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A REVIEW PAPER ON DISINFECTION BY-PRODUCTS FORMATION DURING DRINKING WATER TREATMENT

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Abstract

Water is the basic need of human life. Most of water borne diseases is due to the presence of pathogens in drinking water. In order to combat such pathogens, efforts need to make in two aspects. First one is effective disinfection and second is sufficient disinfection. While the disinfection of drinking water effectively prevents the water-borne diseases, an unintended consequence of disinfection is the formation of disinfectant by-products (DBPs). When disinfectant like chlorine reacts with the naturally organic compound present in water, it forms disinfectant by-products. The genotoxicity and cytotoxicity of disinfectants by-products are highly influenced by the species of the halogen substituted in the disinfection by-products compounds in the order of iodo > bromo > chloro. Gas chromatography (GC) and liquid chromatography (LC) technique is the most commonly available method to detect the disinfection by products in water. Other methods such as ultra-high resolution mass spectroscopy (MS), TOX analysis, ion chromatography, and fluorescence excitation spectroscopy are used for the detection. Common methods that are used for the treatments of DBPs are coagulation, biological filtration, adsorption and membrane filtration. Many countries around the world are regulating the DBPs to protect public health. In order to achieve global DBP regulation over 165 countries have specified the parameter values for DBPs. DBP standard enforcement is an expensive and time consuming process for any nation. 107 to 167 countries have setup a guideline value for the free chlorine, among which 36 have set the value at WHO guideline. 71 countries have marked it less than WHO guidelines. If disinfection is failing what are the likely options to embrace if potable and life sustainable water for all is to become a reality as required in the sustainable development goals.

Keywords

Disinfection by-products (DBPs), GC (gas chromatography), LC (liquid chromatography), WHO (World health organization)



1. Introduction

Water is the basic need of human life. The most affordable, safe and reliable access to water is one of the essential goal of humans but it has remained a worldwide challenge in 21st century. Due to the unavailability of safe and clean water, every year about 1.8 million people die due to waterborne and water related diseases like diarrhea. Out of 1.8 million deaths, 90% are under the age of 5-years. Most of these water borne diseases is due to the presence of pathogens in drinking water.

In order to combat such pathogens, present in the drinking water, efforts need to focus on two aspects, effective disinfection and sufficient disinfection. Effective disinfection is usually required for the inactivation of pathogens (like pathogenic micro-organisms) during the drinking water treatment. While sufficient disinfectant requires, for the prevention of regrowth of microbes in water, to be maintained within a water distribution system (Sharma, *et al.*, 2017).

While the disinfection of drinking water effectively prevents the water-borne diseases, an un-intended consequence of disinfection is the formation of disinfectant by-products (DBPs). Many disinfectants like ozone, chlorine, chloramine and chlorine dioxide might react with the different water constitutes like anthropogenic contaminants, iodide (I-), Bromide (Br-) and natural organic matter (NOM) etc. This is the potential reaction form of

undesirable DBPs which are geno-toxic, carcinogenic and cytotoxic (Ding, *et al.*, 2018).

Since Tri-halo-methanes (THMs) were the first disinfectant by-product identified in 1972 during the chlorination of drinking water, significant efforts have been made in order to investigate the formation mechanism, toxicity, mitigation technologies and occurrence of disinfectant by-products. Haloacetic acids (HAA), haloacetaldehyde (hal) and Tri-halomethans are the three classes of disinfection by-products classes that typically range from several to hundreds of micro-gram per liter in the water. While the other DBPs like halo-nitromethanes (HNM), halo-acetamides (HAM) and halo-acetonitriles (HAN) are formed usually at a lower range from several nano grams per litre to few micro grams per litre. Besides the above mentioned halogenated DBPs the N-Nitrosamines (NAs) represent the non-halogenated disinfectant by product. The well-known example of n-nitrosamines is N-nitrosodi-methylamine (NDMA) with a concentration ranges within several to only few nano gram per litre in the finished water (Bei, *et al.*, 2016).

