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Disinfection methods and by-products formation

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ABSTRACT

Water disinfection is a necessary process for the control of the pathogenic micro-organisms. However, the use of chemical disinfectants leads to the formation of disinfection by-products (DBPs). While the pathogenic micro-organisms are the primary cause of human health risk from water, DBPs also provide an unintended health hazard. Chlorination, chloramination, ozonation, and ultraviolet system are the most common methods used for drinking water and wastewater treatment. However, trihalomethanes (THMs), halogenic acetic acids, haloacetonitrils (HAN), halo-aldehydes and haloketons consist mainly of DBPs. Different types of DBPs are formed depending on a number of significant factors related to the selected method. The overall purpose of this paper was to analyze several disinfection method and compare the results of each one.

Keywords: Disinfection by-products; Chlorination; Ozonation; Drinking water; Wastewater

1. Introduction

At the beginning of the twentieth century, water and wastewater were treated by one principle, "the solution to pollution is dilution." The disinfection of drinking water and wastewater provides significant benefits which focus on the protection from contact with pathogenic organisms including those causing cholera, polio, typhoid, hepatitis,and a number of other bacterial, viral, and parasitic diseases. Disinfection is a process, where a significant percentage of pathogenic organisms is destroyed . Disinfection efficiency is usually measured, using "indicator organisms" [1]. The most common indicator micro-organism used in the evaluation of the quality of drinking water is total coliform (TC), unless there is a reason to focus on a different micro-organism [2]. However, the most common indicator micro-organism for wastewater evaluation is fecal coliform even though the use of *Escherichia coli* (*E. coli*) or total coliform was mentioned in the past [2]. Disinfectants, in addition to effectively killing harmful micro-organisms, are powerful oxidants that oxidize the organic matter and bromide naturally present in most water sources (rivers, lakes, and groundwater), creating several disinfection by-products (DBPs). Chlorine, ozone, chlorine dioxide, and chloramines are the most common disinfectants in

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use, and each produces its own suite of chemical DBPs [3]. DBPs result from the reactions between organic and inorganic matter in water with chemical agents during the water disinfection process.

2. Disinfection methods

Disinfection is usually the final stage in the water treatment process in order to limit the effects of organic material, suspended solids (SS), and other contaminants like pathogenic micro-organisms. The primary methods used for the disinfection of water in very small (25,500 people) and small (501–3,300 people) treatment systems are ozonation, ultraviolet irradiation (UV), and chlorination [4]. There are numerous alternative disinfectants that have been less widely used in small and very small water treatment systems, including chlorine dioxide, potassium permanganate, chloramines and peroxone (ozone/hydrogen peroxide [HP]). An effective disinfectant should be able to: (1) destroy all types of pathogens in whatever number present in the water, (2) destroy the pathogens within the time available for disinfection, (3) function properly regardless of any fluctuations in the composition or condition of the water, (4) function within the temperature range of the water, (5) not cause the water to become toxic or unpalatable, (6) be safe and easy to handle, and (7) determine its concentration in the water and provide residual protection against recontamination.

2.1. Chlorination

Chlorine has been successfully used for the control of waterborne infectious diseases for nearly a century, and chlorination is one of the most effective public health measures ever undertaken [4]. Chlorine is used to disinfect water in either gaseous form (Cl_2), or as hypochlorite salts. All forms of chlorine react with water to produce hypochlorous acid (HOCl), which rapidly dissociates to form the hypochlorite ion according to the following Eq. (1):

$$HOCl \leftrightarrow OCl^- + H^+ \quad (1)$$

In addition to HOCl and the hypochlorite ion (OCl^-), chlorine may also be found in the form of monochloramine (NH_2Cl) and dichloramine ($NHCl_2$). The dominant form of chlorine depends upon the combination of parameters such as temperature, pH and ammonia concentrations. As the pH increases the concentration of the hypochlorite ion relative to hypochlorous (HOCl) acid increases, while the presence of ammonia tends to increase the concentration of monochloramine. Knowledge of the dominant form of chlorine in a particular disinfection process is important. With the differing forms come varying oxidizing strengths and thus biocidal efficiencies. The chlorine disinfection process occurs primarily through oxidation of cell walls leading to cell lysis (bacterial) or inactivation of functional sites on the cell surface. Hypochlorous acid is the most potent of the four main oxidizing forms. In addition to differences in oxidizing strengths between forms of chlorine, the disinfection effectiveness varies across the range of micro-organisms. Protozoans, helminths, and viruses are the most resistant, followed by bacterial pathogens, with each species varying in resistance. Chlorine is very effective against enteric bacteria, such as *E. coli*, but less effective against other bacterial species [5].

2.2. Chloramination

Chloramines are formed during a reaction between chlorine (Cl_2) and ammonia (NH_3). This reaction is according to the following Eq. (2):

$$NH_3 + HOCl \leftrightarrow NH_2Cl + H_2O \quad (2)$$

Chloramines are amines, which contain at least one chlorine atom that is directly bonded to nitrogen atoms (N). Inorganic chloramines are formed when dissolved chlorine and ammonia react. During this reaction, three different inorganic chloramines are formed: monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (NCl_3). There are many similarities between chlorine and chloramine. The most important fact is that both of them provide effective residual disinfection with minimal risk to public health. The difference is that monochloramine is 200 times less effective as a disinfectant than chlorine [6]. On the other hand, chlorine forms many by-products, including trihalomethanes (THM) and haloacetic acids (HAA), whereas chloramine forms a significantly lower amount of THMs and HAAs, but also forms N-nitrosodimethylamine (NDMA) [7].

