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Advanced Oxidation Process for Haloacetic Acid Removal in Tehranpars Water Treatment Using CuO Nanocatalyst

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Abstract

Potentially harmful disinfection byproducts (DBPs), as a significant challenge in water treatment, are formed when oxidizing disinfectants react with natural organic matters (NOM). Unfortunately, an unwanted side effect is the formation of harmful by-products, such as THMs and HAAs, following the chlorination stage. DBPs cause a variety of diseases like cancer in humans. In this study, the Advanced Oxidation Process (AOP) method was used to reduce HAA contamination in Tehranpars Water Treatment Plant. The EPA Method 552/2 was used for detecting HAA compounds by gas chromatography equipped with an ECD detector. The AOP method was performed in a photoreactor equipped with 4 UV lamps. The effects of UV radiation, the concentration of hydrogen peroxide, level of pH, reaction time, number of UV lamps, and amount of CuO nanocatalyst on the oxidation reaction of HAA were investigated. The results showed that the annual mean levels of DCAA and TCAA in Tehranpars tap water were 0.0526 and 0.232, respectively. The optimum level of CuO nanocatalyst in the AOP process was 0.625 with 99.79% removal of DCAA and 99.22% removal of TCAA. The removal percentage increased with increasing treatment time, hydrogen peroxide level, and the number of the UV lamp at neutral and alkaline pH.

Keywords: *Advanced oxidation process, CuO, Disinfection by-products, Chlorination, Haloacetic acids.*

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Introduction

The supply of disinfected water is necessary to protect human health, causing a significant reduction in mortality and infectious diseases. However, the reaction of disinfectants, especially chlorinated compounds, with natural organic matters, bromide, and iodide in water forms DBPs, which are carcinogens. Haloaceticacids (HAAs) are among the most predominant classes of chlorination byproducts and thus are good indicators of the total DBPs in chlorinated water. Due to their potentially deleterious impacts on human health, great attention has been given to HAAs in recent years, and many national or international agencies have set regulations to reduce these hazardous materials in water [1]. According to Richardson (2003), the potential DBPs, as a major concern in water treatment, are formed when oxidizing disinfectants react with natural organic matters (NOMs).

DBPs are a group of chemical contaminants formed in water during the disinfection process. Many DBPs are formed by the reaction between chlorine and natural organic matters in the water (e.g., humic and fulvic substances). Two major groups of DBPs are trihalomethanes (THMs) and haloacetic acids (HAAs). Both THMs and HAAs are the most prevalent class of DBPs, second to trihalomethanes (THMs) in water disinfected by chlorine compounds [1]. HAAs are potentially carcinogenic substances. Currently, four THMs (THM4, chloroform, dibromochloromethane, bromodichloromethane, and bromoform) and five HAAs (HAA5, monochloacetic acid, monobromoacetic acid, dichloroacetic acid, dibromoacetic acid, and trichloroacetic acid) are the U.S. EPA regulated [2]. Compounds of THMs-chloroform, bromodichloromethane, chlorodibromomethane, and bromo form were recognized as potential human or animal carcinogens [3-5].

Haloacetic acids are potentially carcinogenic substances. They are also toxic to aquatic organisms. Trichloroacetic acid and monochloroacetic acid are also phytotoxic and have been used as herbicides until the late 1980s. Haloacetic acids are naturally formed in the atmosphere during the photochemical degradation of chlorinated solvents. Besides, they are regarded as disinfection byproducts resulted from the addition of a chlorine compound, such as hypochlorous acid, hypochlorite, or dichlorine, to water or wastewater for disinfection purposes. Reactions between natural organic matter and chlorine compounds produce haloacetic acids at ppt to ppb ranges in drinking water distribution systems and at ppb to ppm ranges in wastewater. Due to the concern over the carcinogenicity of haloacetic acids, the United States Environmental Protection Agency regulated the allowable concentration of haloacetic acids in drinking water as a part of the Disinfectants and Disinfection Byproducts Rule promulgated in 1998. HAA5, which is expressed as the sum of the concentrations of these acids, is currently limited to 60 ppb [6].

