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Humic substances as precursors for trihalomethanes yields upon chlorination

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ABSTRACT

The role of humic substances (HSs) in the formation of trihalomethanes (THMs) through the chlorination process in drinking water purification plants was investigated. A series of batch experiments, under different experimental conditions (reaction time, levels of HSs, and pH) were designed. In addition, trihalomethanes formation potential (THMFP) was assessed. The results showed that the average concentration of total THMs formed was 7.63 μg/L. Chloroform was the main species of THMs, while bromoform was not generated during this study. Prolonging the reaction time with increasing HSs concentrations and alkaline pH resulted in increasing the total THMs formed. The contribution of humic acid to the THM precursor was greater than fulvic acid. Therefore, the complete removal of HSs, or at least optimizing the operating conditions, is recommended to minimize the formation of THMs.

Keywords: Humic acid; Fulvic acid; Chlorine; Chloroform

1. Introduction

The disinfection of drinking water supplies using chlorine was likely the most important event in the whole history of the water supply industry [1]. The disinfectant action of chlorine with filtration can entirely remove a wide range of disease-causing organisms. Since its introduction, chlorination has been the most important disinfection method due to its significant achievement in reducing waterborne diseases and its low cost [2–4].

However, several other techniques such as ozonation and UV-radiation are also applied in water treatment. During the first 50 years of chlorine disinfection history, no attempts were made to study the negative health effects of chlorination [5]. The formation of trihalomethanes (THMs) as byproducts of the chlorination process was the first evidence that chlorination process had some unwanted features. THMs were the first detected and the largest category of halogenated disinfection byproducts (DBPs) in treated drinking water [6,7], followed by haloacetic acids (HAAs) [8,9] and haloacetonitriles, and haloketones and chloropicrin at lower concentrations [10]. THMs and HAAs are the two largest categories of halogenated DBPs in treated drinking water [11].

Interest in the study of halogenated DBPs formation has stemmed primarily from the biological implications of their presence in drinking water. Halogenated DBPs are classified as possible human carcinogens by the United States Environment Protection Agency [12]. Recently, it has been reported that THMs induce DNA damage and increase the risk of

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cancer [13]. Their occurrence in drinking water could result in public health problems by ingestion, inhalation, and dermal adsorption [14].

Natural organic matter (NOM) itself has no direct impact on drinking water, but it affects water quality by increasing the disinfectant and coagulant demand, providing precursor materials for DBPs and enhancing bacteriological regrowth in the distribution system [15,16]. Humic substances (HSs) are the dominant fraction of NOM in soils, sediments, and water [3,17]. HSs are subdivided according to their water solubility into three categories; humic acid (HA), fulvic acid (FA), and humin. HA is the fraction of HSs that is soluble in water at pH greater than 2 and becomes insoluble below pH 2, while FA is the fraction that is soluble in water at any pH value, and humin is the fraction that is water insoluble at any pH value [18].

HSs in natural water have a documented reactivity with a diversity of oxidants and disinfectants that are used for drinking water purification, particularly chlorine [19]. HSs react with free chlorine to produce halogenated DBPs including THMs, HAAs, HANs, haloaldehydes, haloketones, chloropicrin, and chlorophenols [19].

In addition to HSs, phenolic compounds, β-diketones, and carboxylic acids that can be converted into ketoacids are liable to produce THMs. These compounds may enter the public water supplies through the potential run-off and leaching from contaminated soils. Once entered the water they transform the C, N, and P cycles, and cause serious environmental problems [20]. Chen et al. [21] have reviewed the main soil pollutants and the application of compost for their bioremediation. Also, it has been reported that aquatic algae and their metabolic product are sources of DBPs precursors [22]. Even with the extensive investigations on this topic, answering the question of which kind of NOM is the reason for DBP formation is still a valid research challenge [3]. So, this study focuses on getting a close picture on the role of HSs in the formation of THMs during the chlorination process. A laboratory bench-scale model was performed to assess the formation of THMs during the chlorination process. Some variables such as reaction time, levels of HSs, and pH were studied to obtain reproducible and meaningful results.

2. Materials and methods

2.1. Chemicals and aqueous solutions

HA sodium salt (analytical grade, Aldrich) and fulvic acid (Suwannee river reference 1S101F of IHSS) were used as received without further purification. *n*-hexane (GC-grade, Sigma-Aldrich) was used for THMs extraction. The stock chlorine solution was prepared by bubbling a pure chlorine gas (>98%) through de-ionized water. All other reagents were of analytical grade, and de-ionized water was used to prepare all the solutions.