2.3. Chlorine dioxide

Chlorine dioxide (ClO_2) is used both as a disinfectant and an oxidant in water treatments. It has several distinct chemical advantages, which complement the traditional use of chlorine in water treatments [8]. Chlorine dioxide is highly effective in controlling waterborne pathogens while minimizing halogenated DBPs. Also, a broad-spectrum microbiocide is as effective as chlorine against viruses, bacteria, and

fungi, and more effective than chlorine for the inactivation of the encysted parasites *Giardia* and *Cryptosporidium*. Furthermore it is an effective control strategy for taste, odor, color, and iron and manganese removal. Chlorine dioxide presents several other advantages than other disinfectants, which can be summarized as follows: (1) the bactericidal efficiency is relatively unaffected by pH values between 4 and 10, (2) Chlorine dioxide is clearly superior to chlorine in the destruction of spores, bacteria, viruses, and other pathogenic micro-organisms on an equal residual base, (3) the required contact time for ClO_2 is lower, (4) chlorine dioxide has better solubility, (5) no corrosion associated with high chlorine concentrations, (6) chlorine dioxide does not react with NH_3 or NH_4^+, (7) it destroys THM precursors and increases coagulation, (8) ClO_2 destroys phenols and has no distinct smell, and (9) it is better at removing iron and magnesia compounds than chlorine, especially complex bounds.

2.4. Ozonation

Ozone has been used for water disinfection for about 80 years in France, Germany, and other European countries. It is now undergoing a critical evaluation as a possible alternative to chlorine when used alone or in conjunction with other disinfection systems [6]. Ozone is produced when oxygen (O_2) molecules are dissociated by an energy source into oxygen atoms and subsequently collide with an oxygen molecule to form an unstable gas, ozone (O_3). Disinfection by ozonation is achieved using the formation of free radicals as oxidizing agents. The method is more effective against viruses and bacteria than chlorination. The low solubility of ozone in water is the main factor that greatly reduces its disinfection capacity, and any ozone residual produced rapidly dissipates as a consequence of its reactive nature. The absence of a lasting residual may also be seen as a disadvantage as this may allow possible microbial re-growth and make it difficult to measure the efficiency of the disinfection process.

The mechanisms of disinfection using ozone include, direct oxidation of the cell wall with leakage of cellular constituents outside of the cell, reactions with radical by-products of ozone decomposition, damage to the constituents of the nucleic acids (purines and pyrimidines) and breakage of carbon–nitrogen bonds leading to depolymerization. The effectiveness of disinfection depends on the susceptibility of the target micro-organisms, the contact time, and the concentration of ozone [2,9]. The advantages of the method could be summarized as follows: (1) It is more effective than chlorine in destroying viruses and bacteria, (2) it requires a short contact time (approximately 10–30 min), (3) there are no harmful residuals that need to be removed after ozonation because ozone decomposes rapidly (4) ozone is generated onsite, and thus, there are fewer safety problems associated with shipping and handling, and (5) ozonation elevates the dissolved oxygen (DO) concentration of the effluent. The increase in DO can eliminate the need for re-creation and also raise the level of DO in the receiving stream. The disadvantages of the method could be: (1) low dosage may not effectively inactivate some viruses, spores, and cysts, (2) it is not economical for wastewater with high levels of SS, biochemical oxygen demand (BOD), chemical oxygen demand, or total organic carbon, (3) it is extremely irritating and possibly toxic, so off-gases from the contactor must be destroyed to prevent workers' exposure, and (4) the cost of treatment can be relatively high in capital and in power intensiveness. Fig. 1 presents the desired and undesired effects of ozonation processes. Comparing Ozonation's methods with other disinfectant methods, ozonation presented with several benefits, which could be summarized as follows: (1) it is more effective than chlorination in destroying viruses and bacteria, (2) it utilizes a short contact time (approximately 10–30 min), (3) there are no harmful residuals that need to be removed after ozonation because ozone decomposes rapidly, (4) ozonation elevates the DO concentration of the effluent. The increase in DO can eliminate the need for re-creation and also raise the level of DO in the receiving stream. At the same time, the methods presents some disadvantages which are: (1) low ozone dosage may not effectively inactivate some viruses, spores, and cysts, (2) ozone is very reactive and corrosive, thus requiring corrosion-resistant materials such as stainless steel, (3) it is not economical for wastewater with high levels of SS, BOD, chemical oxygen demand, or total organic carbon, (4) ozone is extremely irritating and possibly toxic, so off-gases from the contactor must be destroyed to prevent workers' exposure, and (5) ozonation is a more complex technology than chlorination or UV disinfection, requiring complicated equipment and efficient contacting systems.

