrophobic bonds are a large group of aromatic compounds with double bonds between carbon atoms, which constitute 50% of TOC. Organic substances belonging to NOM such as humic acids (HA) or fulvic acids (FA) are the main precursors of the formation of OBPs/DBPs products. The formation of intermediate products mainly concerns hydrophobic compounds, but hydrophilic and low molecular weight compounds also influence the formation of OBPs/DBPs [10]. As a result of the reaction of chlorine with compounds in the composition of natural organic substances, not only chlorine derivatives but also bromo- and chloro-bromo-organic derivatives are formed. Mono-, di-, and tri-halogenated chemical compounds are formed depending on the number of atoms that bind to the NOM molecules. Figure 1 presents a general classification of the hitherto identified DBPs and those most frequently determined in water [4,5,11-13].

Table 1. Properties of DBPs [4,5,11-13]

Disinfection by-products DBPs	Chemical formula/ mass molecule	Precursors of DBPs	Range of concentration in water
			µg/L
Sum of Trihalomethanes THM		Humic acids, Chlorofil “a”, Aliphatic hydroxyl-acids, Carboxylic acids, Aromatic carboxylic acids	Up to the value of 127.5
TCM	$CHCl_2$/119.38		Up to the value of 64.4
BDCM	$CHBrCl_2$/169.83		Up to the value of 25.0
DBCM	$CHBr_2Cl$/208.29		Up to the value of 34.9
TBM	$CHBr_2$/252.75		Up to the value of 61.6

Sum of halogenoacetonitriles HAN		Amino acids, proteins, Aspartic acids, Trypthofan, Cinurenine, Tyrosine, Algae	Up to the value of 22.5
TCAN	C_2Cl_3N/144.39		Up to the value of 5.14
DCAN	C_2HNCl_2/109.94		Up to the value of 18.84
BCAN	$C_2HBrClN$/154.39		Up to the value of 7.19
DBAN	C_2HBr_2N/198.84		Up to the value of 8.0
Sum of halogenoketones HK		Fulvic acids, Hydrofobic acids, Hydrofilic acids, Hydrofilic	Up to the value of 22.5
1.1-DCP	$C_3H_4Cl_2O$/126.98		Up to the value of 10.03
1.1.1-TCP	$C_3H_3Cl_3O$/196.0		Up to the value of 19.59
trichloronitromethane - chloropicrin CP	Cl_3CNO_2/164.39	Nitrogenous organic compounds, Humic acids	Up to the value of 4.19
trichloroacetaldehyde- chloral hydrate CH	$C_2H_3Cl_3O_2$/165.4	Aldehydes, Acetaldehydes	Up to the value of 33.2

Due to the concentrations in the water, trihalogenomethanes (THMs) must be replaced first, halogenoacetic acids (HAAs) second, and halogenoacetaldehydes (CHs) third. The presence of such combinations as halogenoketones (HK) was also demonstrated. A special group among the by-products of water disinfection are compounds containing nitrogen in the molecule. These include halogenoacetonitriles (HAN), halogenoacetamides, and halogenonitromethanes (HNM). The most frequently determined compounds in water are four compounds classified as trihalomethanes. They are tri chloromethane (TCM), tribromethane (TBM), and two compounds containing chlorine and bromine: bromodichloromethane (BDCM) and dibromochloromethane (DBCM). Among the halogenoacetonitriles, the most common compounds are two-chlorine derivatives such as trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), and those containing chlorine and bromine: dibromoacetonitrile (DBAN) and bromochloroacetonitrile (BCAN). Nitrogen compounds also include chloropicrin, where nitrogen in the molecule occurs at the third degree of oxidation (nitro group -NO_2^-). Among halogenoketones (HK), 1,1dichloropropropanone (1,1-DCP) and 1,1,1trichloropropanone (1,1,1-TCP) are the most frequently determined [4,5,14]. Some of the above-mentioned compounds are characterized by strong toxic effects on indicator organisms and probably carcinogenic effects on humans. This is confirmed by toxicological studies based on which IARC has classified them