To date, a wide range of analytical methods has been used to analyze an individual HAA or a group of HAAs. These include gas chromatography (GC), liquid chromatography (LC), and ion chromatography (IC). Gas Chromatography-Electron Capture Detector or GC-ECD is the most widely used technique with five approved methods set by the US EPA: the US EPA Method 552.1 (1992), the US EPA Method 552.2 (1995), the US EPA Method 552.3 (2003), the Standard Method 6251 (APHA, 1998) and most recently US EPA Method 557 (2009), which is for detection of haloacetic acids, bromate and dalapon in drinking water by ion chromatography-electrospray ionization tandem mass spectrometry (IC-ESI-MS/MS). In the first four methods, HAAs were extracted from water samples using either methyl tert-butyl ether (MTBE) or anion exchange resins and then converted to their methyl esters using acidic methanol or diazomethane. The GC/ECD US EPA methods are typically reliable and accurate with detection limits for the nine HAAs in the low μg L-1 range but are very labor-intensive due to the extensive extraction procedures [7].

To reduce HAAs, intensive efforts are currently made to remove DBPs precursors and alternative disinfectants are used to yield less regulated DBPs. On the other hand, much fewer efforts have been made on the treatment of HAAs after their formation, such as granular activated carbon, biodegradation, advanced oxidation, zero-valent iron reduction, and electrochemical removal [8]. Oxidation is defined as the transfer of one or more electrons from an electron donor (reductant) to an electron acceptor (oxidant), which has a higher affinity for electrons. The electron transfer (ET) results in the chemical transformation of both the oxidant and reductant and, in some cases, the production of chemical species with an odd number of valence electrons.

These species, known as radicals, tend to be highly unstable and, therefore, highly reactive because of having an unpaired electron. Oxidation reactions that produce radicals tend to be followed by additional oxidation reactions between the radical oxidants and other reactants (both organic andinorganic) until thermodynamically stable oxidation products are formed [9]. Advanced oxidation processes (AOPs) were first proposed for potable water treatment in the 1980s. AOPs are defined as the oxidation processes involving the generation of hydroxyl radicals (OH·) in a sufficient quantity to affect water purification. Later, the AOP concept was extended to the oxidative processes with the sulfate radical anion (SO_4^{2-}). Different from common oxidants, such as chlorine and ozone that have a dual role of decontamination and disinfection, AOPs are applied primarily for the destruction of organic or inorganic contaminants in water and wastewater. Although AOP inactivation of pathogens and pathogenic indicators have been studied, they are rarely employed for disinfection because these radicals have a too short half-life (on the order of microseconds), so that the required detention times for disinfection are prohibitive due to extremely low radical concentrations. When AOPs are applied for wastewater treatment, these radicals, as a powerful oxidizing agent, are expected to sufficiently destruct wastewater pollutants, and transform them into less and even non-toxic products, thereby providing an ultimate solution for wastewater treatment [10]. AOPs, such as TiO2 photocatalysis, rely on the production of nonspecific radical species, which are capable of oxidizing a wide array of contaminants [11].

Experimental

Drinking-Water Characterization

The sample drinking water was tap water in Tehranpars according to EPA 552.2 method in 4 seasons. The average amounts of DCAA and TCAA were examined and the samples prepared for AOP according to average concentration.

Experimental Design and Analytical Methods

In this study, the AOP method was used to reduce the contamination of HAA in Tehran drinking water. The experiments were conducted in a UV-reactor, whereby the samples were decanted to a quart tube surrounded by 4 UV lamps (UV-C) (Figure 1).

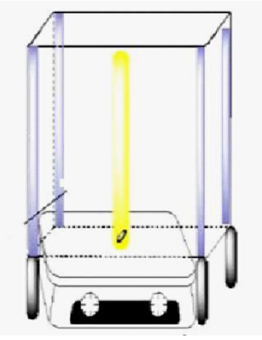

Figure 1. Sketch of photo reactor.

In the reactor corners, different parameters including pH, the number of UV lamps, time, amount of hydrogen peroxide, the amount of CuO nanocatalyst were assessed to achieve optimum levels for DCAA and TCAA removal. For each treatment, 100 ml of the sample was exposed to different parameters according to the experimental design (Table 1).After each treatment, if the sample had suspended particles of CuO nanocatalyst, it underwent a centrifuge process to collect the deposition, which was then added to 60 mL vials to prepare it for the analysis. Residual amount of CuO nanocatalyst was reusable but removal percentage was decreasing after each reuse.

HAA analysis was performed using a Chrompack CP 9001 series gas chromatography equipped with electron capture detectors. EPA 552.2 method was selected as an analytical method.