2.5. UV disinfection

An UV disinfection system transfers electromagnetic energy from a mercury arc lamp to an organism's genetic material (DNA and RNA). When UV radiation penetrates the cell wall of the organism, it

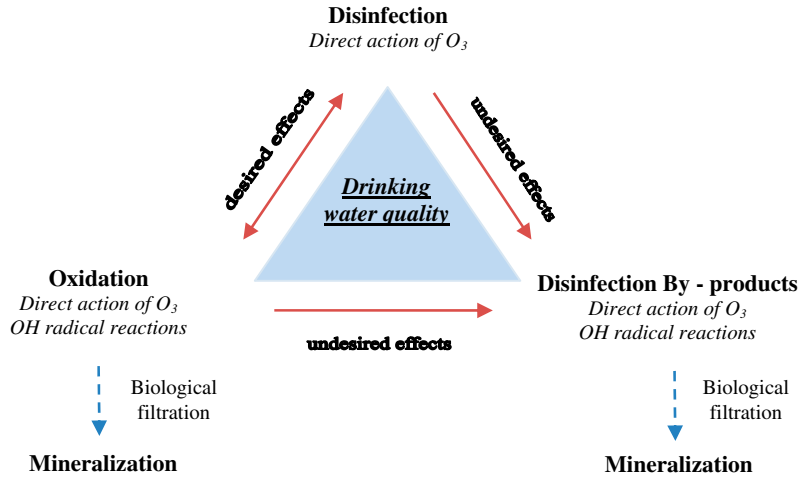

Fig. 1. Desired and undesired effects of ozonation processes [23].

destroys the cell's ability to reproduce. UV radiation, generated by an electrical discharge through mercury vapor, penetrates the genetic material of micro-organisms and retards their ability to reproduce. The effectiveness of a UV disinfection system depends on the characteristics of the wastewater, the intensity of UV radiation, the amount of time the micro-organisms are exposed to the radiation, and the reactor configuration. For any one treatment plant, disinfection success is directly related to the concentration of colloidal and particulate constituents in the wastewater [10]. The optimum wavelength to effectively inactivate micro-organisms is in the range of 250–270 nm. The intensity of the radiation emitted by the lamp dissipates as the distance from the lamp increases. Low-pressure lamps emit essentially monochromatic light at a wavelength of 253.7 nm. Standard lengths of the low-pressure lamps are 0.75 and 1.5 m with diameters of 1.5–2.0 cm. The ideal lamp wall temperature is between 95 and 122 EF [11]. According to Hanzon, 1999 [12], UV disinfection is effective at inactivating most viruses, spores, and cysts as well as it is a physical process rather than a chemical disinfectant, which eliminates the need to generate, handle, transport, or store toxic/hazardous or corrosive chemicals. Also, there is no residual effect that can be harmful to humans or aquatic life. Hence UV method has a shorter contact time when compared with other disinfectants (approximately 20–30 s with low-pressure lamps). On the other hand, UV disinfection is not as cost-effective as chlorination, but costs are competitive when chlorination dechlorination is used and fire codes are met as well as micro-organisms can sometimes repair and reverse the destructive effects of UV through a "repair mechanism," known as photoreactivation, or in the absence of light known as "dark repair." Turbidity and total suspended solids (TSS) in the wastewater can render UV disinfection ineffective. UV disinfection with low-pressure lamps is not effective for secondary effluent with TSS levels above 30 mg/L.

2.6. Peracetic acid

Peracetic acid or peroxyacetic acid (PAA) is the peroxide of acetic acid (AA). PAA is a strong oxidant and disinfectant. Its oxidation potential is larger than that of chlorine or chlorine dioxide. PAA is commercially available in the form of a quaternary equilibrium mixture containing AA, HP, PAA, and water as shown by the following Eq. (3):

$$CH_3CO_2H + H_2O_2 \leftrightarrow CH_3CO_3H + H_2O \quad (3)$$

PAA is a clear, colorless liquid with no foaming capability. It has a strong pungent acetic acid odor (acetic acid is the principal component of vinegar) and has an acidic pH of less than 2. Due to its effectiveness against bacteria and viruses as demonstrated in many industries, the use of PAA as a disinfectant for wastewater effluents has been investigated since 1980s. Major disadvantages associated with PAA disinfection are the increase of organic content in the effluent, the potential microbial regrowth due to remaining acetic acid (AA is also a product of decomposed PAA), and the lower efficiency against some viruses and parasites (e.g. Giardia lamblia cysts and Cryptosporidium parvum oocysts). Another drawback in the use of PAA is its high cost, which is partly due to limited production capacity worldwide [13].

3. Disinfection by-products

DBPs [14] are formed when disinfectants used in water treatment plants react with bromide and/or natural organic matter (NOM) present in the source water. Table 1 presents the basic categories of DBPs, while Table 2 contains the DBPs regulations from the World Health organization (WHO), [2,3,8,15].