In general, the concentrations of carbonaceous disinfectant by-products (C-DBPs) are higher than the nitrogenous disinfectant by-product (N-DBPs). However, toxicology analysis of disinfectant by-products shows that the N-DBPs are more toxic than the C-DBPs (Krasner *et al.*, 2013). More-over most of the halogenated aromatic disinfectant by-products with high toxicity than the halogenated halo-aliphatic

disinfectant by-products were quantified and identified in the various samples of drinking water. It mostly ranges from the several nano-grams per litre to few micro-grams per litre. Therefore, the toxic effects of the halogenated aromatic disinfectant by-products and N-DBPs cannot be ignored because toxicity relies upon the toxic potential and the concentration (Jeong *et al.*, 2015).

2. Identification & Treatment

Gas chromatographic technique is the most commonly available method to detect the disinfection by products in water. Various detectors such as ECD and MS are used in GC analysis. ECD is cheaper than MS and has good chemical selectivity. In order to achieve higher sensitivity MS is preferred. Modified or coupled MS detectors are available which give higher selectivity in detecting DBPs. These modified detectors area included as selected ion monitoring quadrupole MS, multiple reaction monitoring (MRM) MS, time of flight MS, high resolution MS, high resolution time of flight MS etc. Various DBPs such as THMs, HAA, chloral hydrate etc. can be analysed by GC with ECD (Chowdhury *et al.*, 2009).

Liquid chromatic technique is another method which is used in case of highly polar DBPs having a high molecular weight and compounds having low thermal stability. LC uses detectors mostly used in MS and UV spectrometers. Sample with DBPs is firstly treated with SPE and then fed into LC coupled with hybrid quadrupole TOF-MS (Truchado *et al.*, 2018).

2.1 Methods For The Removal Of DBP From Drinking Water

Common methods that are used for the removal of BDPs are coagulation, Biological filtration, membrane filtration and adsorption.

2.1.1 Coagulation

During the disinfection of drinking water, disinfectant like chlorine react with naturally present organic matter to form DBPs like haloacetic acid and tri-halomethanes which are very harmful to humans. Coagulation is a process that is used to treat the precursors of DBPs for the remove the total organic carbon (TOC) from water and to control disinfection by-products generation in water. Benefits of treating these TOC through coagulation process includes the production of less sludge, excellent coagulation efficiency at low coagulant dose, low cost and the no reduction in the alkalinity. The removal of TOC by coagulation method depends on the chemical nature of naturally organic matter, TOC concentration, coagulation PH, coagulation dose and coagulation type (Uyak & Toroz, 2004).

2.1.2 Biological Filtration

Biological active filtration is basically designed not only to remove particles from the water but also to remove the organic matter by microbial process, growing in the form of biofilm attached to a support media. A review on the impact of biological active filtration on the control of precursors of DBP and disinfectant by-products demonstrated that the biological active filtration generally remove the precursors of disinfectant

by-products but some studies also indicated that under the certain condition biological active filtration process also cause the formation of halogenated N-disinfectant by products and N-nitrosamines (Chu *et al.*, 2015).

2.1.3 Adsorption

Adsorption is the process of drinking water treatment in which adsorbents (like molecules, ions and atoms) are accumulated on the surface of adsorbent (Solid). For the environmental purification purpose AC is one of the most popular adsorbent that particularly capture the traceable micro-pollutants in the treatment of drinking water. AC (serving as the adsorbent) in terms of their appearance and shape can be categorized into granular AC (GAC), cylindrical AC (CAC), AC fibre and powder AC (PAC).

The adsorption capacity of AC is ascribed on surface functional group, well-developed pore structure and its large surface area. Adsorption served as an effective method for the removal or reduction of disinfectant by products precursors such as natural organic matter. Study found absorbance as an effective method for the removal of dissolved organic carbon, dissolved inorganic and organic nitrogen, total dissolved nitrogen and bromide (Anna Kwarciak-Kozłowska, 2020)

2.1.4 Membrane Filtration

It is the process that separate two phases via membrane. In the drinking water treatment technology membrane filtration remove both the particulate and dissolved pollutant like natural organic matter from the water. Most common

membrane filtration process in the drinking water treatment is ultrafiltration, reverse osmosis (OS), Nano filtration (NF) and microfiltration (Anna Kwarciak-Kozłowska, 2020).

Membrane filtration process is very effective in minimizing the formation of carcinogenic disinfectant by-product by removing the significant amount of organic matter. Pore size is one of the most important properties of membrane filtration. Removal of natural organic matter increases by decreasing the pore size. When the removing of disinfectant by-products from the drinking water the process of ultrafiltration and microfiltration is often more supported by the coagulation, adsorption and AOX process (Anna Kwarciak-Kozłowska, 2020).