Summary of the EPA 552.2 method

Forty mL of the sample volume was adjusted to pH<0.5 and extracted with 4 mL of MTBE. The HAAs partitioned to the organic phase were then converted into their methyl ester derivatives by adding 10% v/v (H2SO4 in methanol) and heating gently. The acidic extract was neutralized in a reverse extraction by a saturated bicarbonate solution and the target analytes were identified and measured using the gas chromatograph equipped with capillary columns and an electron capture detector (GC/ECD). The analytes were quantified employing standard calibration.

Results and discussion

The 4-season average amounts of DCAA and TCAA in Tehranparstap water were 0.0526 and 0.232, respectively. Average TOC level was79 mg/l. The optimum amount of CuO nanocatalyst in the AOP process was 0.625 with 99.79% removal for DCAA and 99.22% removal for TCAA (Table 2).

Table 1. Experimental design.

Test number	CuO nano Catalyst (g)	Time (min)	H_2O_2 (Ml)	UV(Number of UV-C lamps)	PH
1	0.25	30	2	2	9
2	1	30	2	2	5
3	0.25	120	2	2	5
4	1	120	2	2	9
5	1	30	10	2	9
6	0.25	30	10	2	5
7	0.25	120	10	2	9
8	1	120	10	2	5
9	0.25	30	2	4	5
10	1	30	2	4	9
11	0.25	120	2	4	9
12	1	120	2	2	5
13	0.25	30	10	4	9
14	1	30	10	4	5
15	0.25	120	10	4	5
16	1	120	10	4	9
17	0.625	75	6	3	7
18	0.625	75	6	3	7
19	0.625	75	6	3	7
20	0.625	75	6	3	7
21	0.625	75	6	3	7
22	0.625	75	6	3	7

23	0.25	75	6	3	7
24	1	75	6	3	7
25	0.625	30	6	3	7
26	0.625	120	6	3	7
27	0.625	75	2	3	7
28	0.625	75	10	3	7
29	0.625	75	6	2	7
30	0.625	75	6	4	7
31	0.625	75	6	3	5
32	0.625	75	6	3	9
33	0.625	75	10	3	7

Table 2. AOP removal results withCuO nanocatalyst.

Test number	**DCAA C_{a0}**	**DCAA C_a**	**TCAA C_{a0}**	**TCAA C_a**	**DCAA removal (%)**	**TCAA removal (%)**
	(Mg/L)	**(Mg/L)**	**(Mg/L)**	**(Mg/L)**		
1	0.0526	0.0103	0.232	0.041	80.42%	82.33%
2	0.0526	0.01	0.232	0.038	80.99%	83.62%
3	0.0526	0.0101	0.232	0.039	80.80%	83.19%
4	0.0526	0.0093	0.232	0.039	82.32%	83.19%
5	0.0526	0.0089	0.232	0.044	83.08%	81.03%
6	0.0526	0.0058	0.232	0.039	88.97%	83.19%
7	0.0526	0.0048	0.232	0.031	90.87%	86.64%
8	0.0526	0.0046	0.232	0.029	91.25%	87.50%
9	0.0526	0.0133	0.232	0.068	74.71%	70.69%
10	0.0526	0.0055	0.232	0.027	89.54%	88.36%
11	0.0526	0.004	0.232	0.023	92.40%	90.09%
12	0.0526	0.0053	0.232	0.025	89.92%	89.22%
13	0.0526	0.0039	0.232	0.0229	92.59%	90.13%
14	0.0526	0.0039	0.232	0.0229	92.59%	90.13%
15	0.0526	0.0027	0.232	0.016	94.87%	93.10%
16	0.0526	0.0039	0.232	0.0231	92.59%	90.04%
17	0.0526	0.0016	0.232	0.014	96.96%	93.97%
18	0.0526	0.0016	0.232	0.014	96.96%	93.97%
19	0.0526	0.0016	0.232	0.014	96.96%	93.97%
20	0.0526	0.0016	0.232	0.014	96.96%	93.97%
21	0.0526	0.0016	0.232	0.014	96.96%	93.97%
22	0.0526	0.0016	0.232	0.014	96.96%	93.97%

