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The Effects of Water Ozonation on Disinfection by-Product Formation

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Abstract

Background: The aim of this study was to evaluate the performance of water ozonation on disinfection by-product formation.

Methods: Experiments were carried out on samples taken from Tajan River, Mazandaran province, Iran. Samples of the pre-filtered raw water and from the 3.5-L water tank reservoir (WT) were analyzed for UV-254 absorbance, dissolved organic carbon (DOC), HS and non-HS, chlorine residual, Simulated Distributed System Total Trihalomethanes (SDS TTHMs) and SDS halo acetic acids (SDS HAAs). The gaseous ozone concentration was varied between 1.5 and 10g/m3.

Results: The study showed that use of the ozonation treatment system resulted in significant improvement in water quality compared to the filtered raw water and the levels of DOC, moreover UV absorbing compounds, SDS TTHMs and SDS HAAs were reduced.

Conclusion: Ozonation treatment system can be used instead of other disinfection systems such as chlorination which have potential of Disinfection By-Products (DBPs) formation.

Keywords: Ozonation; DBPs; Formation; Disinfection.

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Introduction

Drinking water safety has received great attention around the world because huge numbers of disinfection by-products (DBPs) have emerged.[1] Disinfection byproducts (DBPs) are a group of chemical compounds formed during the disinfection process.[2] The formation of DBPs in drinking water has caused serious public health concerns since the discovery of chloroform in chlorinated waters.[3] Natural organic matter (NOM) (a complex mixture of many chemical groups, including humic substances, simple carboxylic acids, amino acids, proteins, and carbohydrates) is the main precursor of DBPs,[4] and it can react with chlorine and form trihalomethanes (THMs) and halo acetic acids (HAAs).[5] In detail, THMs including chloroform and Bromo-dichloro -methane (BDCM) are both regulated at 60 μg/L, while dibromochloromethane (DBCM) and bromoform are required to stay below 100 μg/L according to Drinking Water Standards (GB5749-2006) in China.[6] Meanwhile, the dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) were also controlled at 50 and 100 μg/L, respectively.[6] The World Health Organization has suggested guideline values of 20 μg/L for Dichloro-aceto- nitrile (DCAN) and 70 μg/L fordibromoacetonitrile (DBAN).[6] The formation of DBPs in water systems has raised growing attention because of their potentially adverse health effects, e.g., cancer and reproductivedefects, in the past several decades.[7] In conclusion, the control of DBPs including regulated THMs, HAAs and HANs in drinking water treatment is very important to public health.

Ozone has been proven to be able to decrease the concentration of DBP precursors[8] and number of microorganisms[9], react with organic substances and increase their biodegradability.[10] The increase of ozone dosages may be resulted in a concomitant decrease in the concentrations of THMs and HAAs formed from subsequent chlorination.[11] Ozonation results in the formation of more polar compounds and an increase in the biodegradability of the chemicals found in the water as compared to that generated with chlorination. Ozone is an excellent disinfectant and is able to inactivate even more resistant pathogenic microorganisms such as protozoa (Cryptosporidium parvum oocysts) where conventional disinfectants (chlorine, chlorine dioxide) fail.[12] However, the ozone exposure required to inactivate these microorganisms is quite high.[13] This may lead to the formation of excess concentrations of undesired disinfection by-products, in particular bromate, which is considered to be a potential human carcinogen.[13,14] Bromate is particularly problematic because unlike many other organic by-products it is not biodegraded in biological filters which usually follow an ozonation step.[15] Therefore the aim of this study was to evaluate the performance of water ozonation on disinfection by-product formation.

Materials and Methods

A Teflon® tubing and stainless steel and valves were used throughout the system. Figure 1 shows the schematic representation of the ozonation disinfection system. Other components included: 3.5-L water-jacked glass reservoirs made of Pyrex glass and a simple mixer (Salemab, Iran). For ozone generation pure oxygen gas (99.9%) from a pressurized cylinder was dried using a molecular sieve trap, and then fed to the ozone generator (Model X23 Salemab, Iran). Varying the voltage applied to the ozone generator controlled the gaseous ozone concentration. The excess gas was vented after passing the gas through a 2% potassium iodide (KI) solution to destroy any residual ozone gas. The water level in the 3.5-L reservoir was maintained at a constant level during the experiments using a peristaltic pump (PHP 502 Pump, Salemab, Iran). A constant water temperature of 20°C was maintained using a recirculating water system. The gaseous ozone concentration was 2 g/m3.