3. Discussion

Disinfection of water is essential part of water treatment. It is in public interest to disinfect the water/wastewater for reuse in urban & semi-urban area. Chlorination is one the most widely used disinfectant because of its inexpensiveness and easy operation. However, it releases many by-products which are harmful to human health beings and animals. There is enough experimental evidence from the studies conducted on animals, which associates the exposure of disinfection by products with cancer and non-cancer health issues. Effects of DBPs are linked with the bladder cancer with THMs and reproductive malfunctioning such as low sperm quality, menstrual cycle, fetal loss, preterm delivery and congenital malformation.

Exposure to DBPs may occur through ingestion, inhalation or dermal absorption from drinking water or swimming pools (Allen *et al.*, 2017).

Swimming pools are one of the major sources of DBPs. DBPs are formed when disinfectants such as chlorine, chloramines, ozone and chlorine dioxide may react with the organic and inorganic matter (sweat, urine, skin particles, hair, personal care products). This results in high level of DBPs in water and air. Chlorinated DBPs and non-chlorinated DBPs are two types of disinfection by-products found in swimming pools. Exposure of DBPs to swimmers can be of different sources such as direct ingestion of swimming pool water, skin absorption and inhalation. Several studies have linked the DBPs formed by chlorination to the several diseases caused by the chemical exposure. Results have shown that THM uptake via inhalation has been associated with higher risk of cancer than uptake via ingestion or through skins. Disinfection by-products in swimming pool water have shown an increase in damaging effects on CHO cells in comparison with corresponding filling water due to presence of more than one mutagen (Akinola *et al.*, 2020).

There is an increased risk of lung epithelium permeability and risk of developing asthma. Competitive swimmers are most common victims of DBPs. Chlorination with its DBP known as THM and HAAs can cause an increased risk of cancer. Chlorate can cause reduced ability of red blood cells to carry oxygen. Chlorite which is other DBPs can cause anaemia and nervous

system effects. Bromoform, which is a by-product of ozonation, can lead to an increased risk of asthma. Toxicological reports have shown the ability of DBPs in swimming pools can have negative effects on reproduction. Outcomes such as low birth weight, preterm delivery, spontaneous abortions, stillbirth and birth defects are at high risk (Craun *et al.*, 2015). It has been estimated that two-third of DBPs contact through ingestion pathways that come from sources other than drinking water especially food and beverages prepared with tap water. Volatile organic compounds (VOC) are other important food contaminants found in untreated groundwater as a result of industrial pollution and can contaminate food and beverages from the water used in production, wrapping materials, polluted air, and retained solvent used for extraction of natural components. Most studies have reported DBPs in food and beverages in terms of the CHCl_3 content with CHCl_3 level in tea as high as 67 $\mu\text{g/L}$ in one study (Doederer *et al.*, 2014)

THMs are highly abundant and widespread in water distribution system. Various experimental animal studies of exposure to THMs have been used to associate the health risks in humans. Drinking water is also used in bathing, laundering, cooking, dishwashing, thus providing pathway to the THMs. THMs being volatile in nature make their exposure through ingestion, inhalation and absorption routes. Chloroform is also among the DBPs which have been described to have carcinogenic properties

based on the animal studies. Chloroform introduces cytotoxicity in human cell culture. Epidemiological studies suggest that DBPs exposure has a negative impact on sperms morphology and concentration. A decrease in menstrual cycle was observed among the US women at sites with high levels of ingested THM. Stillbirth risk is also increased by 9% due to high exposure of THM (Liu *et al.*, 2018).

HAAs include five of the acetic acids which are regulated in US. HAAs are not regulated in Europe. Animal studies suggest that health related defects with exposure to HAAs can cause reproductive malfunctioning, neurotoxicity and bladder cancer. NDMA (N-Nitrosodimethylamine) is an emerging DBP which is formed in drinking water and wastewater treatment. USEPA has classified NDMA as probable human carcinogen, where some states have regulated the levels. Bromate identified as DBPs is also suspected to be carcinogen. Perchlorate have found to be interfering with the ability of the thyroid gland to produce thyroid hormones, thus it is also has to be regulated by USEPA (Klarich, 2017).

