



Effect of Chlorine dose in formation of Disinfection By-Products in Drinking Water

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Abstract

In the poorest regions in the world, there are more than 783 million people who live without access to clean water (UNICEF, 2016). The earliest Egyptians used to drink the Nile water after purification and the groundwater without disinfectants or sterilization when the pathogens circulating in the drinking water were rather few. In many countries; Aluminum Sulphate still being used for many of water purification and treatment processes such as turbidity removal due to its coagulation properties. Due to the organic material is obviously present in water; Certain types of chlorine can react with certain organic molecules, forming hazardous compounds. The water were collected for 30 cm under water from Zefitta drinking water plant, Gharbia Governorate, Egypt. Next, all characteristics of physical and chemical nature has been identified before use in experiments. This study aimed to highlight the effect of chlorine dose on hazardous organic material formation. The study resulted in the chlorine dose is one of the major parameters in hazardous organic material formation with significant increase in HAAs and Tri Halo Methanes THMs, with the chlorine dosage increase. (p- Values were 0.001, 0.004 and 0.002 for (THMs), DiChloro Acetic Acids (DCAAs) and Tri Chloro Acetic Acids (TCAA) respectively). Thus, chlorine dose in drinking water chlorination process had a major influence on HAAs and THMs levels and must be controlled efficiently.

Keywords: Organic; hazardous; drinking water; chlorine; NOM..

1. Introduction

Chlorination is one of the most important process in water treatment [1]. Chlorination has significantly reduced the risk of pathogenic dirt but could pose a chemical hazard to human health due to formation of various disinfection by-products (DBPs) [2] which are formed by the reaction of chlorine and precursors such as natural organic matter (NOM) [3], [4]. Particularly, perchlorinating is the popular process for drinking water pretreatment globally because of its low costs, its effectiveness for long duration [5]. In addition, chlorination can also help to minimize pollution. such as suspended solids, organics, pathogenic bacteria, virus, and algae in raw water. However, several research have shown that in water treatment processes the chlorine could react with organics and produce a range of disinfection by-products (DBPs) [6]. Studying the carcinogenicity to human, researchers have paid interest to DBPs [7]. Furthermore, among all DBPs, haloacetic acids (HAAs) and trihalomethanes (THMs) characterized by chlorinated and brominated DBPs are found frequently with high concentrations; consequently, THMs and HAAs have attracted more interest [8]. Due to the possibility of carcinogenicity of DBPs [9], various countries have sharp

regulations to control DBPs. For instance, the United States Environmental Protection Agency (US EPA) has established an extreme pollution level for trihalomethanes equal 80, while it has been established a 60 µg/L for five halo acetic acids; European Community legalizes the levels of at 100 µg/L for (Bromoform, Chloroform, Dibromochloromethane and Dichlorobromomethane) [10]. The formation and detection of HAAs and THMs are a complicated problem dependent on many factors, such as the properties and levels of natural organic matter (NOM) [3], [4] and other water quality factors like pH, ammonia, and inorganic matrix [11]. This study aimed to investigate the chlorine dosage effect on the formation DBPs. For this study, water samples were gathered from intake of Zefitta drinking water plant, Gharbia Governorate, Egypt. The raw water samples were chlorinated in different chlorine dosage to predict the concentration of selected DBPs.

2. Experimental

2.1. Materials

All chemical, reagents, reference materials of purgeable volatile organic compounds and inorganic

chemicals used were analytical purity grade. Aluminum Sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), was obtained from Alum Misr Company, Abou Zabal, Egypt. As well, Calcium Hypochlorite ($\text{Ca}(\text{OCl})_2$, 30 % chlorine) was obtained from Misr Chemical Company, Alexandria, Egypt. While Reference Materials and reagents were obtained from Acustandard Co., and Sigma Aldrich Co.

2.2. • Methodology

The operation parameters have been simulated during experiment according to the actual treatment processes. Water was collected from 30 cm under water from Zeftta drinking water plant, Gharbia Governorate, Egypt. The collected water was analyzed to measure the physiochemical parameters. Next, the samples divided into 18 glass flasks, each one of them containing 1 liter of water before the treatment. All samples were with the same properties before treatment due to it were from the same source and collected at the same time. All of them treated with Aluminum sulphate, the final concentration of Aluminum Sulphate was 20 ppm; to remove all turbidity. No adjustment for pH, temperature, or another parameter. Next, samples were treated with Sodium Hypochlorite for 2 hours as contact time. The final concentration of Sodium Hypochlorite was 1,2,3,4,5 and 6 ppm. Then, Sodium thiosulphate used to remove the chlorine residue. Then the organic disinfection byproducts as Trihalomethanes (Chloroform, Bromodichloromethane, Chlorodibromomethane) and Haloacetic acids as (Dichloroacetic acids, Trichloroacetic acids) has been analyzed. The experiments were repeated three times, average of values has been shown in this study. Methods of chemical analysis, sample preservation, handling, and storage are provided in Table (1).

