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Concederations Concerning the Formation of Non volatile Chlorinated Organic Compounds in the Chlorination Process of Water

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Abstract: In this study, the influence of organic precursors concentration and nature, chlorine dose, pH, contact time and temperature on organic non-volatile compounds occurrence (TOCINV) as a result of certain waters chlorination was investigated. The quantity of organic chlorinated compounds increased with the increase of the chlorine-resorcinol ratio, the maximum values being obtained for the 10-12.8 chlorine-resorcinol ratio. The synthetic waters used for the testing had a content of humic acids ranging between 10-30 mg dm⁻³ humic acids. Using a dose of 30 mg dm⁻³ chlorine and 30 mg dm⁻³ humic acids at constant pH and temperature values, the contract time was varied along 0.25-25 h.

Key words: Drinking water, organic halogenated compounds, humic acids, resorcinol

INTRODUCTION

A present time priority in drinking water supply with a view to ensure the consumers protection, is represented by organic halogenated compounds occurrence at natural water chlorination. Studies reported by Haag (1983), Marinsky (1986), Boller (1994, 1995) and Hoehn (1987) have proved that organic volatile and non volatile halogenated compounds to be found in drinking water are unhealthy for human consumers, being considered as potentially causing human cancer, mutations teratogenies and embryo-toxic. Egging *et al.* (1997) investigated semiconductor photocatalysis as an alternative. Aldrich humic acid solutions 100 mg dm⁻³, filtered through 0.22 µm Millipore filters) were photolysed in a 0.1% suspension of Degussa P25 titanium dioxide using a mercury lamp.

On account of the studies in the field that have been published so far being mainly concerned with the presence of the organic volatile halogenated compounds (TOXV), the present paper deals with organic non-volatile compounds (TOXNV). The main objective of this study is to investigate the formation of non-volatile chlorinated organic compounds (humic acid) in the drinking water of Tafila city in the southern district of Jordan. Samples were taken from Zapda spring, Abour water station and Twana spring and then subjected to chemical analysis. This study was promoted by the ministry of water and irrigation and the ministry of environment since little studies were conducted to solve this problem.

MATERIALS AND METHODS

The experiments that have been carried out traced the influence of several parameters (organic precursors concentration and nature, chlorine dose, pH, contact time, temperature) on organic non-volatile compounds occurrence (TOCINV) as a result of certain waters chlorination. The studies made use of synthetic waters with various contents of resorcinol and humic acids and of raw surface water samples. the chlorination agent employed was sodium hypochlorite.

Kolle (1975) has published a method for the analysis of organic non-volatile chlorinated compounds (TOCINV) by pyrohydrolysis. This method consists in the organic non-volatile chlorinated compounds concentration by their coagulation and adsorption on activated carbon as published by Huhn (1978). Following the concentration there took place, by pyrohydrolysis at 1100°C, the mineralization of the adsorbed compounds and the chlorine ion determining, by using the specific electrode ion, chlorine ion meter OP-261, having 10⁻¹-10⁻⁵ g dm⁻³ measuring range.

Cochechi (1994) reported a method by which humic acids determining was achieved by their precipitation with concentrated H₂SO₄ at pH = 1.5, followed by the precipitate maturation for 48 hours and its filtering and dissolution in a NaOH 9.1 n solution.

Resorcinol determining in water was accomplished by spectrophotometric method in UV with SPECORD UV-VIS instrument.

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Total Organic Carbon (TOC) was determined with a Beckman 915A analyzer; pH was measured with a pH meter of Radelkis OP-207 type.

RESULTS AND DISCUSSION

The first set testing made use of synthetic waters having a resorcinol content of 5-25 mg dm⁻³. Resorcinol is considered as one of the most important precursors with a polyhydroxibenzenic structure, characteristic of humic macromolecular substances that are often met in surface waters.

Variable chlorine doses were added to each of the synthetically waters.

Table 1 synthetically presents organic non-volatile chlorinated compounds obtained during the process by analyzing the influence of the reactant concentration, namely chlorine-resorcinol reactants ratio.

It has been found out that the quantity of organic chlorinated compounds increased with the increase of the chlorine-resorcinol ratio, the maximum values being obtained for the 10-12.8 chlorine-resorcinol ratio.

Figure 1 represents the variation of TOCINV quantity formed for the synthetic water with a resorcinol content of 25 mg dm⁻³ for the pH values ranging between 6-12.