[15]. The group of 2B compounds with carcinogenic effects on humans includes TCM, BDCM, and DBAN. According to EPA, the carcinogenic and teratogenic effect is shown by TCM, whereas TCM and BDCM are potentially carcinogenic to humans - Table 2. Due to toxic effects, the presence of these compounds in water should be monitored on an ongoing basis. It should be emphasized that not all the above-mentioned identified disinfection process derivatives are referenced in the legislation on drinking water. In the Regulation of the Minister of Health in force in Poland, the admissible concentration of only four trihalomethanes is given [16]. The maximum permissible total concentration of trichloromethane (chloroform), bromodichloromethane, dibromochloromethane, and tribromethane (bromoform) shall not exceed 100µg/L. The additional requirements laid down in that Regulation indicate that at the consumer inlet point, if the water is disinfected with chlorine or its compounds, the concentration of trichloromethane (TCM) should not exceed 30µg/L and that of bromodichloromethane (BDCM) should not exceed 15µg/L. These regulations are in line with the European Union guidelines for the quality of drinking water [17]. However, the acceptable concentration of trihalomethane according to the US EPA is set at 80µg/L. The toxicity and acceptable concentrations of selected OBPs/DBP are presented in Table 2.

Table 2. Toxicity and limit values for selected OBPs/DBPs [4,5,12,13,16,17]

Disinfection by-products DBPs	Toxicity according to IARC/ Carcinogenicity EPA/ influence for health	Limit concentration WHO/US EPA/Polish legislation in drinking water
		µg/L
Sum of THM	n.g	n. g /no higher than 80 / no higher than 100
TCM	2B/P-N/ carcinogenic, teratogenic	300/80/30
BDCM	2B/P/n.g	60/80/15
DBCM	3/N/n.g	100/80
TBM	3/N/ teratogenic, nefrotoxic	100/80
Sum of HAN	n.g	-
TCAN	3/n.g/genotoxic	-
DCAN	3/n.g/ mutagenic, genotoxic	20/-
BCAN	3/n.g/ mutagenic, genotoxic	70/-
DBAN	2B/n.g/n.g	-

Sum of HK		
1.1-DCP	n.g/n.g/mutagenic	-
1.1.1-TCP	n.g/n.g/mutagenic	-
CP	3/n.g/n.g	-
CH	3/n.g/n.g	-

Halogen organic compounds are not only present in water but are also identified in municipal and industrial wastewater. The presence of these compounds has been confirmed in detergents, plant protection products, organic solvents, additives for paints, varnishes and petrol, cleaning preparations, cooling liquids, and other chemical products. The carriers of chlorinated organic derivatives are leachate from landfills, cellulose and paper sewage, and hospital sewage [2,6-8]. The source of these compounds in cellulose-paper wastewater is the reaction of organic residues leached from wood with chlorine ions used to bleach cellulose [7]. Gonzales and Zaror [18] studied the formation of halides during bleaching of cellulose and extraction with chlorine/chlorine dioxide and NaOH and H_2O_2, respectively. It was shown that about 8% of the amount of introduced chloride ions form connections with dissolved organic compounds. The main source of AOX in hospital wastewater is from the use of contrast agents and iodine. Concentrations of these compounds in hospital wastewater reached 1mg/l, but the highest concentrations (14mg Cl/l) were determined in outflows from rooms where medical procedures were performed [18]. In raw urban wastewater, the AOX concentration is lower by an order of magnitude and does not exceed 0.1mgCl/l. Studies on changes of concentration in the sewage treatment plant showed that the source of these compounds are anaerobic processes taking place in the treatment plant, as increased numbers of these compounds were recorded despite the decrease of concentration in raw sewage [8]. In the literature, information can be found confirming that domestic wastewater brings about 33% adsorbable organic halogens to municipal wastewater treatment plants on activated carbon, while the remaining load comes from industrial wastewater. Schultz and Hahn [19] conducted a study to determine the conditions for the formation of organic halogens in urban wastewater. The dependence of AOX generation on the concentration of dissolved organic compounds, pH value, time, temperature, and the presence of oxidizing and reducing compounds was determined. There was a 13-fold increase in AOX concentration after sodium hypochlorite was introduced to wastewater, where dissolved organic carbon concentration was at the level of 25mg/l. The number of organic halogens adsorbed on activated carbon varied depending on the type of organic compounds present in the sewage (phenol, oleic acid). The amount of generated AOX was the highest in the first 10 minutes of the process and when the process was carried out at 40°C. It was shown that, with an increase in pH value, the number of halides formed decreased and at pH level 5.5, more than 0.6mg/l was formed, and at pH level 10 - about 10 times less AOX was formed [19]. The formation of AOX in wastewater during photochemical oxidation was also studied by Baycan and colleagues [20]. The authors demonstrated that the formation of halogen connections took place after 6-18 minutes. The number of formed halogen compounds depended on the concentration of chloride ions and the pH value. When the reaction time was prolonged to 4 hours, a slow decrease in AOX concentration was observed regardless of pH value, and the highest degree of removal was 95%. This proves the possibility of degradation of newly formed halides in the presence of hydrogen dioxide and UV radiation [20].

