



Removal of Trihalomethans in Tehran Drinking Water by an Advanced Oxidation Process

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Abstract

Due to growing population and increasing contamination of surface and ground water, it is necessary to protect public health by drinking water disinfected with chlorine, the most common method of disinfection. Despite enormous benefits of the chlorination method, there are also disadvantages to human health. Disinfection by-products cause a variety of diseases like cancers in humans. The main group of these by-products is THMs. Different methods such as Adsorption, Air Stripping Packed-Column, Nano-filtration, and Granular Activated Carbon have been applied to eliminate THMs from water resources. In this study, Advanced Oxidation Process (AOP) method is used to reduce the contamination of THMs in Tehran drinking water. EPA method 551/1 was used for quantitating the analysis of trihalomethane compounds applying a gas chromatography equipped with an ECD detector. AOP method was performed in a photoreactor equipped with 4 UV lamps. The effects of UV radiation, concentration of hydrogen peroxide, and amount of ZnO nanocatalyst on oxidation reaction of THMs have been investigated. Results show that an optimum amount of hydrogen peroxide with and without applying the catalyst was 5 mL of concentrated solution (30%), and the optimum amount of catalyst with this amount of hydrogen peroxide was 0/5 g in 100 ml of drinking water samples with constant reaction time (1hr) and UV irradiation. The yield of THMs removal reaction in these conditions has been determined 91.78 %. One of the most important superiority of this method, in comparison with other THMS removing methods, is the reduction of THMs contamination of drinking water in trace amounts.

Keywords: Disinfection by-products–THMs–AOP–ZnO nanocatalyst–hydrogen peroxide

1. INTRODUCTION

Chlorine was accepted to disinfect the treatment of drinking water in early 1900s. Because of the chlorination, it has dramatically reduced the incidence of waterborne diseases and improved the quality of life. (Ellis, 1991, Calderon, R. L. 2000.) Unfortunately, an unwanted side effect was the formation of harmful by-products upon chlorination. The most significant group of disinfection by-products (DBPs) formed during chlorination is the trihaloromethanes (THMs). Compounds of this group—chloroform, bromodichloromethane, chlorodibromomethane, and bromoform were recognized as potential human or animal carcinogens (Bull and Kopfter, 1991; U.S.EPA, 1991, Gordon, Gilbert, William J. Cooper, 1987). THMs are formed by the aqueous chlorination of humic substances, of soluble compounds secreted from algae, and of

naturally occurring nitrogenous compounds. THMs consist primarily of chloroform, bromodichloromethane, dibromochloromethane, and bromoform. Concentration of THMs in drinking-water varies widely and ranges from not-detectable to 1 mg/liter or more. Formation of THMs can be minimized by avoiding pre-chlorination and effective coagulation, sedimentation, and filtration to remove organic precursors before final disinfection. Removal of THMs after their formation is difficult and involves resource-intensive processes, such as activated carbon adsorption, air stripping, or advanced oxidation process methods. (IARC, 1991; Morris, 1982; Canada, 1993, Bull R.J., Kopfler F.C. 1991)

Oxidation is defined as the transfer of one or more electrons from an electron donor (reductant) to an electron acceptor (oxidant) having a higher affinity for electrons. The electron transfers result in the chemical transformation of both the oxidant and the

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reductant and, in some cases, producing chemical species with an odd number of valence electrons. These species, known as radicals, tend to be highly unstable and, therefore, highly reactive because one of their electrons is unpaired. Oxidation reactions that produce radicals tend to be followed by additional oxidation reactions between the radical oxidants and other reactants (both organic and inorganic) until thermodynamically stable oxidation products are formed (Dorfman and Adams, 1973). "Advanced Oxidation Techniques" (AOPs) are promising techniques to efficiently and effectively convert these compounds into better biodegradable or less harmful substances. Several types of AOPs are being developed. Often these techniques are based on ozone, hydrogen peroxide, UV irradiation, and combinations of these techniques. Advanced Oxidation Processes are based on these natural processes. They mainly rely on the formation of reactive and short-lived oxygen containing intermediates, such as hydroxyl radicals ($\bullet\text{OH}$). These radicals are formed under the influence of UV irradiance, and they are powerful, non-selective oxidants which can be used to convert also those compounds that are not sensitive to photolysis (Oppenländer 2002, Reckhow, D., 1999, Sierka, R., Amy, G., 1985).