Table 1: TOCINV quantity for various values of chlorine: resorcinol ration (Cl₂/R)

Resorcinol (mg dm ⁻³)	TOCINV (mg dm ⁻³)			
	Cl ₂ /R = 5	Cl ₂ /R = 6	Cl ₂ /R = 10	Cl ₂ /R = 12.8
5	1.7	2.1	4.7	5.9
10	-	-	-	7.65
15	3.0	3.6	7.0	10.4
25	3.2	4.4	10.4	16.0

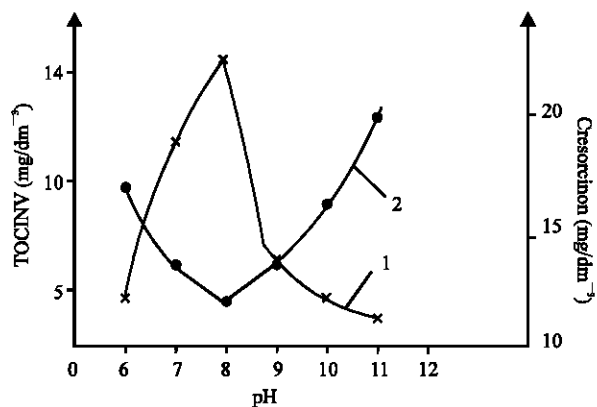


Fig.1: TOCINV concentration vibration as function of pH 1-TOCINV concentration; 2-Resorcinol residual concentration

The formed TOCINV is highly dependent on the reaction medium pH and presents maximum values for pH values ranging between 7.5-8; pH values ranging between 9-11 substantially reduce the maximum value, making it three times smaller.

Figure 2 presents the variation of organic chlorinated products quantities resulting as function of the operating temperature. An increase of the medium temperature with 10°C results in an increase of the resulted reaction products quantity, it being two times bigger.

Table 2 illustrates chlorinated products formation as a function of the reaction duration for two temperature values, namely 5° and 20°C.

Starting with a water sample containing g mg dm⁻³ resorcinol and 22.8 mg dm⁻³ chlorine, TOCINV is being substantially formed during the first 15-30 h of the reaction (about 50%), followed by a shown increase of its quantity.

The second set of testing studied TOCINV formation at the chlorination of waters containing humic acids.

Humic substances represent final produces of chemical and microbiological processes in natural waters flora and fauna transforming.

Humic acids represent an important class of the precursors of organic chlorinated compounds.

The synthetic waters used for the testing had a content of humic acids ranging between 10-30 mg dm⁻³ umic acids. Using a dose of 30 mg dm⁻³ chlorine and 30 mg dm⁻³ humic acids at constant pH and temperature values, the contract time was varied along 0.25-25 h (Fig. 3). Consequently, TOCINV increases along with the

Table 2: TOCINV quantity for various reaction time values

Temp (°C)	TOCINV (mg dm ⁻³)				
	t = 2 h	t = 9 h	t = 26 h	t = 74 h	t = 170 h
5	2.0	3.45	4.8	11.2	13.0
20	4.0	4.20	8.4	16.0	16.5

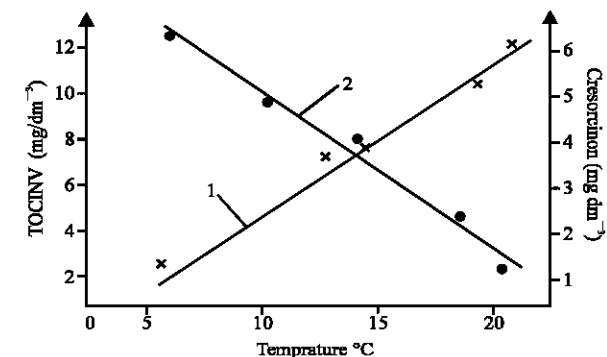


Fig.2: OCINV concentration variation as function of temperature 1-TOCINV concentration; Resorcinol residual concentration

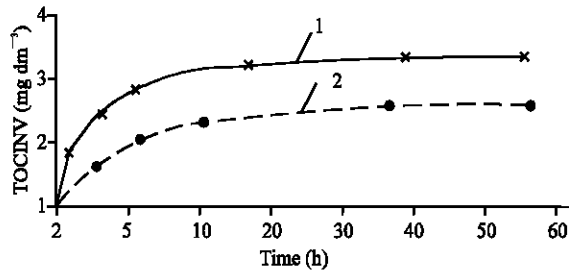


Fig. 3: Contact time influence on TOCINV formation
1-TOCINV concentration; 2- chlorine residual concentration

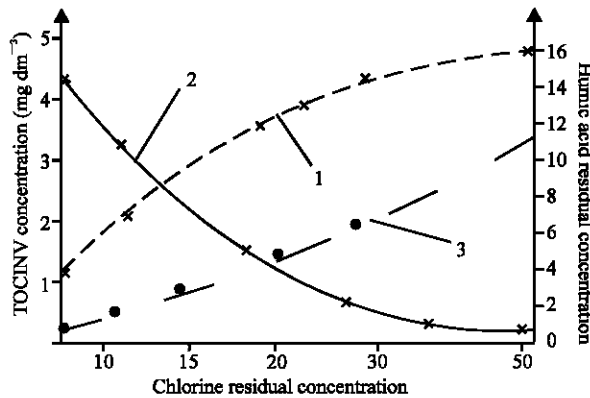


Fig. 4: Chlorine dose influence on TOCINV formation

contact time, as shown by the Fig. 3 and by the UV absorption curves, the maximum quantity obtained being 7.7 mg dm^{-3} , after 26 h.