Different disinfectants produce different types or amounts of DBPs (Table 3) [15]. The types of DBPs that are formed depend on a number of influential factors: (1) the type of disinfectant, (2) the disinfection dose, (3) the disinfection residue, (4) circumstances of disinfection: reaction time, temperature, and pH, (5) the constituents of water, and (6) concentrations and properties of naturally present organic matter (NOM) in the water. When the dose and residue of the disinfectant are higher, more disinfection by-products are formed. Although when the reaction time is shorter, higher concentrations of trihalomethanes (THM) and halogenic acetic acids (HAA) may be formed. Hence, when the reaction time is longer, some temporary forms of DBPs may become disinfection end products, such as tribromine acetic acid and bromoform. Haloacetonitrils (HAN) and haloketons (HK) are decomposed. While temperatures increase, reactions take place faster, causing a higher chlorine concentration to be required for a proper disinfection. This causes more halogenic disinfection by-products to be formed. An increase in temperatures also enhances the decomposition of tribromine acetic acids, HAN, and HK. When pH values are high, more hypochlorite ions are formed, causing the effeciency of chlorine disinfection to decrease. At higher pH values, more THM is formed, whereas more HAA is formed when pH values are lower. At high pH values, HAN and HK are decomposed by hydrolysis, because of an increase in hydrolysis reactions at higher pH values. The levels of trihalomethanes in drinking water are often higher in the distribution network than at drinking water production companies. When hydrolysis takes place, many DBPs become trihalomethanes [14].

Trihalomethanes (THMs–CHX_3) were among the first DBPs to be discovered in chlorinated water. These substances are formed during chlorine disinfection and disinfection by chlorinated disinfectants. Trihalomethanes can be divided into trichloromethane (chloroform, $CHCl_3$), bromine dichloromethane (BDCM, $CHBrCl_2$), chlorine dibromomethane ($CHBr_2Cl$), and tribromomethane ($CHBr_3$).When bromine is present, brominated propanon is formed, causing brominated trihalomethanes to form. Trihalomethanes are formed during hydrolysis reactions of various trihalogenic DBPs and transition products, such as trihaloacetonnitrils, trihaloacetyldehydes, and brominated trihalo acetic acids [16]. HAA are an important type of chlorinated DBPs. Acetic acids consist of three hydrogen atoms that are fixed to a COOH-group. H-atoms of HAA are partly replaced by halogen atoms. HAA are non-volatile compounds. HAA can also be formed during a reaction between propanon and chlorine. When pH values are low, trichloropropanon is oxidized further to form tetra-, penta-, and hexachloropropanon. When these compounds are hydrolyzed, mono-, di-, and trichloro acetic acids will form [16]. The reaction mechanisms are described by the following Eqs. (4) and (5).

$$CH_3COCCl_3 + HOCl \rightarrow CHCl_2COCCl_3 \quad (4)$$

$$CHCl_2COCHCl_3 + H_2O \rightarrow CHCl_2COOH + CHCl_3 \quad (5)$$

Haloacetonitrils (HAN), halo-aldehydes and haloketons: These DBPs are usually present in lower amounts than THM and HAA. These compounds are usually formed immediately during water disinfection, but are decomposed quickly during hydrolysis reactions or reactions with residual disinfectants [17]. The compounds can also be products of reactions of other DBPs, such as THM and HAA. When pH values are high, these compounds cannot be formed. The reaction mechanism of acetaldehyde and chlorine is given from the following Eq. (6):

$$CH_3CH + HOCl \rightarrow CCl_3CHO \quad (6)$$

NDMA is a potent carcinogen formed during chloramination of water and wastewater treatment plant effluents [18]. NDMA is a yellow, volatile, and oily liquid, which is characterized by low viscosity. It is highly soluble in water, alcohols, and other organic solvents as well as in fat. The compound is sensitive to light, especially in UV and it undergoes fast photolytic degradation. Monochloramine and organic compounds containing nitrogen such as dimethylamine or tertiary amines containing dimethyl groups are the compounds that take part in the formation of NDMA. Other compounds containing nitrogen such as amino acids and proteins do not form significant concentrations of NDMA.

The mechanism of NDMA formation was originally connected with the reaction of secondary amines with nitrite, in which NO^+ played a particular role. Tertiary amines do not react with nitrite. In the case of primary amines, the reaction led to the formation of ammonia, and NDMA was the only intermediate

Table 1
Disinfection by-products [2,3,8,14,15]