Samples of the pre-filtered raw water (feed raw water) and from the 3.5-L water tank reservoir (WT) were analyzed for UV-254 absorbance, dissolved organic carbon (DOC), HS and non-HS, chlorine residual, simulated distributed system total trihalomethanes (SDS TTHMs) and SDS halo acetic acids (SDS HAAs). The gaseous ozone concentration was varied between 1.5 and 10 g/m3. After the optimization by factorial design, the ozonation were applied in the treatment of pre-

filtered raw water using a batch wise mode. For this, different scenarios were tested with regard to ozone concentration of 1.5, 5 and 10 g/m3 and contact times of 0 and 6 hours.

Experiments were carried out on samples taken from TajanRiver, Mazandaran Province, Iran. The samples were taken from the middle of river and from a depth of 30 cm. The maximum storage period was 3 days. Water samples were pre-filtered through a 0.45-μm mixed Millipore filter before testing.

The experiments were carried out in a batch mode reactor (1.14 L) in a water bath (20 ± 2°C). The synthetic water was added into the reactor firstly before a saturated ozone solution was added by using a syringe through septa on the top of the reactor (16). The saturated ozone solution (at about 30 mg /l) was prepared freshly by continuously bubbling ozone-containing oxygen gas (from an ozone generator (Model X23 Salemab, Iran) into cold de-ionized water (at 4°C) using a diffuser. The respective volumes of the simulated natural water and saturated ozone solution were determined by the required ozone dosage (ranging from 0 to 6 mg /l). The reaction will last for 20 min (16 and then 5 min of nitrogen stripping were used to quench the residual O3 (16). One aliquot of sample filtered with a 0.45 μm membrane was taken for the analysis of bromide, bromate, UV254, and DOC. Another aliquot of sample was taken forformation potentialsdetermination of the concerned DBPs according to the uniform formation conditions (UFC) protocol.[17] After incubation for 24 h, a stoichiometric amount of sodium thiosulfate was added to quench the residual chlorine.

The absorbance of ozone in the gas phase was measured at 254 nm with a biomate 3S spectrophotometer (Thermoscientific, US) with Split-beam; Quartz Coated optical design. An extinction coefficient of 3000/M.cm [11] were used to calculate the ozone concentration. The UV absorbance of the water samples was measured at a wavelength of 254 nm with a biomate 3S spectrophotometer (Thermoscientific, US). DOC was analyzed using an 8 port sampler for TOC analyzer (Shimadzu, Japan). The TOC analyzer uses the UV/persulfate method (Standard Method, 2005). The humicsubstances (HS) and non-humic substances (non-HS) in the samples were isolated from the water samples by adsorption on XAD-8 resin according to Method 5510C.[18] Chlorine residual was measured using the Iodometric method, method 4500B.[18]

Water samples were dosed with a chlorine concentration that ensured a residual chlorine concentration in the range of 0.5-2 mg/L according to the procedures in standard method 2350.[18] The THM compounds, chloroform (CHCl3), bromodichloromethane(CHBrCl2), dibromochloromethane (CHBr2Cl), and bromoform (CHBr3), were extracted from the water samples using hexane and analyzed by gas chromatography (method 5710, .[19] A GC-2010 plus High-end gas chromatograph (Shimadzu, Japan) equipped with an electron capture detector (ECD), an auto-sampler, and a 30 m×0.25 mm ID, 1 μm DB-5ms column (Shimadzu, Japan) was used for the analysis. The oven temperature was ramped from 60 to 130°C at a rate of 8°C/min. The flow rate of the carrier gas (N2) was 12.0 mL/min. The injector and detector temperatures were 265 and 330°C, respectively.

SDS HAAs were produced by chlorination as described above. The concentrations of monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), trichloroacetic acid (TCAA), and dibromoacetic acid (DBAA) were determined using US EPA method 552.2. A GC-2010 plus High-end gas chromatograph (Shimadzu, Japan) equipped with an electron capture detector (ECD), an auto-sampler, and a 30 m×0.25 mm ID, 1 μm DB-5ms column (Shimadzu, Japan) was used for the analysis. The oven temperature was programmed to hold for 13 min at 31°C, then increased to 72 C at a rate of 4.3 °C/min and held 5 min, then increased to 92°C at a rate of 4.3 °C/min. The carrier gas flow was 10 mL/min with the injector and detector temperatures at 195 and 250°C, respectively.

Results

The characteristics of the water are given in Table 1, and table 2 shows the results of water ozonation. All data are reported as a percent decrease as compared to the concentrations present in the raw feed water.

The effects of ozonation time on the removal efficiencies can be observed by comparing the results for permeate 1 and 2 in table 3. Permeate samples were collected in covered bottles and stored in cool box. The first 500mL of permeate collected was labeled as P1 and the latter 1000 ml as P2. P1 and P2 samples were collected to study the effect of ozone contact time on the water quality.