Humic acids reduction during the first 15 minutes was of 89%, they being transformed in TOCINV and THM, respectively, by chlorination.

The reduction degree in humic acids concentration will be slower, if the contact time is longer (Fig. 4).

A constant dose of 30 mg dm^{-3} humic acids was used to study the influence of the chlorine dose of the formed TOCINV quantity during 30 min contact time, for the various chlorine quantity-ranging between 5-50 mg dm^{-3} (Fig. 5).

The results presented in Fig. 5 were obtained by using doses of 25 mg dm^{-3} humic acids and 10 mg dm^{-3} chlorine, with pH values ranging between 5-11, which shows that high pH values the TOCINV content decreases, larger quantity of THM formation being thus favoured.

The third set of testing studied the influence of the organic precursors concentration represented by the global TOC parameters in raw surface water, over the formation of organic non-volatile chlorinated compounds.

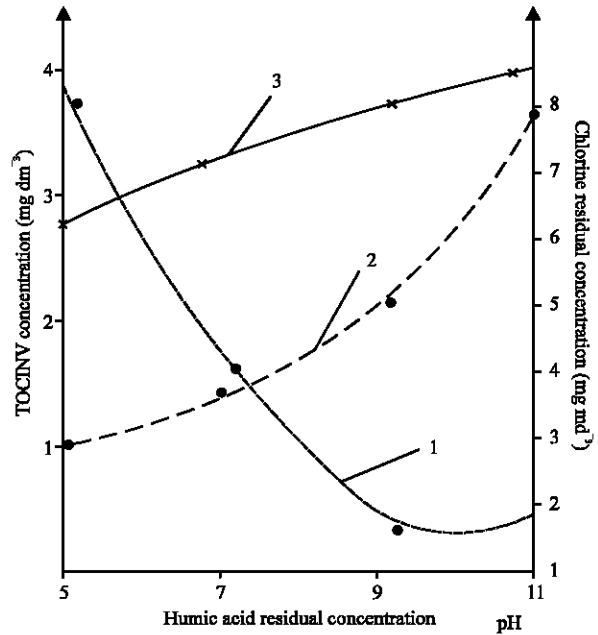


Fig.5: pH influence on the chlorination process for water containing 25 mg dm^{-3} humic acids

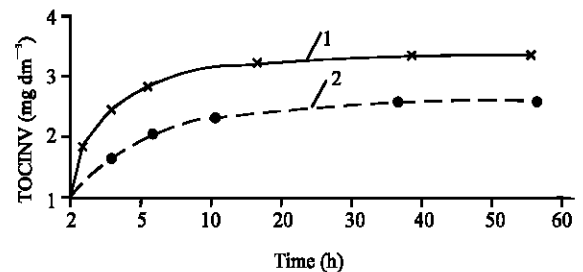


Fig. 6: TOCINV formation in waters with different organic content -TOC = 6 mg dm^{-3} ; 2- 12.5 mg dm^{-3}

Figure 6 presents TOCIV values obtained after the chlorination of water samples with different organic loadings, of 6 and 12.5 mg dm^{-3} , respectively, for the same chlorine: TOC ratio, which show that TOCINV values does not increase directly proportional to TOC global parameters, but in influenced by the nature of the organic species that are present in water.

The subsequent studies traced the possibility of the organic non-volatile compounds elimination out of raw water undergoing chlorination by coagulating them with aluminum sulphate, followed by absorption on activated carbon (Table 3). A reduction of about 50% TOCINV is obtained in water treated by coagulation and adsorption a activated active a carbon, TOCINV concentration being practically negligible in the water thus treated.

Table 3: TOCINV elimination through coagulation and adsorption

TOC mg dm ⁻³ raw water	TOCINV mg dm ⁻³		
	Chlorination	Coagulation	Coagulation and adsorption
6.2	2.5	1.30	0.23
7.8	4.0	2.08	0.03

CONCLUSIONS

The studies hereby referred to are concerned with the influence of the precursors concentration, chlorine dose, contact time temperature and pH are TOCINV formation with regard to quantity and rate of occurrence when using synthetic waters as well as raw surface water.

TOCINV quantity and rate of occurrence increases with the chlorine dose, contact time, organic content and temperature.

A minimum chlorine does to be added in the process of water treatment has to be established, since chlorine excess results in toxic compounds that might endanger the lives of human consumers.

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