EPA 500 series methods are a number of extracting and analyzing methods for these by-products. 551.1 EPA method is intended as a stand-alone procedure for either the analysis of only the Trihalomethans (THMs) or for all the chlorination disinfection by-products (DBPs) with the chlorinated organic solvents and gas chromatography. Methyl-t-butyl ether (MTBE) is recommended as the primary extraction solvent in this method. However, due to safety concerns associated with MTBE and the current use of pentane by some laboratories for certain method analyses, pentane is offered as an optional extraction solvent for all analyses except chloral hydrate. (G.A 1977 and Hodgeson, J.W., Cohen, A.L.1988,)

2. MATERIALS & METHODS:

2.1 Drinking water characterization:

The drinking source water was taken from water tap in 3 areas in north, west, and east of Tehran according to EPA 551.1 method. Two sets of 60 mL vials were prepared for sampling. 1, 1-dichloro-2-propanone was added to samples as a dechlorinating agent. All samples collected were duplicated and chilled to 4°C on the day of collection and maintained at that temperature until analysis.

2.3 Experimental design and analytical methods:

In this study, advanced oxidation process (AOP) method was used to reduce contamination of THMs in Tehran drinking water. The experiments were conducted in a UV-reactor whereby samples were decanted to a quart tube surrounded by 4 UV lamps in the reactor corners (figure 1). The 3 treatments examined were UV- H_2O_2 , UV- several amount of ZnO nanocatalyst using optimum amount of H_2O_2 , and UV- several amount of H_2O_2 by applying an optimum amount of ZnO nanocatalyst. For each treatment 100 ml of samples was affected by 4 UV lamps in 1 hour.

In the first treatment 3, 5, and 7 ml of H_2O_2 , and in the second one, 0.25g, 0.5g, 0.75g, and 1g of ZnO nanocatalyst were examined by applying an optimum amount of H_2O_2 according to the first treatment result. In addition, in the last treatment, 3, 5, and 7 ml of H_2O_2 were tested applying an optimum amount of ZnO according to previous treatment result.

After each treatment, if samples had suspended particles of ZnO nanocatalyst, a centrifuge was used for depositing and was added to 60 mL vials in which they were prepared for analyzing.

THM analysis was performed using a Chrompack CP 9001 series Gas chromatography equipped with electron capture detectors. EPA 551.1 was selected as an analytical method.

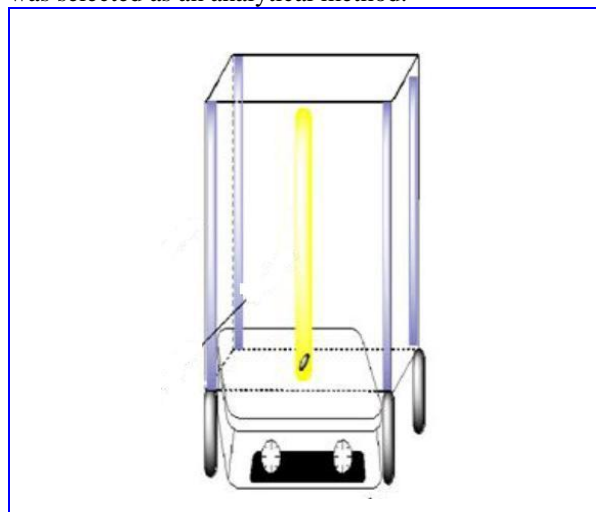


Fig. 1: photoreactor

2.4 The synthesis of ZnO nanoparticles process:

ZnO nanocatalyst was synthesized according to sol-gel method. In this process, 1 mol $\text{Zn}(\text{NO}_3)_2$ and

2mol (NH₂)₂CO Were dissolved in de-ionized water. By ammonia, solution's pH was raised to 7 in the water bath for 4 hours. At this time, the solution became a white gel. Then, it was burned in an auto-combustion process. In the end, the powder made in the previous step was placed in an oven at 600 ° C for 2 hours.