3. METHODS OF REDUCING THE FORMATION/REMOVAL OF HALOGEN ORGANIC COMPOUNDS

In view of the observed increasing amount of NOM in environmentally derived waters, the most important problem in the preparation of drinking water today is the prevention of the formation of intermediate products of the oxidation process (OBPs) and the intermediate products of the DBPs disinfection process. One option is to phase out chlorine in the pre-treatment processes and apply chlorine compounds only to the final stage of water treatment to disinfect the water before it is fed into the network. On the other hand, the removal of NOM from raw water by physical or chemical/photochemical processes during the initial treatment phase is increasingly being introduced. This reduces or removes certain precursors to the intermediate products of oxidation and disinfection. Partial removal of NOM is also achieved in processes used in conventional water treatment plants [21]. One of them is coagulation, allowing the removal of compounds causing water colour and turbidity, including carcinogenic compounds such as polycyclic aromatic hydrocarbons of PAHs, and to reduce the potential for DBPs formation [22,23]. The most commonly used coagulant in water treatment plants is aluminium sulphate (VI), however, currently, this is replaced by coagulants, which are initially hydrolysed salts [5,13,22-25]. These reagents are more effective than aluminium sulphate (VI) in removing substances influencing water turbidity and organic contaminants. In addition, they are more resistant to changes in temperature and pH [22,26-30]. Comparative studies on the efficiency of reduction of the potential for formation of selected halogenoacetonitriles, trihalomethanes, halogenonitromethane, haloacetaldehyde, and halogenoketones were conducted by co-authors. These studies were carried out with the use of aluminium sulphate (VI) and coagulants classified as initially hydrolysed (polyaluminium chloride, di-aluminium chloride pentahydroxide, and di-aluminium chloride hydroxide sulphate). These studies showed that in the coagulation process, it is possible to obtain a decrease in the potential for the formation of the above-mentioned products within the range of 60 to 82%. For particular analysed compounds, the decrease in the formation potential was within the limits of halogenoacetronitriles: 14-95%, trihalomethanes, respectively: 33-95%, halogenonitromethanes such as chloropicrin: 45-72%, halogenoketones: 50-90% and for halogacetaldehyde such as chloral hydrate: 41-75% [23]. However, in water treatment plants, in most cases, only the final disinfection process is monitored, and other unit processes are omitted. Co-author studies conducted on a real water treatment facility showed that the AOX value fluctuated after subsequent processes and the final value was slightly higher than the initial one, which confirms the formation of halogen AOX compounds during water treatment [22]. High efficiency in the removal of NOM from water is obtained in the processes included in the deepened oxidation process AOP (advanced oxidation process). These methods include chemical, photochemical, catalytic, and integrated processes. In the processes O_3-H_2O_2, O_3-UV, H_2O_2-UV, catalyst -UV, H_2O_2 - catalyst, Fenton reagent, Fenton-UV reagent or ultrasound process support are used. The catalyst is usually titanium dioxide TiO_2 [14,31-33]. In the above-mentioned processes, the efficiency of organic (and some inorganic) compounds expressed as the COD index usually exceeds 90%. Equally high is the removal efficiency of organic compounds expressed as UV254 absorbance. The results of the research indicate the dependence of the process efficiency not only on the process conditions (type of oxidant, dose, reaction time or ratio between Fe^{2+} and H_2O_2 ions in the Fenton process) but also on the initial concentration and type of substances included in the NOM and on the presence of other compounds, including inorganic ones [14,31-34]. AOP processes are also highly effective in removing organic halogens marked as AOX from wastewater. The studies described in the literature focus on wastewater highly loaded with these compounds, which includes cellulose-paper or pharmaceutical wastewater [9]. The possibility of complete removal of organic halogens during photochemical oxidation or chemical oxidation with the use of Fenton reagent or during the catalytic oxidation process has been demonstrated [31-32].