Table 1 Methods of chemical analysis for purgeable volatile organic compounds, sample preservation, handling, and storage.

Preservatives, De-chlorinating agents	Sampling Bottle	Storage Temp.	Max. hold period (days)	Method
For each 40 ml bottle 3 mg $\text{Na}_2\text{S}_2\text{O}_3$ were added and acidified using HCl to pH < 2.0	Amber Glass	4°C	14	EPA 524.4**

** U.S. EPA (2014) "U.S. EPA Drinking Water Methods for Chemical Contaminants Office of Ground Water and Drinking Water [12], [13].

2.2.1. pH, temperature, and Electrical Conductivity measuring:

The pH was measured using an analytical pH meter (HANNA pH 211- Romania); the instrument was calibrated using standard pH buffers (4, 7 and 10). While temperature and Electrical Conductivity (EC) was measured using an analytical Electrical Conductivity including analytical thermometer embedded unit - Cond.720 WTW series-Germany; after being calibrated by standards of 413, 1413 and 2776 $\mu\text{mohs/cm}$. The measurements for pH and (EC) were done on-site according to standard methods SM4500- H+B* and SM2510- B* respectively [14].

2.2.2. Total Organic Carbon (TOC)

TOC was determined according to SMWW; 500 ml of sample were filtered through 0.45 μm membrane filter and then acidified to less than pH 2. Measurements were done by Sievers 5310 C Laboratory TOC analyzer - USA. The instrument was calibrated daily by using dipotassium phthalate at 0.7, 2.5 and 5 ppm [14].

2.2.3. Organic Parameters

Purgeble Organic Complexes in Water were determination of by Capillary Column Gas Chromatography (GC) Agilent 7890B GC system column interfaced to a mass spectrometer (MS). This is a general-purpose method for identifying and measuring purgeable volatile organic chemicals in water at any treatment stage. The process can be used to measure a variety of organic materials. Purge and trap processes can eliminate this substance from water samples because of its high volatility and low water solubility. Purge and trap processes can eliminate this substance from water samples because of its high volatility and low water solubility; by bubbling an inert gas such as Helium (^4He) through the aqueous sample into the sample matrix with low water solubility Volatile organic compounds is removed (purged). In a tube containing sufficient sorbent materials, purged sample components are trapped. The sorbent tube is heated and reverse flushed with helium once purging is complete to desorb the trapped sample components into a capillary gas. The temperature of the column is controlled to aid separation of the method analytes, which are subsequently detected using the MS. By comparing observed mass spectra and retention times to reference spectra and retention durations in a database, compounds eluting from the GC column are identified and used to column Agilent DB-624 Ultra inert 60m /250mm / 0.25 μm . Reference spectra and retention times for analytes measuring calibration standards has been used under the same conditions as samples are measured in. Analytes are quantitated using procedural standard calibration. Each identified component's concentration is determined by comparing the MS response of the quantitation ion produced by that chemical to the MS response of the quantitation ion produced by an internal standard compound. The oven's temperature program for analyzing purgeble organic compounds is provided in Table (2). While the inlet condition: split mode, initial temperature 200 °C, column flow 0.8 ml/min., split ratio 40:100.

Table 2 Temperature program for analyzing purgeble Organic Compounds

Level	Ramping (°C /min)	Final Temp. °C	hold time (min)
1		30	12
2	2.5	60	1
3	5	100	15
4	5	180	6

The instrument was calibrated by using Purgeble Organic Compounds. Standards corresponding EPA 524.4 have a fixed Concentration of all Compounds (60 Purgeble Organic Compounds) and dilute that fixed slandered under special conditions to more one variable concentration to calibrate the

GC-MS System by nine points at 1, 4, 8,10,20,40,60,80 and 100 µg/L to construct Calibration Curve [12].