Trihalomethans concentrations were examined in 3 area of Tehran. The highest amount of THMs is related to west of Tehran in Gisha street. In Gisha's samples, THM concentration was 21.91 ppb, and these samples were used for AOP tests in next steps (Chromatogram 1).

3. RESULTS

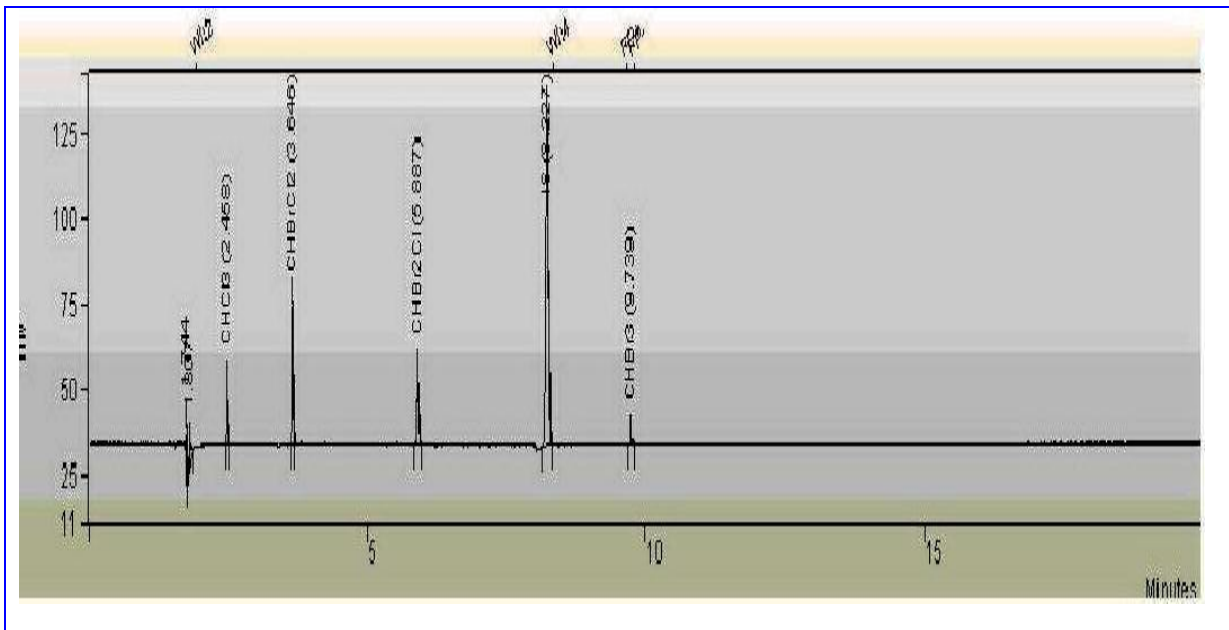


Fig. 2. Chromatogram 1- Gisha's samples

An optimum amount of H₂O₂ without applying nanocatalyst, was 5 ml, and THM concentration reduced to 5.04 ppb. (Table1) (Chromatogram 2).

Table 1. Optimum amount of hydrogen peroxide without applying catalyst

$X = \frac{C_{a0} - C_a}{C_{a0}} \times 100$	C_a ($\mu\text{g/L}$)	C_{a0} ($\mu\text{g/L}$)	H ₂ O ₂ (ml)	Time
%68.86	6.86	21.9	3	1hr
%77	5.04		5	
%74.44	5.60		7	

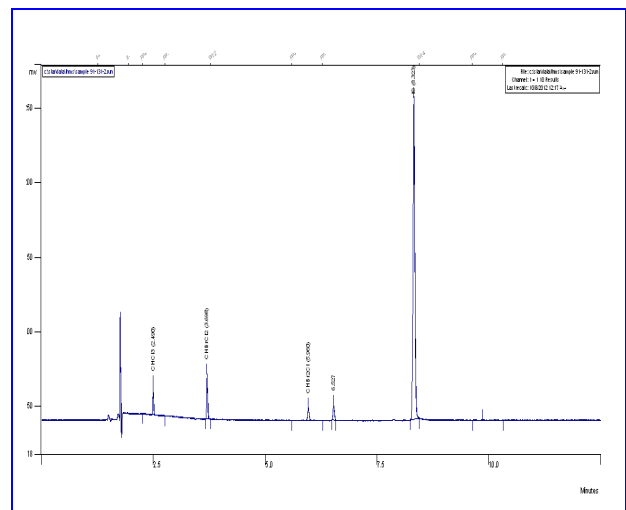


Fig 3. Chromatogram 2: The result of Optimum amount of H₂O₂ without applying nanocatalyst (5 ml) samples