4. CONCLUSION

Numerous studies described in literature, as well as co-author studies, confirm the formation of OBPs treatment by-products and DBPs disinfection by-products during treatment processes. This is related to the presence of naturally occurring organic compounds in waters taken from the environment, which are precursors to the formation of derivatives. In the process of water preparation for consumption, as a result of chemical reactions with disinfectants or oxidants, mono-, di-, and tri-halogen derivative chemical compounds are formed. However, the concentration of these compounds is not routinely determined in drinking water as the legislation sets a limit of only four compounds belonging to trihalomethane. This is important because some of them are toxic to test organisms and potentially toxic to humans. Partial removal of precursors of halogen derivatives is achieved during coagulation, but additional processes are introduced in water treatment plants to ensure highly efficient initial removal of NOM from water. This results in a reduction in the potential for the formation of halogen organic bonds which are the processes of deepened oxidation of AOP (chemical, photochemical, and catalytic). However, the use of a single process is not always sufficient to remove the precursors of OBPs/DBPs formation so, some of the by-products of the treatment processes are traceable in the water. Taking the above into account, and the confirmed toxicity of certain water disinfection products, there is an urgent need to supplement the legislation with these contaminants and to make it mandatory to monitor their concentration in water entering the network and intended for consumption. From the point of view of water protection, it is important to prevent the formation of halogen products in wastewater or the final treatment of wastewater before discharge into a receiving body.

REFERENCES

1. Anielak, A 2015. Wysokoefektywne metody oczyszczania wody. Wydawnictwo Naukowe PWN, Warszawa.
2. Jancewicz, A, Dmitruk, U and Kwiatkowska, A 2011. Badania zawartości wybranych substancji halogenoorganicznych (AOX) w wodzie i ściekach. Ochrona Środowiska. 33, 1.
3. Włodyka-Bergier, A and Bergier, T 2015. Lotne organiczne produkty uboczne chlorowania w wodzie z krakowskich systemów dystrybucji. Wydawnictwa AGH, Kraków.
4. Włodyka-Bergier, A, Bergier, T and Zając, W 2017. Assessment of applicability of UV irradiation in swimming pool water treatment – a case study. Environment Protection, 39, 1, 53-56.
5. Rak, M and Świderska-Bróż, M 2001. On the advantages of using prehydrolysed aluminum coagulants. Environment Protection Engineering. 27, 3-4, 5-17.
6. Cherif, S, Fraaj, RB and Jrad, A 2006. Quality of treated wastewater method validation of AOX, Accreditation and Quality Assurance, 11, 632-637.
7. Savant, DV, Abdul-Rahman, R and Ranade DR 2006. Anaaerobic degradation of adsorbable organic halides (AOX) from pulp and paper industry wastewater. Bioresource Technology. 97, 1092-1104.

8. Shomar, B 2007. Sources of adsorbable organic halogens (AOX) in sludge of Gaza. Chemosphere, 69, 1130-1135.
9. Luyten, J, Sniegowski, K, Van Eyck, K, Maertens, D, Timmermans, S, Liers, S and Braeken, L 2013. AOX removal from industrial wastewaters using advanced oxidation processes: assessement of a combined chemical-biological oxidation. Water Science and Technology, 68, 9, 2048- 2054.
10. Zhang, X, Cui, C and Yu, S 2017. Identyfying oxidation intermediates fordem during ozone-UV of fulvic acid, Desalination and Water Treatment 74, 258-268.
11. Kowalska, M 2014. The effectiveness of removal of haloacetic acids from water using bioreactor with native enzymes. Membranes and Membrane Processes in Environmental Protection, Monografie Komitetu Inżynierii Środowiska PAN, 49–59.
12. Jung, C and Son, H 2008. The relationship between disinfection by-products formation and characteristics of natural organic matter in raw water. Korean Journal of Chemical Engineering 25, 4, 714–720.
13. Gregory, J and Duan, V 2014. Properties of flocs produced by water treatment coagulants. Water Sci. Technol.44(10), 231-236.
14. Moncayo-Lasso, A, Pulgarin C and Benitez, N 2008. Degradation of DBPs precursors in river water before and after slow sand filtration by photo-Fentonprocess at pH 5 in a solar CPC reactor. Water Research. 42, 15,4125-4132.
15. IARC - International Agency of Research on Cancer, 1991, 1999, 2002, 2004.
16. Rozporządzenie Ministra Zdrowia z dnia 7 grudnia 2017 r. w sprawie jakości wody przeznaczonej do spożycia przez ludzi Dz U, 2017, poz. 2294.
17. 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, 84-97.
18. Gonzales, P and Zaror, C 2000. Effect of process modification on AOX emission from kraft pulp bleaching using Chilean pine and eucalyptus. Journal of Cleaner Production, 8, 233-241.
19. Schultz, S and Hahn, H 1998. Generation of halogenated organic compounds in municipal wastewater. Water Science and technology, 1, 303-309.
20. Baycan, N, Thomanetz, E and Sengul, F 2007. Influence of chloride concentration on the formation of AOX in UV oxidative system. Journal of Hazardous Materials. 143, 171-176.
21. Kabsch-Korbutowicz, M, Urbanowska, A, Majewska-Nowak, K and Kawiecka-Skowron, J 2010. Removal of organic substances from aqueous