23	0.0526	0.0039	0.232	0.019	92.59%	91.81%
24	0.0526	0.0027	0.232	0.01	94.87%	95.69%
25	0.0526	0.0049	0.232	0.0011	90.68%	99.53%
26	0.0526	0.0019	0.232	0.008	96.39%	96.55%
27	0.0526	0.0018	0.232	0.0041	96.58%	98.23%
28	0.0526	0.0001	0.232	0.002	99.79%	99.14%
29	0.0526	0.003	0.232	0.0029	94.30%	98.75%
30	0.0526	0.0009	0.232	0.0018	98.29%	99.22%
31	0.0526	0.0028	0.232	0.0025	94.68%	98.92%
32	0.0526	0.0009	0.232	0.0018	98.29%	99.22%
33	0.0526	0.0009	0.232	0.0018	98.29%	99.22%

According to the results, the removal percentage increases with increasing treatment time, hydrogen peroxide content, and the number of UV lamps in neutral and alkaline pH. The possible errors in this study is mixer grade & environment temperature. The efficiency of this method was achieved through the recombination of radical hydroxyls. In comparison with biologically active carbon filtration; this method has high efficiency and suitable removal percentage (Figures 2 and 3).

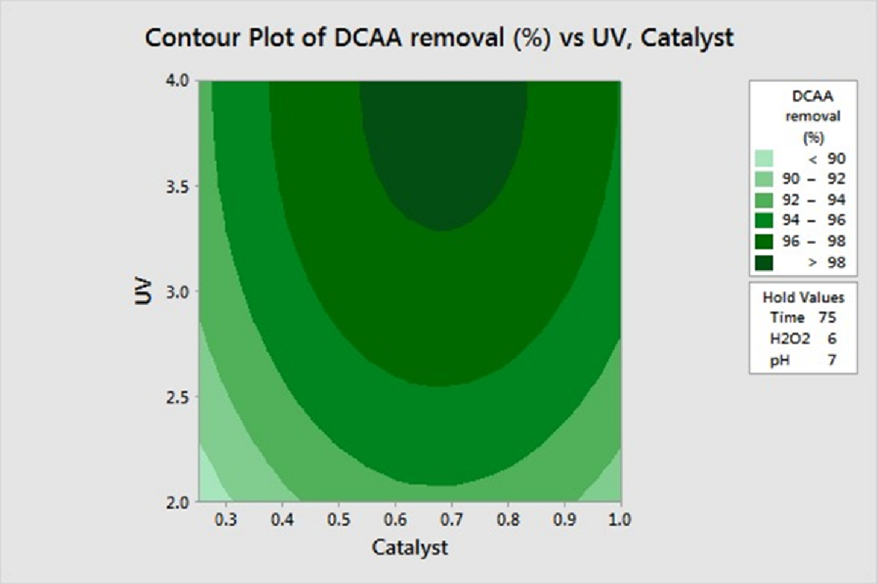

Figure 2. Optimum amount of CuO nanocatalyst for DCAA removal.

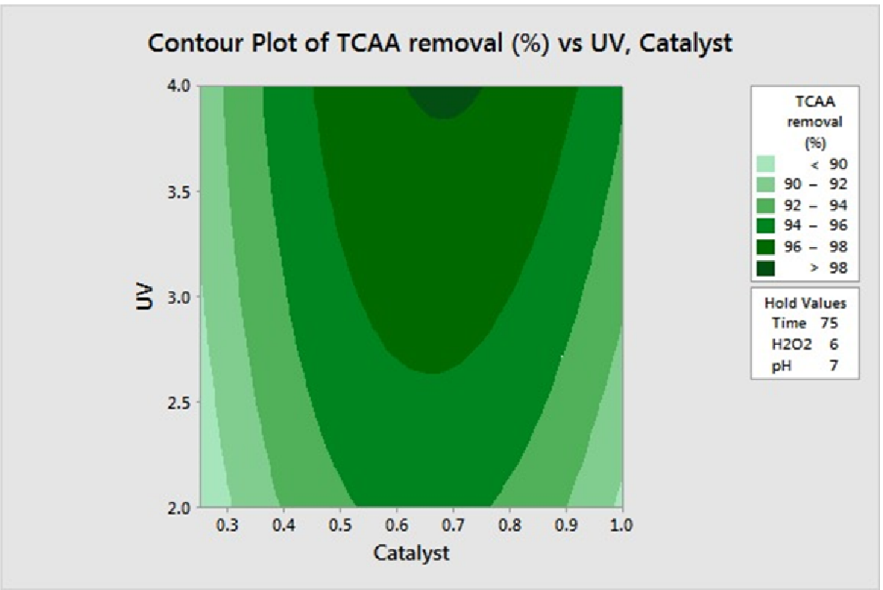

Figure 3. Optimum amount of CuO nanocatalyst for TCAA removal.