Discussion

The apparatus illustrated in Fig. 1 was used for this experiment. As the table 2 shows, ozonation was more effective on removal of SDS TTHMs and SDS HAAs dissolved organic carbon, humic substances and non humic because of more degradability of these compounds. The table also shows variations in the gaseous ozone concentration (over the range from 1.5 to 10 g/m3) had little effect on the extent DOC and other compounds removal. An explanation for the behavior is is based on the dosages used in this experiment, only a small fraction of the DOC is mineralized (converted to CO2 and water) and that ozone simply converts larger molecules into smaller ones, which then pass through the membrane. Study has been done by Wang et al (2014) confirmed the results.[16]

The longer ozone contact time did not result in a large increase in the removal efficiency for UV-254 (62.3% vs. 73.6%), suggesting that most of the UV-254 absorbing material were degraded in the time necessary to collect the first 500mL of sample (i.e., within 6-7 h). On the contrary, the removal efficiencies of DOC, SDS TTHMs, and SDS HAAs for permeate 2 were roughly twice that for permeate 1, indicating that the reaction of ozone with TTHM and HAA precursors is slower than ozone with UV-absorbing materials.[17,18] a. SDS THM and SDS HAA were measured using standard method 5710 and US EPA method 552.2, respectively. The values are reported in actual concentration values (Mean ± S.D) n= 6, duplicate experiments with each analysis run in triplicate

Table 1. Characteristics of Tajan River water

Parameters	Value	Parameters	Value
TOC (mg/L)	6.8–10.1	SDS THMs[a] (µg/L)	175
pH	7.2–7.5	SDS HAAs[a] (µg/L)	60
Alkalinity (mg/L as CaCO3)	120–132	BDOC (mg/L)	0.86–2.9
UV-254 (abs.)	0.132–0.155	Nitrate (mg/L)	0.23
Total phosphate (mg/L)	0.04	Hardness (mg/L as CaCO3)	158–171

Table 2.Effect of water ozonation on DBPs formation

Parameter	Effect of ozone doses[a], (natural pH 7.2–7.5)		
	10	2.5	1.5
UV-254 (abs)	0.12± 0.008	0.12± 0.008	0.12± 0.008
Dissolved organic carbon (mg/L)	13.5±0.42	14.3±0.31	14.5±0.24
Humicsubstances (mg/L)	6.1± 0.29	6.5± 0.17	6.4± 0.35
Non humicsubstances (mg/L)	3.5 ± 0.76	3.8 ± 0.54	3.8 ± 0.97
SDS TTHMs (mg/L)	231±0.75	233.6±0.42	238.2±0.68
SDS HAAs (mg/L)	78.92± 0.36	79.12± 0.21	79.51± 0.44

Table 3. Comparison of parameter for the evaluation of ozonation performance

Parameter	Feed raw water initial values	Permeate 1 (% reduction)	Permeate 2 (% reduction)
UV-254 (abs)	0.12± 0.008	62.3 ± 5.6	72.6± 3.7
Dissolved organic carbon (mg/L)	13.5±0.42	19.9 ± 0.26	71.6±2.4
Humiccubstances (mg/L)	6.1± 0.29	39.6± 2.5	51.5±5.6
Non humicsubstances (mg/L) (% increase)	-3.5 ± 0.76	-13.6±0.52	-17.2± 0.64
SDS TTHMs (mg/L)	231±0.75	16.8±2.3	32.1±3.1
SDS HAAs (mg/L)	78.92± 0.36	11.8±0.69	20.7±2.4
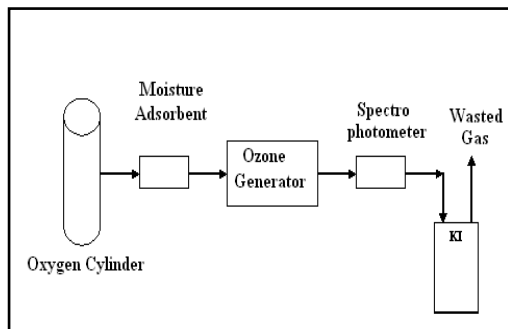
Figure 1. Schematic representation of the ozone disinfection system

Increasing the gaseous ozone concentration from 1.5 to 2.5 g/m3 resulted in an increasing the percent reduction of both UV-254 in the P1 samples, suggesting that, at the lower ozone gas concentration, the ozone dosage was not sufficient to remove the reactive UV-254 absorbing compounds.

The study showed that the use of ozonation treatment system resulted in significant improvements in water quality ascompared to the filtered raw water and the levels of DOC, UV absorbing compounds. SDS TTHMs and SDS HAAs were also reduced.

Acknowledgements

Conflict to Interest

The authors declare that they have no conflict of interest.

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