Trihalomethanes THMs		*Iodo-THMs and other THMs*	
Chloroform	$CHCl_3$	Dichloroiodomethane	$CHClI_2$
Bromodichloromethane	$CHCl_2Br$	Bromochloroiodomethane	CHBrClI
Chlorodibromomethane	$CHBr_2CI$	Dibromoiodomethane	$CHBr_2I$
Bromoform	$CHBr_3$	Chlorodiiodomethane	$CHClI_2$
		Bromodiiodomethane	$CHBrI_2$
Haloacetic acids HAAs		*Iodoform*	
Chloroacetic acid	$CH_2ClCOOH$	Dichloromethane	CH_2Cl_2
Bromoacetic acid	$CH_2BrCOOH$	Bromochloromethane	CH_2BrCl
Dichloroacetic acid	$CHCl_2COOH$	Dibromomethane	CH_2Br_2
Dibromoacetic acid	$CHBr_2COOH$		
Trichloroacetic acid	$CHC1_3COOH$		
Oxyhalides		*Haloamides*	
Bromate	BrO_3-	Chloroacetamide	C_2H_4ClNO
Chlorite	ClO_2-	Bromoacetamide	C_2H_4BrNO
		Iodoacetamide	C_2H_4INO
Halonitromethanes HNMs		Dichloroacetamide	$C_2H_3Cl_2NO$
Chloronitromethane	CH_2ClNO_2	Bromochloroacetamide	$C_2H_3BrClNO$
Bromonitromethane	CH_2BrNO_2	Dibromoacetamide	$C_2H_3Br_2NO$
Dichloronitromethane	$CHCl_2NO_2$	Bromoiodoacetamide	C_2H_3BrINO
Dibromonitromethane	$CHBr_2NO_2$	Trichloroacetamide	$C_2H_2Cl_3NO$
Bromochloronitromethane	$CHBrClNO_2$	Bromodichloracetamide	$C_2H_2BrCl_2NO$
Trichloronitromethane (chloropicrin)	CCl_3NO_2	Dibromochloroacetamide	$C_2H_2ClBr_2NO$
		Tribromoacetamide	C_2H_2BrNO
		Diiodoacetamide	C_2H3I_2NO
		Chloroiodoacetamide	C_2H_2ClINO
Iodo-acids		*Trichloroacetonitrile*	
Iodoacetic acid	$C_2H_3IO_2$	Bromodichloroacetonitrile	C_2BrCl_2N
Bromoiodoacetic acid	$C_2H_2BrIO_2$	Dibromochloroacetonitrile	C_2Br_2ClN
		Tribromoacetonitrile	C_2Br_3N
Other halo-acids		*Haloacetonitriles*	
Bromochloroacetic acid	$C_2H_2BrClO_2$	Chloroacetonitrile	C_2H_2ClN
Bromodichloroacetic acid	$C_2HBrCl_2O_2$	Bromoacetonitrile	C_2H_2BrN
Dibromochloroacetic acid	$C_2HBrClO_2$	Iodoacetonitrile	C_2H_2IN
Tribromoacetic acid	C_2HBrO_2	Dichloroacetonitrile	C_2HCl_2N
		Bromochloroacetonitrile	$C_2HBrClN$
		Dibromoacetonitrile	C_2HBr_2N
Nitrosamines		*Aldehydes*	
NDMA	$C_2H_6N_2O$	Formaldehyde	CH_2O
N-Nitrosopyrrolidine	$C_4H_8N_2O$	Acetaldehyde	C_2H_4O
N-Nitrosomorpholine	$C_4H_8N_2O$	Chloroacetaldehyde	C_2H_3ClO
N-Nitrosopiperidine	C_5H10N_2O	Dichloroacetaldehyde	$C_2H_2Cl_2O$
N-Nitrosodiphenylamine	$C1_2H_{10}N_2O$	Bromochloroacetaldehyde	$C_2HBrClO$
Other DBPs		Trichloroacetaldehyde (chloral hydrate)	C_2HCl_3O
Chlorate	ClO_3^-	Tribromoacetaldehyde	C_2HBr_3O

product of the reaction. Only the reaction with secondary amines resulted in the formation of the appropriate nitrosoamines [19].

4. Analytical methods

Analysis techniques play a key role in understanding reactions and processing in water treatment and

Table 2
WHO guidelines [3]

DBP	Guideline value mg/L
Total THMs	0.1
Chloroform	0.2
Bromodichloromethane	0.06
Chlorodibromomethane	0.1
Bromoform	0.1
Dichloroacetic acid	0.05
Trichloroacetic acid	0.2
Bromate	0.01
Chlrorite	0.7
Chloral hydrate (trichoroacetaldeyde)	0.01
Dichloroacetonitrile	0.02
Cyanogen chloride	0.07

can therefore contribute considerably to minimizing DBPs in drinking water. Toxicological assessment of DBPs also depends on compound identification and quantification. GC–MS is still the major analysis method for DBPs, so highly polar and high molecular weight fractions are not completely known. However LC–MS has already reached the status of a routinely used method in water analysis. LC–MS offers distinct advantages such as : (1) the investigation of direct analysis of highly polar hydrophilic DBPs and direct analysis of high molecular weight and non-volatile compounds, (2) LC–MS2 might be able to distinguish between structural isomers that cannot be distinguished using GC–MS, and (3) improvements in instrumentation and analytical techniques are allowing low lg/L and ng/L limits of detection for LC–MS, which offers promise for measuring DBPs that are present at trace levels [20,21].