Tang and Xie studied biologically active carbon filtration for haloacetic acid removal from swimming pool water. In this study, a biologically activated carbon (BAC) filter was continuously operated on-site for the treatment of haloacetic acids (HAAs) in an outdoor swimming pool at an average empty bed contact time (EBCT) of 5.8 min. Results showed that BAC filtration was a viable technology for direct removal of HAAs from the pool water with a nominal efficiency of 57.7% while the chlorine residuals were 1.71 ± 0.90 mg/L during the study. THMs and TOC were not removed and thus were not regarded as indicators of the BAC filtration effectiveness. Increased EBCT in the range of 4.5 and 6.4 min led to improved HAA removal performance, which could be fitted well by a logarithmic regression model. BAC filtration also affected the HAA speciation by removing more dichloroacetic acid (DCAA) than trichloroacetic acid (TCAA), resulting in a lower ratio of DCAA/TCAA in the filtered effluent. However, the observation of an overall constant ratio could be attributable to a complex formation and degradation mechanism occurring in swimming pools [12].

In some studies, they have reduced the potential of DBPs formation with UV and O3. The efficiency of this method was lower than the suggested method in this study. Chin and Brube studied the removal of disinfection by-product precursors with the ozone-UV advanced oxidation process. In this study, the efficacy of using ozone (O3), ultraviolet irradiation (UV), and the combined O3-UV advanced oxidation process (AOP) to remove 2 classes of DBP precursors from raw surface water samples were assessed and compared. In particular, trihalomethane and haloacetic acid formation potentials were measured. Laboratory batch scale experiments were carried out as a function of ozone and UV dosage to study the removal kinetics. It is concluded that the combined O3-UV AOP was more effective than both the ozone and UV treatment alone. Ozone-UV AOP is capable of mineralizing up to 50% of the total organic carbon from the raw source water at an ozone dose of 0:620:019 mg O3=mL and a UV dose of 1:61Ws/cm^2. Besides, O3-UV AOP can reduce trihalomethane formation potential by roughly 80% and haloacetic acid formation potential by roughly 70% at the same ozone and UV dosage [13].

Kiattisaksiri et al. studied the photodegradation of haloacetonitriles in water by vacuum ultraviolet (VUV) irradiation. In this study, photodegradation of haloacetonitriles (HANs), highly carcinogenic nitrogenous disinfection by-products, in water was investigated in comparison with ultraviolet (UV, only 254 nm) using vacuum ultraviolet (VUV, 185 þ 254 nm). Monochloroacetonitrile (MCAN), dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), and dibromoacetonitrile (DBAN) were species of HANs under investigation. The effect of gas purging and intermediate formation under VUV was examined. The results showed that the pseudo-first-order rate constants for the reduction of HANs under VUV were approximately 2-7 times better than UV. The order of degradation efficiency under VUV and UV was MCAN < DCAN < TCAN < DBAN. The degradation efficiencies of individual HANs under VUV were higher than those of mixed HANs, suggesting competitive effects among HANs. Under nitrogen purging, the removal rate constants of mixed HANs were much higher than those of the aerated condition by 34.4, 34.9, 10.1, and 3.8 times for MCAN, DCAN, TCAN, and DBAN, respectively. The major degradation mechanism for HANs varied depending on HANs species. Degradation intermediates of HANs, such as 2-chloropropionitrile, 2,2-dimethylpropanenitrile, and fumaronitrile, were produced from the substitution, addition, and polymerization reactions. Besides, chlorinated HANs with a lower number of chlorine atoms including MCAN and DCAN were found to be the intermediates of DCAN and TCAN degradation, respectively [14].

Conclusion

CuO nanocatalyst efficiently removed DCAA and TCAA in an advance oxidation process using a photoreactor. The most important result of this research was the high percentage of PPB removal. The optimum amount of CuO nanocatalyst in the AOP process was 0.625 with 99.79% removal for DCAA and 99.22% removal for TCAA .CuO nanocatalyst is a suitable choice to use in AOP methods for removing disinfection by-products. Mixer grade & environment temperature may be errors of this study and can investigate in further experiments.

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