2.2.4. Statistical analysis

The results of chlorine dose, the concentrations of CHCl_3 , BDCM, CDBM, THMs, DCAA, TCAA, HAAs and the THMs/HAAs ratio were handled by EXCEL 365. To guarantee the quality of experiment results, distilled water was used as a blank; furthermore, all the samples and blanks were analyzed in duplicate.

3. Results and Discussion

3.1. Raw water analysis:

The raw water quality during the sampling process was shown in Table (3). Considering that all the quantity of water required for these experiments has been sampled, treated and analyzed under the same conditions. The average values were shown to discuss in the next paragraph.

Table 3 Characteristics of water quality

Water quality index	Range	Average
pH	4.1 – 4.6	4.45
Temperature °C	25 – 28	26.1
Turbidity (NTU)	0.5 – 1	0.6
UV254 cm^{-1}	0.043 – 0.058	0.049
TOC mg/L	3.8 – 4.3	4.1
Electrical Conductivity ($\mu\text{mohs/cm}$)	330 – 390	367
Free Chlorine ppm.	ND	--
THMs ($\mu\text{g/L}$)	ND	--
HAA ($\mu\text{g/L}$)	ND	--

Table (4) shows the Chlorine doses and Disinfection By products (DBPs); which explain the organic DBPs as Trihalomethanes and Haloacetic acids as (dichloro acetic acids, Trichloroacetic acids).

Table 4 Chlorine dose effect on THMs and HAAs formations

Chlorine Dose (ppm.)	CHCl_3 $\mu\text{g/L}$	BDCM $\mu\text{g/L}$	CDBM $\mu\text{g/L}$	THMs $\mu\text{g/L}$	DCAA $\mu\text{g/L}$	TCAA $\mu\text{g/L}$
1	38.42	12.78	3.72	54.92	12.31	23.19
2	46.9	16.36	4.14	67.4	18.64	28.38
3	61.22	15.45	3.75	80.42	25.86	33.77
4	75.33	18.42	4.08	97.83	36.71	46.11
5	111.91	21.82	4.29	138.02	49.22	68.73
6	135.05	31.95	6.53	173.53	67.13	87.11

The concentrations of CHCl_3 , BDCM, CDBM, THMs, DCAA, TCAA, HAAs were 38.42, 12.78, 3.72, 54.92, 12.31 and 23.19 $\mu\text{g/L}$ in the treated water with 1 ppm chlorine dose while it is increased with increasing the chlorine dose, reached to 135.05, 31.95, 6.53, 173.53, 67.13 and 87.11 for CHCl_3 , BDCM, CDBM, THMs, DCAA, TCAA, HAAs respectively. These results indicating the positive significant relation between Chlorine doses and DBPs species, these finding agreed with the results stated by Bond and co-authors [15]. The correlation coefficient was equal 0.9369, 0.9637 and 0.9260 for THMs, DCAA and TCAA respectively, the same relation found by Xin Gu and his research team [16]. Figure (1) explain the relation between DBPs and chlorine dose.

Initial concentration of trihalomethanes was 54.92 $\mu\text{g/L}$ when the disinfectant dose 1 ppm, final concentration of Total trihalomethanes 173.53 $\mu\text{g/L}$, last concentration is very high corresponding Criteria of world Health organization (WHO), the criteria of total trihalomethanes corresponding (WHO) 100 ppm [10]. Figure (2) which show the Relation between Chlorine doses and dichloroacetic acid as organic Disinfection By products (DBPs). From just looking on the result the initial concentration of dichloroacetic acid 12.31 $\mu\text{g/L}$ when concentration equal 1 ppm of disinfectant, last concentration of dichloroacetic acid 67.13 $\mu\text{g/L}$ when concentration of disinfectant equal 6 ppm, last concentration is very high corresponding (WHO), which certain the danger of chlorine as disinfectant in surface water. While Figure (3) shows the Relation between Chlorine doses and Trichloroacetic acid as organic Disinfection By products (DBPs), this agreed with Hua, et.al (2008) [17]. Trichloroacetic acids as organic disinfection by product which produce when uses chlorine as disinfectant, from table (1) results the initial concentration 23.19 ppm when chlorine dose 1ppm, last concentration of Trichloroacetic acid 87.11 $\mu\text{g/L}$, Although the last concentration with in rang but near of fin of (WHO) criteria, fin of (WHO) 100 $\mu\text{g/L}$ of Trichloroacetic acid [10]. All samples have the same contact time between a variable Chlorine doses and treated water, that time was two hours and preserved by thiosulphate to analyze corresponding DPBs methods. Worthy mentioning all sample have the same Total Organic Carbon (TOC) before treated by Chlorine doses, after treated by Chlorine (TOC) differ slightly. As explained in Table (5), The formation of THMs, DCAA and TCAA are significant positive correlation.