5. Discussion

Water DBPs have been studied for the last 30 years. DBPs have become a concern for water because human epidemiological studies have indicated somewhat consistent association between increased risk of bladder cancer and long-term consumption of chlorinated drinking water. More than 600 DBPs have been previously identified [22], and in recent years the research focuses on the identification of emerging DBPs such as nitrosamines and iodinated DBPs. Various studies focus on the formation of DBPs and the NOM in drinking water during the chlorination treatment [4,23]. As referred by Goslan et al. [24], the DBPs produced by chlorination were trichalomethanes, haloacetonitriles, haloacetic acid, bromochloacetic acid, bromodichloroacetic acid, tribromomethane, dichlorobromomethane, trichloromethane, dibromochloromethane, chloropicrin, dibromacetic acid, dibromoacetonitrile, dibromochloroacetic acid, dichloroacetic acid, and dichloroacetonitrile. As previously reported, NOM and various DBPs are produced during drinking water ozonation. The

Table 3
Important groups of DBPs produced using different types of disinfectants [14]

Class of DBPs	Common example	Chlorine	Ozone	ClO_2	Chloramines
Trihalomethanes (THM)	Chloroform	×	×		×
Other haloalkanes		×			
Haloalkenes		×			
Haloacetic acids (HAA)	Chloroacetic	×			×
Haloaromatic acids		×			
Haloketones		×	×	×	
Haloacetonitrile (HAN)	Chloroacetonitrile	×	×		
Other halonitrile	Cyanogen chloride	×			×
Haloaldehyde	Chloral hydrate	×			×
Haloalcohals		×			×
Phenols	2-Chlorophenol	×	×		
Halonitromethane	Chloropicrin	×			
Ketones	Acetone	×	×	×	
Carboxylic acids	Acetic acid	×	×	×	
Aromatic acids	Benzoic acid	×	×	×	
Aldo and Ketoacids			×	×	
Hydroxy acids		×	×		
Others		×	×	×	×

produced DBPs were monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, bromochloroacetic acid, trichloroacetic acid, dibromoacetic acid, dichlorobromethane, dibrochloromethane, and tribromethane and the analytical methods used were GC-ECD and GC-MS [25,26]. Also, various studies showed that the application of other disinfection methods such as UV method might generate various DBPs of NOM during drinking water treatment [27]. As reported by Dotson et al. [10], the produced DBPs were the monohalogenated, dihalogenated and trihalogenated acetic acids and also the trichalomethanes, haloacetonitriles.

Apart from drinking water, researchers showed great interest in the treatment of wastewater with chlorination and ozonation and their DBPs. Wert et al. [28] and Silva et al. [29] studied DBPs produced during the ozonation of wastewater. The analytical method GC-ECD was used for the determination of these DBPs. Various DBPs were generated such as formaldehyde, acetaldehyde, glyoxal, methylglyoxal cetaldehyde, butanal, formaldehyde, pentanal, propanal, acetate, fomate, ketomalonate, oxalate, propionate, and pyruvate. Additionally, various studies were done regarding the identification of various DBPs produced during the treatment with chlorination of wastewater. The analytical methods were used for the identification all these DBPs were GC-ECD and GC-MS. The DBPs that have been determined were the bromochloroacetic acid, bromodichloroacetic acid, chloroacetic acid, chlorodibromoacetic acid, dibromoacetic acid, dichloroacetic acid, trichloroacetic acid, bromodichloromethane, chloroform, dibromochloromethane, bromoacetic acid, tribromoacetic acid, trichloroacetic acid, and dichloroacetic acid [30,31].

Very interesting results were also presented in the study carried out from Kitis et al. [13], which are reported on the formation of DBPs during the treatment of wastewater using peracetic acid. The most important DBPs which were produced include aldehydes, halogenated phenols, brominated phenols and aldehydes, and monosubstituted chlorophenols. Other research [32] has focused on specific NOMs such as dimethylamine (DMA), humic and fulvic acids, vanillic acid, p-hydroxybenzoic acid, and phenols. As previously reported, the main disinfection method of DMA was the use of monochloramine and one of the main DBPs which had been produced was NDMA.

From the existing literature review [6,14,19,24,25,33–44] the most common disinfection method used during the treatment of drinking water is chlorination which is followed by ozonation (Fig. 1). Figs. 2 and 3 present the most used disinfection method for the treatment of urban wastewater. Form the same review, the most common analytical method used (for the identification of DBPs during the drinking water and wastewater disinfection) is GC/ECD, followed by GC/MS (Figs. 4 and 5). Chlorination and ozonation were the two most common disinfection methods used.

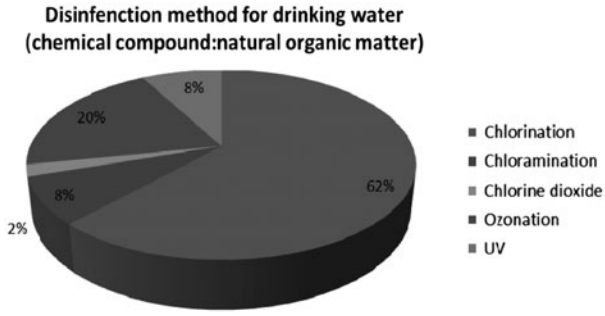

Fig. 2. Disinfection method for drinking water (chemical compound: natural organic matter).

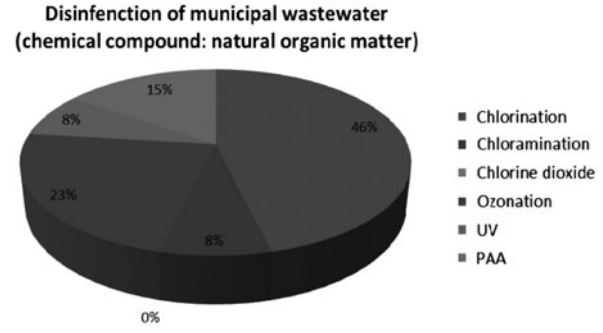

Fig. 3. Disinfection method for municipal water (chemical compound: natural organic matter).