solutions with the use of ceramic membrane. Annual Set the Environment Protection. 12, 467-478.

22. Nowacka, A and Włodarczyk-Makuła, M 2015. Effectiveness of priority PAH removal in a water coagulation process, Water Science and Technology: Water Supply. 15, 4, 683–692.
23. Nowacka, A, Włodarczyk-Makuła, M and Macherzyński, B 2014. Comparison of effectiveness of coagulation with aluminum sulfate and pre-hydrolyzed aluminum coagulants. Desalination and Water Treatment. 52, 3843-3851.
24. Pernitsky, D and Edzwald, J 2006. Selection of alum and polyaluminum coagulants: Principles and applications. Journal of Water Supply: Research and Technology-AQUA. 55, 121–141.
25. Krupińska, I 2014. Effect of the type of aluminium coagulant on effectiveness at removing pollutants from groundwater in the process of coagulation. Selected Papers, Section: Water Engineering 9th International Conference "Environmental Engineering", Vilnus, Lithuania, May 22–23 VGTU Press. http://leidykla.vgtu.lt/conferences/ENVIRO_2014/Articles/2/082_Krupinska.pdf.
26. Gumińska, J and Kłos, M 2012. Analysis of post-coagulation properties of flocs in terms of coagulant choice. Environment Protection Engineering. 38, 103-113.
27. Sinha, S, Yoon, Y, Amy, G and Yoon, J 2004. Determining the effectiveness of conventional and alternative coagulants through effective characterization schemes. Chemosphere. 57(9), 1115-1122.
28. Zhanmeng, L, Simin, L, Haixia, Z, Fahui, N and Qunhui, W 2013. Preparation, characterisation and coagulation behavior of a novel inorganic coagulant – polyferric(III)-magnesium(II)-sulfate. Environment Protection Engineering. 39, 3, 57-71.
29. Ghernaout, D, Ghernaout, B and Kellil, A 2009. Natural organic matter removal and enhanced coagulation. Desalination and Water Treatment. 2, 203-222.
30. Włodarczyk-Makuła, M and Nowacka-Klusek, A 2019. Decrease in the chloride disinfection by-products (DBPs) formation potential in water as a result of coagulation process, Desalination and Water Treatment, 167, 96-104.
31. Matilainen, A and Sillanpaa, M 2010. Removal of natural organic matter from drinking water by advanced oxidation processes, Chemosphere, 80,4 351-365.
32. Murray, CA and Parsons, SA 2004. Comparison of AOPs for the removal of natural organic matter: performance and economic assessment. Water Science and Technology. 49, 4, 267-272.

33. Murray, CA and Parsons, SA 2004. Removal of NOM from drinking water: Fenton's and photo-Fenton's processes. Chemosphere, 54,7, 1017-1023.
34. Han, Q, Wanga, Y, Yan, H, Gaoa, B, Maa, D, Suna, S, Jianya Lingb and Yong-bao Chu 2016. Photocatalysis of THM precursors in reclaimed water: the application of TiO_2 in UV irradiation, Desalination and Water Treatment. 57, 9136-9147.

Editor received the manuscript: 03.11.2019