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THM FORMATION AND REMOVAL WITH DISINFECTION IN DRINKING WATER

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ABSTRACT

Chlorine, which is widely used in the disinfection process of waters, forms trihalomethanes from disinfection by-products by entering into a reaction with natural organic substances in water resources. Control of trihalomethane (THM) formations is possible by the removal of substances that lead to these formation. In recent years Advance Oxidation Procedures are the preferred methods of treatment for removing humic substances from the main THM precursors.The purpose of this study is; evaluation of the researches about the formation of THMs formed as a result of disinfection process in drinking water, health effects, differences between the practices applied in Turkey and the world and control methods and their advantages and disadvantages. A limited number of scientific studies on the subject in our country, have been widely preferred due to the low cost of it is still widely preferred and the negative effects on the health of the formed byproducts constitute the most important reasons for the study.

Key words
Disinfection by Product, THM Precursors, Ozone, Hydrogen peroxide, , Advanced Oxidation Process, Humic Substances.

INTRODUCTION

Disinfection of water developed for health human health is one of the most important developments. In the process of disinfection, chlorine and its compouns are widely used for the purpose of removing pathogenic micro-organisms from water. These disinfectants are preferred not only because they are effective in the removal of many microorganisms but also because they are economical and permanent in distribution networks. By contrast; reaction of chlorine with natural organic matters in water leads to formatin of disinfection by products (DBP). These formations are occurred by substitution of natural organic and chemical structures and reactive moieties with chlorine, bromine or iodine, which is called halogen. Basic chlorinated disinfection by-products are defined as Trihalomethanes, Haloacetic acids, Haloacetonitriles, other disinfection by-products are Haloaldehyde, Haloketone, Halonitromethane Phenols (1). The trihalomethanes (THMs) contained in these compounds are mainly; Chlorinated, bromodichloromethane, dibromochloro methane and bromoform, which are toxic and cancerogenic (2-4). In this study; The researches related to formation of THMs during disinfection process in drinking water, the health effects, applied the standards in Turkey and world and the differences in the applications of control methods and their advantages and disadvantages is evaluated.

MATERIALS AND METHODS

In the preparation of this study, the Ph.D. thesis study titled "Removal of THM Precursors in Drinking Water by Ozone / Hydrogen Peroxide Process" prepared at Hacettepe University Department of Environmental Engineering (5). Also; a project with number 05 01 602 003 studied on the same topic at Unit of Scientific Research at Hacettepe University has contributed to the study (6).

Factors Affecting the Formation of THM in Drinking Water

Natural organic substances are the precursors of THM Formation and the amount of THM formation in drinking water depends on the water quality parameters as well as on the operating conditions of the disinfection process. These are; factors such as the type and concentration of natural organic matter, temperature, alkalinity and pH (7,8). In addition to affecting the rate of THM formation, these factors also influence the concentration of each THM demonstrated in various studies (9-12). Humic substances. constitute a large part of natural substances in water.

The Negative Effects of THM on Health

The carcinogenic and toxic effects of DBP, which occurs as a result of disinfection in drinking water, have been reported in several toxicological and epidemiological studies (3,4). Experiment performed on laboratory animals showed that Chloroform, bromochloromethane, and bromoform AS THMs located in DBP, have toxic and cancerogenic effects (2). In addition, based on the study of Walter et al. (13), it is stated that high THM concentrations especially of bromodichloromethane may cause early stages of pregnancy in drinking water. In addition, epidemiological studies associated with cancer have showed that there may be a link between human exposed to chlorinated surface waters and cancer formations in general (14). Though it is argued that there is a number of uncertainties between cancer and by-products in chlorinated water from obtained data, based on available epidemiological and toxicological datas, THMs in water has been recognized as potentially harmful to human health.

The USEPA has introduced the regulation of drinking water that adversely affects the human health of DBP, especially cancer and diseases caused by them. Table 1. indicates that organized by USEPA in 1999, DBP's harmful effects and proved by epidemiological / laboratory studies (15).

THM Standards

The World Health Organization, the US EPA and the EU have published drinking water guidelines for some important DBPs. In our country, an arrangement made in TSE 266, (2005) has only introduced a restriction for Total THMs. All the standards for THMs are given in Table 2.

Table 1. Harmful effect of DBP on health (16)

DBP	Compound	Ratio	Harm Effect
Trihalometanhans	Chloroform	B2	Cancer, liver and kidney damage
	Dibromochloromethane	C	Nervous system, liver and kidney damage
	Bromodichloromethane	B2	Cancer, Nervous system., liver and kidney damage
	Bromoform	B2	Cancer, Nervous system, liver and kidney damage
Haloacetonitriles	Trikloroacetonitrile	C	Cancer, Mutagenic and clastogenic effects
Halogenated Aldehyde And ketone	Formaldehyde	B1	Cancer, Mutagenic and clastogenic effects
Halophenol	2-Chlorophenol	D	Cancer,, Tumor pioneer
Haloacetic acid	Dichloroaceticacid	B2	Cancer, Developmental disorder
	Trichloroaceticacid	C	Liver, kidney, spleen, developmental disorder
Inorganic Compound	Bromate	B2	Cancer
	Chloride	D	Developmental Disorder