It has been found that chlorine disinfection causes spread of resistant genes in wastewater treatment plant, which have caused an increase in the antibiotic resistant genes. Pesticides such as neonictinoids act as a precursor to the disinfection by products in water distribution system. It has been found that use of treated water for the irrigation purposes is beneficial for the good quality crop and preventing the damage

to be caused by pathogens. But DBPs or residual chemicals in irrigation water may damage the ecosystem (Klarich, 2017)

3.1 Global DBP Regulatory Compliance Framework

Chlorine is the most commonly used disinfectant in world. Although new disinfectants are being introduced, these disinfectants are chemicals. And like every other chemicals there are by products which can be of harmful nature to human health. Many countries around the world are regulating the DBPs to protect public health. Most of the research is being conducted on trihalomethanes (THMs) and haloacetic acids (HAAs). In order to achieve global DBP regulation over 165 countries have specified the parameter values for DBPs. DBP standard enforcement is an expensive and time consuming process for any nation. 107 to 167 countries have setup a guideline value for the free chlorine, among which 36 have set the value at WHO's guideline. 71 countries have marked it less than WHO guidelines. Enforcement of guideline can be done on following basis, rural and urban, ground water and surface water and small, medium and large scale water utilities. There is a need of phased reinforcement in order to take up this crucial task (Organization, 2018).

4. Conclusion

In the sustainable development goals, provision of potable water is a must for all. But until the discovery of DBPs in disinfected water, the major health concern with drinking water is the presence of pathogenic microorganisms which

have been associated with outbreaks of water borne diseases typically cholera, salmonella infections, shigellosis, and intestinal parasites. Further, it is difficult to generate data on DBPs in drinking water and assess their health impact in communities where research facilities are not available or accessible. The fall out of this is that information on the health implication on DBPs has originated from America and Europe mostly with scanty reports from China and India. Notwithstanding, the scope of epidemiological studies even in developed countries should also include the socio-demography of the community, the role of transportation as it involves migration and the psychological effect knowing water is a harbour of dangerous chemicals. If disinfection is failing what are the likely options to embrace if potable and life sustainable water for all is to become a reality as required in the sustainable development goals.

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Table 1: Shows the Drinking Water DBPs Limits In Different Countries

Sr No.	DBPs	China (2006)	US (2012)	Japan (2015)	WHO (4 th Edition)
1	Total Trihalomethanes	The sum of the ratio of the concentration of each to its respective limit should not exceed 1	0.08*	0.1	The sum of the ratio of the concentration of each to its respective limit should not exceed 1
2	Bromate	0.01	0.01	0.01	0.01
3	Chlorite	0.7	1	0.6	0.7
4	Chlorate	0.7	-	0.6	0.7
5	Haloaceticacids	-	0.06*	-	-
6	Formaldehyade	0.9	-	0.08	-
7	Beomofom	0.1	0.08	0.09	0.1
8	Chloroform	0.06	0.08	0.06	0.3
9	Dobromochloromethane	0.1	0.08	0.1	0.1
10	Bromodichloromethane	0.06	0.08	0.03	0.06
11	Dichloroactate	0.05	0.06	0.02	0.02
12	Trichloroacetate	0.1	0.06	0.03	0.05
13	Dibromoacetone	-	-	-	0.07
14	Dichloroacetone	-	-	0.01	0.02
15	Cyanogen Chloride	0.07	-	-	-
16	Trichloroacetaldehyde	0.01	-	0.02	-
17	2,4,6-Trichlorophenol	0.2	-	-	0.2
18	N-nitrosodimethylamine (NDMA)	-	-	0.0001	0.0001

Table 2: Shows the DBPs Water Source And Health Effects

Water Source	DBPs	Health Effects
Drinking Water	Bromate	Increased Risk Of Cancer
Drinking Water	Chlorite	Affects Nervous System, Causes Anaemia In Infants, Children And Fetuses Of Pregnant Women
Drinking Water	Haloacetic Acid	Increased Risk Of Cancer
Drinking Water	Trihalomethanes	Affects Liver, Kidney And Central Nervous System And Causes Cancer
Tap Water		Increased Risk Of Bladder Cancer In Men
		Increased Risk Of Stillbirth
		Affects The Time Of Pregnancy For Women