2.2. Chlorination procedure

Chlorine stock solution concentration was determined iodometrically, while the residual chlorine was determined by the DPD colorimetric method according to APHA [23]. HA sodium salt (analytical grade, Aldrich) and fulvic acid (Suwannee river reference 1S101F of IHSS) were used as received. Batch chlorination trials were performed using a series of 1-L TFE-lined screw cap amber glass bottles. A volume of de-ionized water that contains humic and fulvic acid to produce a concentration of 2, 4, and 6 mg/L of each acid was transferred to the bottles in a single component system. Each sample bottle was adjusted to the desired pH value (pH 5, 7, and 9).

Conditions of the chlorination test were designed to simulate chlorine dose that was applied in the pre-chlorination process at the water treatment plants. With a graduated pipette, a certain volume of the chlorine dosing solution was transferred into the glass bottle (containing humic or fulvic acid solution) to produce 5 mg/L initial chlorine dose. Immediately, the bottle was agitated and stored in the dark at 25 ± 2°C. The reaction periods were adjusted at 5 min, 1 and 2 h on the base of separate sample bottle. A reagent blank was prepared with each batch of samples by the same manner in the absence of HSs.

2.3. Trihalomethanes formation potential (THMFP)

The samples were buffered at pH 7, chlorinated with an excess of chlorine, and incubated at 25 ± 2°C for 7 d to let the reaction come near completion. At the end of the incubation period, the free chlorine residual was ranging between 3 and 5 mg Cl_2/L.

2.4. Trihalomethanes quantification

THMs concentrations were determined using simple liquid–liquid extraction gas chromatographic method (GC, EPA method 501.2). A Varian 4000 gas chromatograph equipped with Varian auto-injector model CP 8410 and 30-meter CP-selected 624CB fused silica capillary column and an electron capture detector (ECD) was used for analysis of THM. Concentration of THMs was calculated using the external standard calibration method. A certified mixture standards of THMs (chloroform (Cl_3CH), bromodichloromethane ($BrCl_2CH$), dibromochloromethane (Br_2ClCH), and bromoform (Br_3CH)) obtained from Suppelco were used. High purity (99.99%) grade gases were used. Helium (flow of 1 mL/min) was used as a carrier gas, while nitrogen (flow of 25 mL/min) was used as makeup gas. All sample extracts including standards and blanks were injected in splitless mode. The injector and detector temperatures were 200 and 270℃ isothermally, respectively. The capillary column temperature program was started with 104℃ for 3 min, ramp 40℃/min to 160℃, and held for 2.6 min.

2.5. Quality control and data analysis

Minimum duplicates samples were analyzed, a procedural blank and the certified standards were analyzed routinely with each batch of samples. Deionized water spiked with known concentrations of THM was used to calculate the percentage recovery of the method and was analyzed regularly with the samples. The average recoveries varied between 85 ± 4%, but not applied in calculating the concentrations of these compounds in the samples. The detection limits of the method was verified and carefully noticed. Observing the linear response of ECD for THMs compounds, in area count, shown that it was responding linearly for all compounds. Mean concentrations of individual compounds in addition to the sum of compounds were calculated. Standard error (±SE) was used as a statistical measurement to verify the accuracy of the results. The statistical variation among the chlorination experiment conditions was determined using a simple *t*-test and analysis of variance.

3. Result and discussion

3.1. Trihalomethanes yields

Generally, the concentration of total trihalomethanes (TTHMs) formed in all samples ranged from 5.45 to 10.24 μg/L with an overall average of 7.63 μg/L (Tables 1–3). This level of TTHMs is very low when compared to the value set by EPA guidelines for drinking water (80 μg/L). In addition, the maximum permissible level of TTHMs in the Egyptian standard for drinking water is 100 μg/L (Decree No. 458, 2007). Most literature studies focused on the chlorination of natural HSs that present or extracted from natural environments with the ambient conditions. Therefore, the levels of THMs detected in the present study were very low than those reported in the literature. However, understanding the process of the formation of trihalomethanes is crucial to apply adequate practices in municipal treatment utilities to supply safe water. Therefore, the operational parameters which influence the occurrence of trihalomethanes, such as HSs concentration, pH, and reaction time were investigated, see below.