An optimum amount of ZnO nanocatalyst, by applying an optimum amount of Hydrogen peroxide, was 0.5g, and THMs concentration reduced to 1.80 ppb. (Table 2) (Chromatogram 3).

Table 2. optimum amount of ZnO

$X = \frac{C_{a0} - C_a}{C_{a0}} \times 100$	C_a ($\mu\text{g/L}$)	C_{a0} ($\mu\text{g/L}$)	H_2O_2 (ml)	catalyst (g_{cat})	Time
% 87.31	2.78	21.91	5	0.25	1hr
91.78 %	1.80			0.5	
78.50 %	4.71			0.75	
76.90 %	5.06			1	

The optimum amount of H_2O_2 , by applying an optimum amount of ZnO nanocatalyst, was 5 ml, and THMs concentration reduced to 1.80 ppb (Table 3) (chromatogram 3).

Table 3. optimum amount of hydrogen peroxide with applying catalyst

$X = \frac{C_{a0} - C_a}{C_{a0}} \times 100$	C_a ($\mu\text{g/L}$)	C_{a0} ($\mu\text{g/L}$)	H_2O_2 (ml)	catalyst (g_{cat})	Time
%63.35	8.03	21.91	3	0.5	1hr
%91.78	1.80		5		
%76.54	5.14		7		

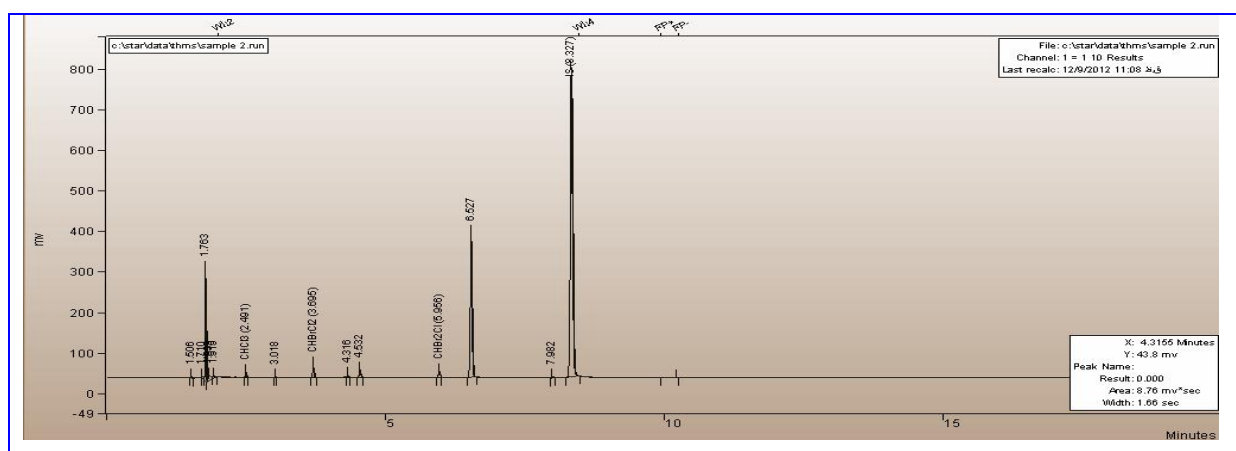


Fig. 4: Chromatogram 3: The result of the optimum amount of ZnO nanocatalyst by applying an optimum amount of Hydrogen peroxide (0.5 g), and an optimum amount of H₂O₂ by applying an optimum amount of ZnO nanocatalyst (5 ml) samples

