

•OH Mineralization of Sulfadiazine during the Treatment of Algae Bloom Water based on a Drinking Water Treatment System with a Capacity of 500 M³/H

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Abstract: The accumulation of antibiotics in river watersheds and lakes would induce spread of antibiotic resistance genes in drinking water. For the mineralization of sulfadiazine (SD), •OH equipment was installed in a drinking water treatment system with a capacity of 500 m³/h. The •OH was produced by strong ionization discharge combined with water jet cavitation. During the transfer of algae bloom water, in only 20 s, a dose of 1.0 mg/L and 0.5 mg/L •OH completely degraded the SD after coagulation sedimentation and sand filtration, respectively. All algae bloom was inactivated by disinfection with 0.5 mg/L •OH; the 106 drinking water quality indexes satisfied the Chinese Standards; and disinfection by-products, such as bromate was not formed. Based on NaClO disinfection, the total THM content increased to 188 µg/L, which is 2.35 times higher than the concentration limit regulated by United States Environmental Protection Agency (80 µg/L). Advanced •OH oxidation based on strong ionization discharge can be used to completely mineralize antibiotics during drinking water treatment.

1 INTRODUCTION

Antibiotics which occur and accumulate in various of water systems, this condition will generate the spreading of the antibiotic resistance genes which affects human health, and as one of the biggest threats it is taken into consideration by the World Health Organization. Lately, antibiotic contamination in The Jiulong River in China has occurred frequently, while the concentrations have varied from nanograms to micrograms per liter. Beyond that, due to severe eutrophication pollution, river basins and lakes often experience massive blue algal blooms. Nevertheless, the used techniques of the water treatment, like coagulation and sedimentation, sand filtration and chlorine disinfection which cannot continue to play important roles in the remove of antibiotics from algal blooms efficiently. To hold back the separation of antibiotics in humans it is essential to exploit practical therapeutic techniques before getting the available potable water.

Advanced Oxidation Technologies (AOT) refer to the process of generating hydroxyl radical (•OH), after that a series of chain reactions in •OH are triggered. and finally degrading organic pollutants

into CO₂, H₂O and inorganic salts. In Fenton system, •OH completely degrades 0.025 mM sulfadiazine (SD) in glass cells with a diameter of 5.0 cm within 30 minutes, and inactivated 94.7% of *Pseudomonas aeruginosa* cells after 5 minutes in a cylindrical reactor. In the photocatalytic system, •OH degraded 100% pure water SD in 100 mL reactor after 2h., and 100% *Microcystis Aeruginosa* was inactivated after 4 h in 100 mL reactor. whereas, the present small laboratory-scale AOT for antibiotic degradation and algal bloom removal requires a long reaction time.

For this article, •OH mineralization in SD during algal bloom water treatment was completed in a 500 m³/h drinking water treatment system (DWTS) during algal bloom. Because SD is widely used to treat some common bacterial infections in humans, animals and aquatic environments SD was selected to be the representative to show the effects and mechanisms in the degradation of •OH. What's more, we also studied the influence of the •OH disinfection on water quality, algae and DBPs which may exist in the drinking water treatment. The comparison of the ordinary disinfectant sodium hypochlorite (NaClO).

2 MATERIALS AND METHODS

2.1 Experimental Procedures

During the algae bloom, the total content of algae in the source water reached 168,000 cells /mL, which include 92.1% *M. Aeruginosa* and 1.2% *Pseudanabaena* sp. and 0.31% *Cyclotella* sp., as shown in Figure 1.

The potable water treatment system consists of "coagulation sedimentation, sand filtration, •OH/NaClO disinfection, antibiotic degradation and a clean water tank" with a capacity of 500 m³/h. For •OH disinfection, part of the sand filter is pumped into •OH equipment, and •OH solution is generated through a series of plasma chemical reactions such as water jet cavitation. After sand filtration, algal bloom water flows to the clean water tank along the pipe at a flow rate of 500 m³/h. After the injection of resulting •OH solution to the liquid/liquid mixer, it will be mixed with water and transferred to the main pipe. For NaClO disinfection, a peristaltic pump is used to inject NaClO solution. The treated water flows through pink pipes to clean tanks. The treatment lasted for 20 s.

To simulate the severe pollution of antibiotic, part of algal bloom water was diverted from the main pipe at a flow rate of 1.0 m³/h into a treatment tank. The prepared SD solution was pumped into the bypass pipe and then injected with •OH or NaClO solution for the degradation SD. The reaction time in the bypass tube is 20 s.

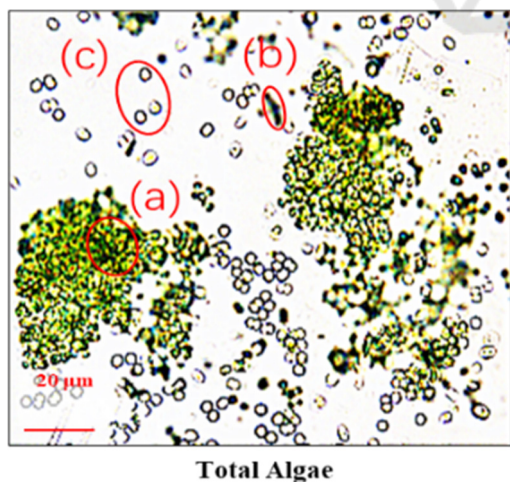


Figure 1: Images of the total algae and three main algae species (amplification factor: 400×)

- (a) *M. aeruginosa* (b) *Pseudanabaena* sp. (c) *Cyclotella* sp.