B1: The possibility of cancer is very high (epidemiological) B2: The possibility of cancer is high (Lab) C: There is a possibility of cancer D: Uncategorized

Table 2. THM Standarts (15, 1, 17)

THM / Standards Unit (µg/l)	WHO (1993)	USEPA(2001)	EU (2003)	Turkey(2005)
Total THM	-	80	150	150
Trichloromethane	200	-	-	-
Bromodichloromethane	60	60	-	-
Dibromochloromethane	100	-	-	-
Tribromomethane	100	-	-	-
DYÜ / Standards Unit (□g/1)	**Canada (2001)**	**Austria (2000)**	**England and Ireland (1999)**	
Total THM	100	250	100	

THM Control Methods

The control of THM formations in the water is possible by the removal of precursors these formations. Scientific studies on the removal of THM precursors from water generally include coagulation, filtration, adsorption and chemical oxidation methods (18, 19, 20, 21, 22, 23, 24, 25). In general, coagulation and subsequent sedimentation and filtration processes are predicted to cause a 50-60% reduction in THM (18, 26). In the oxidation process, one of the methods used to remove THM precursors, a number of oxidants have been investigated for use in precursor removal. Leaders of oxidants used in applications and researches; can be given as Ozone, hydrogen peroxide, potassium permanganate, chlorine dioxide and advanced oxidation systems. Studies conducted so far have shown that; the chemical oxidation method is one of the purification methods with a positive effect in removing the humic precursors from the water. In particular, chemical oxidants used in the presence of homogeneous and heterogeneous catalysts have been found to be more effective than individual oxidants in the degredation of humic substances (7). The hydroxyl radicals $OH^{\cdot}$, which are believed to be the result of reactions to the productivity of these systems, are described as Advanced Oxidation Techniques.

In these processes generally used to produce the hydroxyl radical, an oxidizing agent such as O3 and / or H2O2, is a light source (28,29) such as ultraviolet rays, and a catalyst such as dissolved metals or metal oxides (30-35) are used together.

In advanced oxidation processes, reactions generally begin with degradation presence of catalysts, and subsequent chain reactions produce hydroxyl radicals.

Some of the basic advanced oxidation processes due to free radical reactions are given in Table 3 (36).

Table 3. Basic Advanced Oxidation Processes

ADVANCED OXIDATION PROCESSES	
Homogeneous systems where light is not used	O_3/H_2O_2, O_3/OH^-, H_2O_2/Fe^{+2} (Fenton reagent)
Homogeneous systems where light is used	O_3/UV, H_2O_2/UV, O_3/H_2O_2/UV, Photo-Fenton, Electron beams, Ultrason, Vakuum-UV
Heterogeneous systems where light is not used	H_2O_2/FeOOH, Electro-Fenton
Heterogeneous systems where light is used	TiO_2/O_2/UV

Some of the Advanced Oxidation Processes given in Table 3 are used in drinking water and wastewater treatment, with a large majority still in laboratory research. Systems employing them together with various combinations of ozone for water and wastewater treatment and chemical oxidation to increase the power developed to overcome both selectivity of O_3 oxidation and applied. (37, 38, 35).

Combined oxidation processes such as O_3 / H_2O_2 and O_3 / UV radiation are methods used to produce the hydroxyl radical. The intensity of the UV radiation, the H_2O_2 / O_3 ratio, the pH and the presence of radical consuming are the factors affecting these processes.

The O_3 / H_2O_2 system produces ($OH^{\cdot}$) radicals with a complex chain mechanism. This mechanism which is formed by deprotonation of hydrogen peroxide provides a control reaction between hydroperoxide anions and O_3. Therefore, in O_3/H_2O_2 Advanced Oxidation Process, the production of (OH•) radical is pH dependent. Except that the source H_2O_2, O_3/UV system has the same mechanism. In O_3/UV process, H_2O_2 is produced by reaction between the O_3 and UV instead of externally added. O_3/UV system is also dependent on pH.

H_2O_2 /UV system related Ozone Advanced Oxidation Process at a much lower rate of (OH•) radical is generated because H_2O_2 has a much lower molar coefficient of consumption than

Ozone. In other words, at the same concentration, higher concentrations of H_2O_2 is required to generate the (OH·) radical (35).

Catalytic oxidation processes have been shown to be effective in removing various natural and synthetic organic materials from surface and groundwater. The most important advantage offered by these technologies is that many organic substances can be oxidized to end products such as simple alcohols and acids and / or carbon dioxide and water. However, alternative technologies such as activated carbon and resin adsorption, reverse osmosis are another phase transfer process and require additional purification. On the other hand, biodegradation processes can be ineffective in the disintegration of contaminants due to microorganism toxicity and fluctuations in pollutant concentrations and pollutant concentrations from the tough nature of pollutants. There is a disadvantage that the use of advanced oxidation processes in water treatment is limited, which means that free radicals produced can be consumed by species such as carbonate, bicarbonate ions and natural organic substances (DOC). This disadvantage can be reduced to an insignificant degree by the use of appropriate oxidant doses (39-41).

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