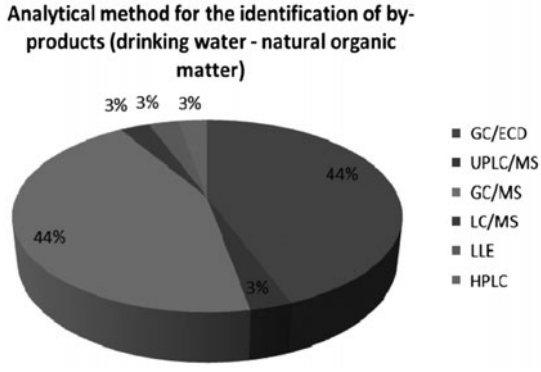

Fig. 4. Analytical method for the identification of by-products (drinking water, natural organic matter).

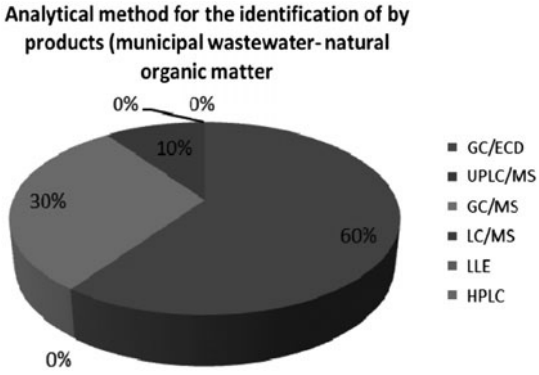

Fig. 5. Analytical method for the identification of by-products (wastewater, natural organic matter).

There are more than 600 DBPs [45,46], and in the near future, the research will be focused on the identification of emerging DBPs such as nitrosamines and iodinated DBPs.

Several studies (qualitative and quantitative Tables 1 and 4, respectively) focus on the formation of DBPs (Table 5 indicate the conditions of the DBPs formation regarding Table 4) and the NOM in drinking water during the chlorination treatment [24,33–35,39,47,48]. As Goslan et al. [24] state, the DBPs produced by the chlorination were trichalomethanes, haloacetonitriles, haloacetic acids, bromochloacetic acid, bromodichloroacetic acid, tribromomethane, dichlorobromomethane, trichloromethane, dibromochloromethane, chloropicrin, dibromacetic acid, dibromoacetonitrile, dibromochloroacetic acid, dichloroacetic acid, and dichloroacetonitrile [44,49–54].

NOM and numerous DBPs are produced during drinking water ozonation. The created DBPs were monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, bromochloroacetic acid, trichloroacetic acid, dibromoacetic acid, dichlorobromethane, dibrochloromethane, and tribromethane and the analytical methods used were GC-ECD and GC-MS [6,25,26,52].

Table 4
Concentrations of DBPs in wastewater and drinking water

DBPs	[49]	[50]	[51]	[52]	[53] Drinking water	[53] Wastewater	[54]	[44]
THMs (μg/L)	21–189		2.6 to 66	1.2–10.2	92.50–118.47	232.60–229.28		29–149
HAAs (μg/L)	18–149		5.0–69	2.3–69.2	89.46–108.08	229.20–273.03		
HKs (μg/L)			0.37–3.9					
THANs (μg/L)			0.023–5.5		3.90–4.43	15.30–18.39		
Chloroform (μg/L)		3.86–73			53.00 −81.01	146–153.27	8.0–29.3	7.3–88
Bromodichloromethane (μg/L)		2.88–24.20						
Dibromochloromethane (μg/L)		1.28–6.94						
Chloroacetic acid (μg/L)		3.95–37.98						
Trichloroacetic acid (μg/L)		8.53–94.39	1.0–40		20−41.85	63–79.71	4.3–18.1	
Dichloroacetic acid (μg/L)			2.5–22		29–39.62	84.20–109.30		
Dihalogenated acetic acid (μg/L)					46.35−50.84	118.7–142.10		
Trihalogenated acetic acid (μg/L)					41.44–55.52	103.80−117.63		
NDMA (μg/L)					24–33.31	574–692.83		
Dichloroacetonitrile (μg/L)					2.20–2.34	7.60–9.57		
Monochloroacetic acid ((μg/L)							4.6–44.6	
Chlorodibromomethane (μg/L)							1.7–14.2	
Bromoform (μg/L).							0.2–1.0	2.3–13
Dichloropropanone (1,1-DCP) (μg/L)							0.4–1.5	
1,1-trichloropropanone (1,1-TCP), (μg/L)							0.2–1.8	
Monobromoacetic acid (μg/L)							0.1–0.7	1.1–2.4
Dibromoacetic acid (μg/L)							6.0–24.5	1.3–2.4
Bromochloroacetic acid (μg/L)							1.8–6.6	
Dichlorobromoacetic acid (μg/L)							0.6–1.7	
Dibromochloroacetic acid (μg/L)							1.3–14.8	
Dibromoacetonitrile (μg/L)								2–3.2
Dichlorobromoform (μg/L)								6.9–36
Dibromochloroform (μg/L)								9.7–21