4. DISCUSSION

The highest percentage of THM removal was 91.78 % related to 5ML Hydrogen peroxide and 0.5g ZnO nanocatalyst in each 100 ml Gisha’s tap water samples (Table 4). Reduced efficiency was caused by recombination of hydroxyl radicals, the most important factor in AOP method. This recombination occurs when we have an extra amount of hydrogen peroxide than an optimum amount. The other cause of efficiency reduction is related to a high amount of suspended nanoparticles which reducing UV radiation to a radical hydroxyl and declined the oxidation process. (Chart1-3)

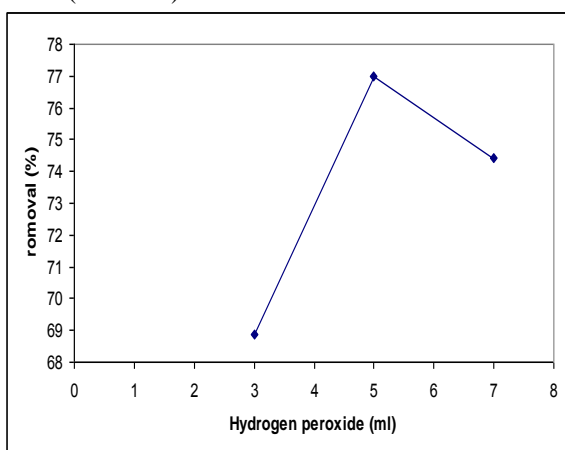


Chart 1: The removal percentage according to Hydrogen peroxide amounts (without nanocatalyst)

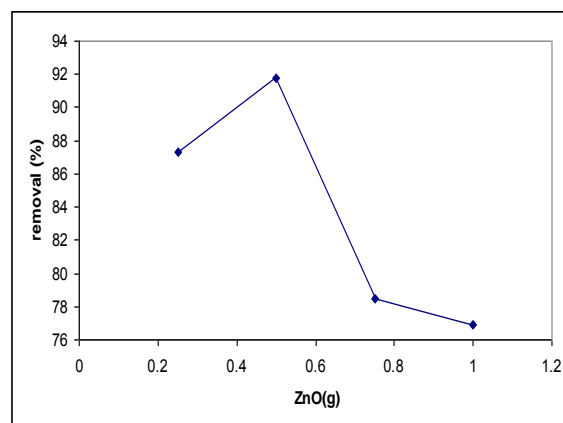


Chart 2: The removal percentage according to Nanocatalyst amounts

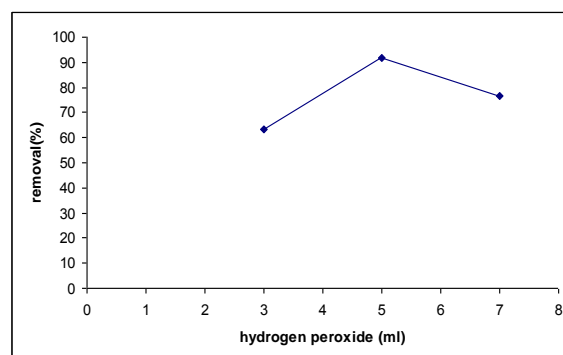


Chart 3 : The removal percentage according to Hydrogen peroxide amounts (with catalyst)

Table 4: determination of optimum amount of hydrogen peroxide and catalyst for 100 ml of tapwater sample in oxidation process

$X = C_{a0} - C_a / C_{a0} \times 100$	C_a ($\mu\text{g/L}$)	C_{a0} ($\mu\text{g/L}$)	H_2O_2 (ml)	catalyst (g_{cat})	Time
87.31 %	2.78	21.91	5	0.25	1 hr
91.78 %	1.80			0.5	
78.50 %	4.71			0.75	
76.90 %	5.06			1	
63.35 %	8.03		3	0.5	
76.54 %	5.14		7		
68.86 %	6.86		3		
77 %	5.04		5		
74.44 %	5.60		7		

5. CONCLUSION

The most important achievement of this research is reducing the total amount of Trihalomethans contamination in drinking water (in Gisha Street) to low concentrations (21.91 ppb to 1.8 ppb) with high efficiency (91.78%) which is not possible in any of the methods listed.

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