Table 1
Trihalomethanes yields (μg/L) after chlorination of humic and fulvic acid as a function of pH 5 and percentage of initial yields (in parenthesis)

	Cl_3CH	Br $CHCl_2$	Br_2CHCl	TTHMs	Cl_3CH	Br $CHCl_2$	Br_2CHCl	TTHMs
Parameters	Humic acid 2 mg/L				Fulvic acid 2 mg/L			
5 min	3.15	1.22	1.63	6.00 (85)	3.00	1.10	1.35	5.45 (82)
1 h	3.36	1.38	1.72	6.46	3.22	1.32	1.65	6.19
2 h	3.90	1.42	1.77	7.09	3.84	1.08	1.74	6.66
	Humic acid 4 mg/L				Fulvic acid 4 mg/L			
5 min	3.25	1.26	1.65	6.16 (77)	3.19	1.16	1.46	5.81 (75)
1 h	3.96	1.37	1.80	7.13	3.80	1.30	1.73	6.83
2 h	4.68	1.44	1.83	7.95	4.53	1.40	1.80	7.73
	Humic acid 6 mg/L				Fulvic acid 6 mg/L			
5 min	3.41	1.31	1.81	6.53 (80)	3.30	1.29	1.79	6.38 (81)
1 h	4.55	1.36	1.87	7.78	4.35	1.19	1.80	7.34
2 h	4.88	1.37	1.95	8.20	4.71	1.23	1.90	7.84

Table 2
Trihalomethanes yields (µg/L) after chlorination of humic and fulvic acid as a function of pH 7 and percentage of initial yields (in parenthesis)

	Cl_3CH	Br $CHCl_2$	Br_2CHCl	TTHMs	Cl_3CH	Br $CHCl_2$	Br_2CHCl	TTHMs
Parameters	Humic acid 2 mg/L				Fulvic acid 2 mg/L			
5 min	3.30	1.30	1.71	6.31 (82)	3.19	1.21	1.62	6.02 (81)
1 h	3.90	1.41	1.83	7.14	3.76	1.38	1.80	6.94
2 h	4.39	1.47	1.83	7.69	4.17	1.45	1.80	7.42
	Humic acid 4 mg/L				Fulvic acid 4 mg/L			
5 min	4.30	1.38	1.82	7.50 (81)	3.51	1.19	1.40	6.10 (73)
1 h	4.52	1.49	1.84	7.85	4.24	1.40	1.41	7.05
2 h	5.86	1.55	1.86	9.27	5.24	1.52	1.56	8.32
	Humic acid 6 mg/L				Fulvic acid 6 mg/L			
5 min	4.49	1.40	1.84	7.73 (84)	4.20	1.20	1.78	7.18 (79)
1 h	5.50	1.53	1.89	8.92	5.04	1.41	1.87	8.32
2 h	5.73	1.56	1.92	9.21	5.64	1.57	1.91	9.12

Table 3
Trihalomethanes yields (µg/L) after chlorination of humic and fulvic acid as a function of pH 9 and percentage of initial yields (in parenthesis)

	Cl_3CH	Br $CHCl_2$	Br_2CHCl	TTHMs	Cl_3CH	Br $CHCl_2$	Br_2CHCl	TTHMs
Parameters	Humic acid 2 mg/L				Fulvic acid 2 mg/L			
5 min	3.54	1.36	1.72	6.62 (76)	3.27	1.34	1.70	6.31
1 h	4.07	1.44	1.93	7.44	3.83	0.92	1.85	(74)
2 h	5.26	1.48	2.01	8.75	5.08	1.47	1.96	6.608.51
	Humic acid 4 mg/L				Fulvic acid 4 mg/L			
5 min	4.38	1.37	1.76	7.51 (76)	3.73	1.30	1.67	6.70 (72)
1 h	5.45	1.41	1.79	8.65	4.67	1.38	1.43	7.48
2 h	6.16	1.81	1.87	9.84	5.90	1.73	1.64	9.27
	Humic acid 6 mg/L				Fulvic acid 6 mg/L			
5 min	5.53	1.41	1.77	8.71 (85)	5.26	1.38	1.73	8.37 (83)
1 h	6.63	1.42	1.79	9.84	6.05	1.40	1.78	9.23
2 h	6.85	1.44	1.95	10.24	6.66	1.51	1.97	10.14