Table 5
Conditions of the DBPs formation

Chemical compound	Type of water	Disinfection method	Analytical method	Refs.
Natural organic matter (NOM)	Drinking water	Chlorination	Gas chromatograph with an electron capture detector (GC/MS)	[49]
1-methyl-3-nitro-1-nitrosoguanidine	Drinking water	Non-chlorine-based secondary disinfectant comprised of silver and hydrogen peroxide (Ag^+/H_2O_2)	Liquid-liquid extraction-diazomethane methylation gas chromatographic	[50]
Natural organic matter (NOM)	Drinking water	Chlorination (Cl_2:NOM=3:1 on weight basis) –monochloramination (Cl_2:N=3:1)	Gas chromatography electron capture detection (GC/ECD)	[51]
Natural organic matter (NOM)	Drinking water	Ozonation (ozone dose: 2.2–2.5mgO_3/L)		[52]
Natural organic matter (NOM)	Municipal wastewater Drinking water	-Chlorination –Chloramination (Cl_2/N=4:1)		[53]
Humic and fulvic acids	Drinking water	Chlorination	Gas chromatography-mass spectrometry (GC/MS)	[54]
Natural organic matter (NOM)	Drinking water	UV/H_2O_2 (800–1000 mJ/cm^2)	High performance size exclusion chromatography	[44]

The application of other disinfection methods such as UV method might generate various DBPs of NOM during drinking water treatment [10,27]. As reported by Dotson et al. [10], the produced DBPs were the monohalogenated, dihalogenated, and trihalogenated acetic acids and also the trichalomethanes and haloacetonitriles.

Apart from drinking water, researchers showed great interest in the treatment of wastewater with chlorination and ozonation and their DBPs. Silva et al. [29] and Wert et al. [28] studied the formation of DBPs during the ozonation of wastewater. The analytical method GC-ECD was used for the determination of these DBPs. Various DBPs were generated such as formaldehyde, acetaldehyde, glyoxal, methylglyoxal cetaldehyde, butanal, formaldehyde, pentanal, propanal, acetate, fomate, ketomalonate, oxalate, propionate, and pyruvate. Very interesting results were presented also in the studies of Kitis et al. [13] and Dell'Erba et al. [55], which are reported on the formation of DBPs during the treatment of wastewater using peracetic acid. The most important DBPs which were produced were aldehydes, halogenated phenols, brominated phenols and aldehydes, and monosubstituted chlorophenols.

Water disinfection has a primary goal to protect human health from microbial disease. However, the new goal of decreasing human exposure to DBPs and reducing health risk from these compounds has certainly advanced through the years. New concerns arise which include adverse reproductive and developmental effects recently observed in human populations, the types of cancer observed in laboratory animals (for regulated DBPs) do not correlate with the cancers observed in human populations (indicating that other DBPs may be important), and studies on human-exposure that show other routes besides ingestion (inhalation and dermal adsorption) are also significant sources of DBP exposures. Epidemiological studies have looked at the associations between exposure to DBPs in drinking water with cancers, adverse birth outcomes and birth defects. Meta-analyses and pooled analyses of these studies have demonstrated consistent associations for bladder cancer and for babies being born small for gestational age, but not for congenital anomalies. Early-term miscarriages have also been reported in some studies. The exact putative agent remains unknown, however, in the epidemiological studies since the number of DBPs in a water sample ishigh and exposure surrogates such as monitoring data of a specific by-product (often total trihalomethanes) are used in lieu of more detailed exposure assessment. The WHO has stated that "the risk of death from pathogens is at least 100–1,000 times greater than the risk of cancer from DBPs" {and} the "risk of illness from pathogens is at least 10,000–1 million times greater than the risk of cancer from DBPs" [22].

As reported by Monarca et al. [56], the difficulties encountered in performing chemical analyses, long-term carcinogenicity tests and epidemiological studies have encouraged the analysis of drinking water using

short-term mutagenicity tests, which are rapid, relatively cheap, and can predict carcinogenic activity, and evaluate the combined action of DBPs present in drinking water as complex mixtures. When using *in vitro* tests, mainly the Salmonella/microsome test, high mutagenic activity was found in chlorinated surface drinking water. Most of this mutagenicity is probably due to the reaction of chlorine with natural water constituents, such as humic acid and fulvic acid, and has been attributed mostly to the presence of chlorinated furanones, such as 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX). Genotoxicity has also been measured directly in treatedwater using *in vivo* tests with aquatic animals (fish, newts or molluscs) or plants (Vicia faba, Allium cepa and Tradescantia spp).

6. Conclusion

Water disinfection is a necessary process that will continue to exist over time. Even though disinfection target is to reduce the microbial risk, it however exposes consumers to the dangerous action of DBPs. These by-products have been studied for the last 30 years but the problem arising from them has not yet been solved. Research which focus on toxicity and estrogenicity of DBPs will continue to take place in laboratories, but the question is whether we should focus on the products or on the disinfection method used for the water treatment and how it is possible to find out the condition that leads to the production of fewer and non hazardous products.

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