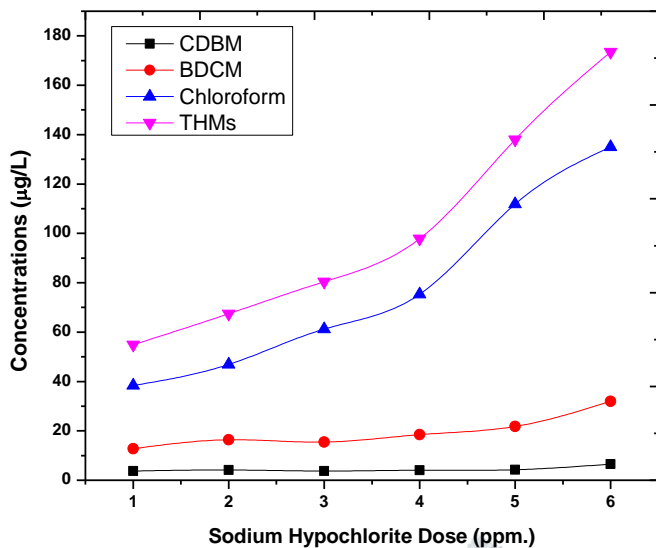


Figure 1 Effect of chlorine dose on THMs formation

Table 5 p-Values and R2 for THMs, DCAA and TCAA formation

	<i>P-value</i>	<i>R²</i>
THMs	0.001	0.9369
DCAA	0.004	0.9637
TCAA	0.002	0.9260

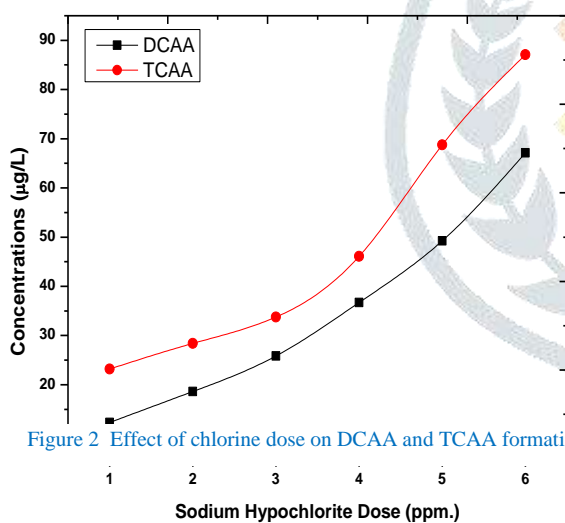


Figure 2 Effect of chlorine dose on DCAA and TCAA formation

In this study, the influence of temperature on the ratio of THMs to HAAs was discounted due to the fact that the sampling and analysis were done at the same time and the temperature. Several research also indicated that the formation of THMs was higher than HAAs [18], [19]. However, Roberts et al. (2002) found that the contents of HAAs were higher than THMs or the same, respectively [20]. Therefore, the relative advantage is primarily determined by the quality of the raw water characteristics, such as the pH, organic matter, and other factors. In total, the chlorine dosage in chlorination process plays a critical influence on the ratio of THMs to HAAs [16], [21].

4. Conclusion and Recommendations

In this study, levels of THMs and HAAs has been analyzed after simulated coagulation and chlorination process with dissimilar chlorine dosage (1, 2, 3, 4, 5 and 6 ppm.), and the changes and ratio of THMs to HAAs were also observed. According to our study, we can conclude that, The THMs and HAAs levels increased with the increasing the chlorine dosage. Chloroform was the main component of four kinds of THMs, while Bromoform not detected in all samples. Additionally, the increase of DCAA and TCAA was the most understandable among all HAAs. The ratio of THMs / HAAs for the chlorine dosage of 1 ppm was 0.646 and increased with chlorine dose reached 0.888 with 6 ppm as chlorine dose. Due to the carcinogenicity of DBPs to human, the dosage of chlorine must be controlled strictly in drinking water treatment plants. Thus, this study recommended to continue the research to find alternative disinfectant to control the THMs and HAAs formation in drinking water disinfection processes.

5. Conflicts of interest

“There are no conflicts to declare”.

6. Funding sources

“There is no fund for this research”.

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