3.1.1. Effect of HSs concentration, pH, and contact time in THMs formation

It can be seen from Figs. 1–3 that, TTHMs formation levels relatively increases as the concentrations of HSs increases, as the pH value increases (alkaline) and as the reaction time passed. However, the variation in TTHMs concentrations with all variables was statistically insignificant ($p > 0.05$), possibly due to the small limitations of the experimental variables. These results are in agreement with several studies, respecting the increased THMs formation levels as the concentrations of HSs, pH values, and contact time with free chlorine increased [24–26]. The results revealed that the kinetics of the THMs formation was very rapid, where most of the THM species were formed about after 5 min of the reaction time. The initial yields of TTHMs

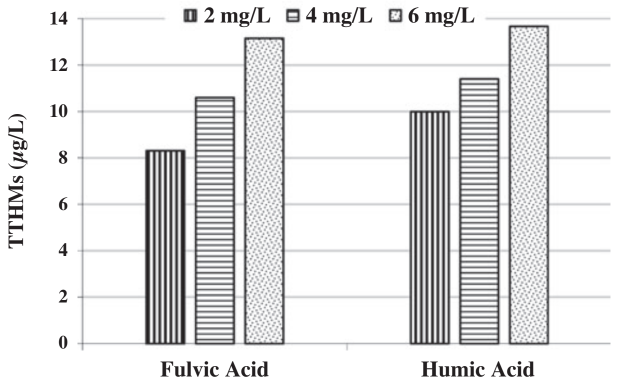

Fig. 1. Variation in total trihalomethanes (TTHMs) with the HS concentration.

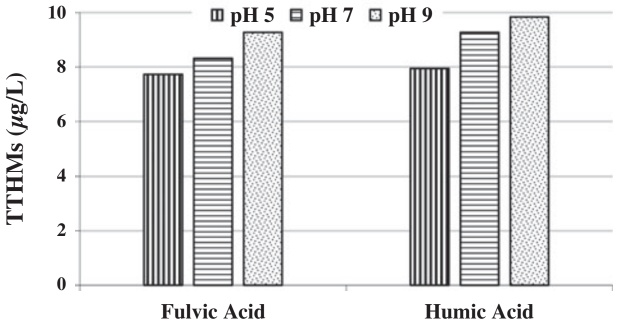

Fig. 2. Variation in total trihalomethanes (TTHMs) with pH value.

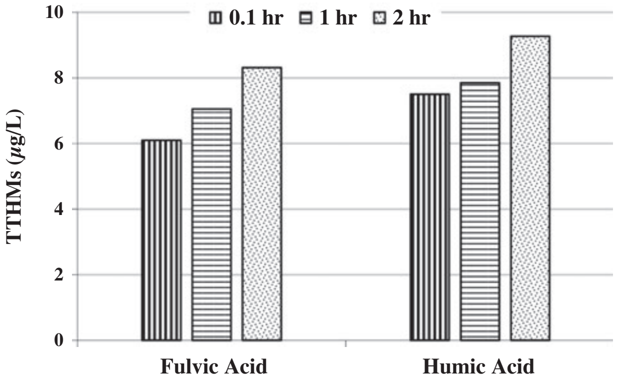

Fig. 3. Variation in total trihalomethanes (TTHMs) with reaction time.

Table 4
Trihalomethanes formation potential after chlorination of HSs

Parameters	Concentration (mg/L)	TTHMFP (μg/L)
Humic acid	2	10.00
	4	11.41
	6	13.67
Fulvic acid	2	8.31
	4	10.60
	6	13.15

insignificantly varied ($p > 0.05$) with the different concentrations of HSs, reaction time, and pH ranging from 72 to 85%. It can be explained that the initial THM formation corresponds to the fast reacting of THM precursors with chlorine within the first 5 min. Thereafter, THMs were slowly produced during 2 h; the plateau phase might be not reached in this short-term experiment.

3.2. Trihalomethanes speciation

Table 4 and Fig. 4 shows the percentage composition of individual THMs compounds to TTHMs as a function of chlorination of HSs with different variables. Chloroform was the dominant species of THMs, while bromoform was not generated at all during this experiment. Chloroform constituted as much as 52–67% of the total trihalomethanes (TTHMs) with both humic and fulvic acids in all conditions with insignificant difference ($p > 0.05$) between both compounds. The predominance of chloroform had been reported by other literatures [22,27]. Generally, the formation of specific compounds of THMs (e.g. chloroform) correlated mainly with the properties and relative abundance of organic matter species present in the water sample that react with the free chlorine [25,28,29]. THMs speciation in chlorinated (chloroform) and brominated (bromodichloromethane, dichlorobromomethane, and bromoform) compounds is mainly influenced by organic matter and bromide ion concentration [30,31]. In the current study, chloroform constitutes more than 50% of TTHMs in all tests due to the using deionized of water, which is almost free of bromide ion.

3.3. Trihalomethanes formation potential

Fig. 5 shows TTHMs formation potential (TTHMFP) as a function of initial chlorine dose (estimated from chlorine demand test) and different concentrations of HSs, namely 2, 4, and 6 mg/L at laboratory temperature (≈25˚C) for a reaction time of 7 d. The estimated TTHMFP increases as the concentrations of humic or fulvic acid increase (Fig. 5). Also, it can be noticed from Fig. 5 that THMFP was highly influenced by HA than with fulvic acid. This is due to

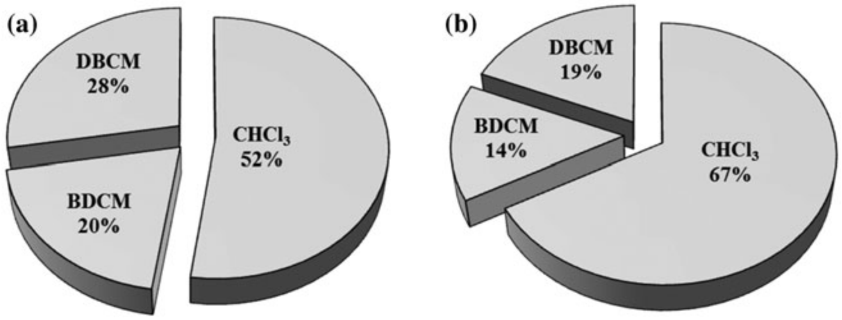

Fig. 4. Percentage composition of individual THMs compounds to TTHMs: (a) pH 5 and (b) pH 9.

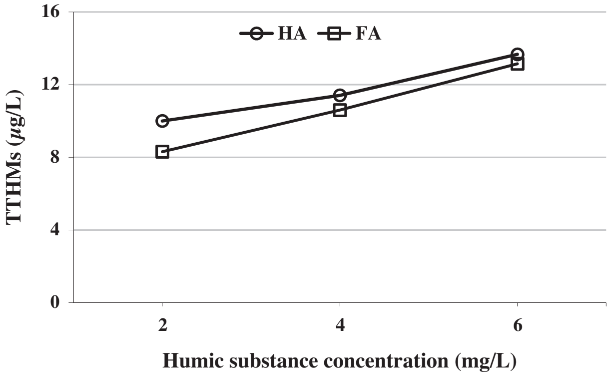

Fig. 5. Variation in total trihalomethanes formation potential with the HS concentration.

the higher hydrophobicity (deduced from the H/C ratio) of HA. It has been reported that the THMFP increases as the hydrophobicity increase [32]. The H/C of the HA sodium salt and fulvic acid are 0.72 [33] and 0.99 [34], respectively, indicating that HA is more aromatic (hydrophobic) than fulvic acid. In the present study, the structural and chemical characteristics of both HSs (humic and fulvic acid) have not been examined. It has been reported that the THMFP produced is influenced by structural and chemical characteristics of HSs such as aromaticity and functionality [29,35–37]. Molecular characterizations, such as ^{13}C NMR and FTIR, are needed to verify this hypothesis.

4. Conclusions

This study focused on understanding the role of HSs in the formation of trihalomethanes during the chlorination process. The effect of reaction time, levels of HSs, and pH on the formation of THMs during the chlorination process was studied. Also, trihalomethanes formation potential (THMFP) was evaluated. The results showed that the average concentration of total trihalomethanes formed was lower than the value set by EPA guidelines for drinking water and the permissible level of total trihalomethanes in the Egyptian standard for drinking water. Chloroform was the main species of THMs, while bromoform was not produced in this study. The total trihalomethanes yield increased with increasing reaction time, HSs concentrations, and alkaline pH. THMFP was greatly influenced by HA than fulvic acid.

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