2.2 Analytical Methods

2.2.1 Determination of the Total Reactive Oxidants and •OH Concentration

•OH and other oxygen radical concentrations as well as NaClO concentrations were defined as total reactive oxidants (TRO) concentrations using an online chlorine analyzer (Hash CL17, USA). As a free radical probe, 4-hydroxybenzoic acid (4-HBA) was used for measuring •OH which will form the hydroxylated derivative 3,4-dihydroxybenzoic acid (3,4-DHBA). The analysis was performed using a high-performance liquid chromatograph (HPLC, Dionex 113 Co. Ltd., USA) equipped with a diode array detector at 210 nm. When TRO concentration is 1.0 mg/L and 0.5 mg/L, the corresponding •OH concentration is 6.35 µM and 3.67 µM, respectively.

2.2.2 Determination of SD, DBPs, and Water Qualities

SD was analyzed by high-performance liquid chromatograph-mass spectrometry (HPLC-MS/MS, Agilent 1290-6410 B, USA) on a 3.5 µm C-18 column (2.1 mm × 100 mm, Waters, USA). The flow rate was 0.6 mL/min. Haloalkanes, formaldehyde and chloral were analyzed according to EPA methods 556, 524.2 and 551.1 using gas chromatography-mass spectrometry (QP2020Plus, Japan) and electron capture detector. Haloacetic acid (HAAs) and rock salts (including BrO₃⁻, ClO₃⁻, and ClO₂⁻) were used by ion chromatographs (Thermo 2100, USA), 557 and 300.1, respectively, according to the USEPA method. Water quality indexes such as total colony, turbidity and conductivity were measured according to GB-5750.1-10.

3 RESULTS AND DISCUSSION

3.1 Degradation of Sulfadiazine during Drinking Water Treatment

Thorough mineralization of antibiotics in drinking water can prevent the further induction of antibiotic resistance in humans by residual antibiotics. The chromatogram of SD degradation by •OH or NaClO is shown in Figure 2. •OH degraded SD from 68 ng/L to below detection limit (B.D.L) at TRO concentration of 1.0 mg/L within 20 s after coagulation, while NaClO degraded SD to 52 ng/L after 20 s and B.D.L after 2 h. •OH degraded SD from 64 ng/L to B.D.L after 20 s and NaClO degraded SD

to 62.7 ng/L after 20 s and to B.D.L after 120 minutes after sand filtration with injection of 0.5 mg/L TRO. Similarly, chlorides produced by electrochemical methods did not degrade SD until 3 hours later. •OH

produced by strong ionization discharge has the prospect of large-scale industrial application in antibiotic degradation.

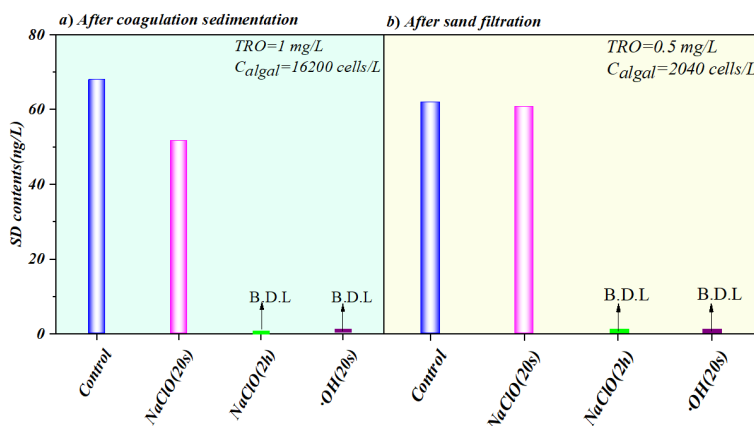


Figure 2: Degradation of SD by •OH/NaClO (B.D.L =bellow detection limit).

3.2 Effect of •OH Disinfection on Algae and the Water Quality

•OH disinfection at 500 m³/h was performed to inactivate algae, bacteria, virus and protozoa to inhibit their regeneration in the water supply network. After sand filtration, •OH solution was injected into the main pipe for disinfection after 20 s reaction. The results of inactivation of algae and bacteria are shown in Fig.3. In the source water, the total content of algae reached 179100 cells/mL. After coagulation and sand filtration, *M. aeruginosa* and other algae decreased to 2000 cells/mL and 40 cells/mL, respectively. No live algae was detected after •OH disinfection.

Escherichia coli, heat-resistant coliform group and total coliform group were detected. No bacteria were detected after •OH disinfection at 0.5 mg/L. After •OH disinfection, the COD_{Mn} decreased from 1.0 mg/L to 0.9 mg/L which indicates that •OH effectively oxidized the reductants and reduced the relative organic content. •OH enhances hydrophilicity by oxidizing hydroxyl and carboxyl groups, reducing turbidity from 0.18 NTU to 0.14 NTU. No obvious change in color, conductivity, hardness, taste, odour, visible organisms and ammonia was observed, and 106 indicators of drinking water quality which could meet the Chinese Sanitary Standards for Drinking Water (GB5749, China, 2006). In consequence, advanced •OH oxidation technology based on strong ionization discharge can be used for drinking water treatment when algal blooms occur.

The heterotrophic plate count in the source water decreased from 300 cfu/mL to 57 cfu/mL by coagulation sedimentation and sand filtration, and no

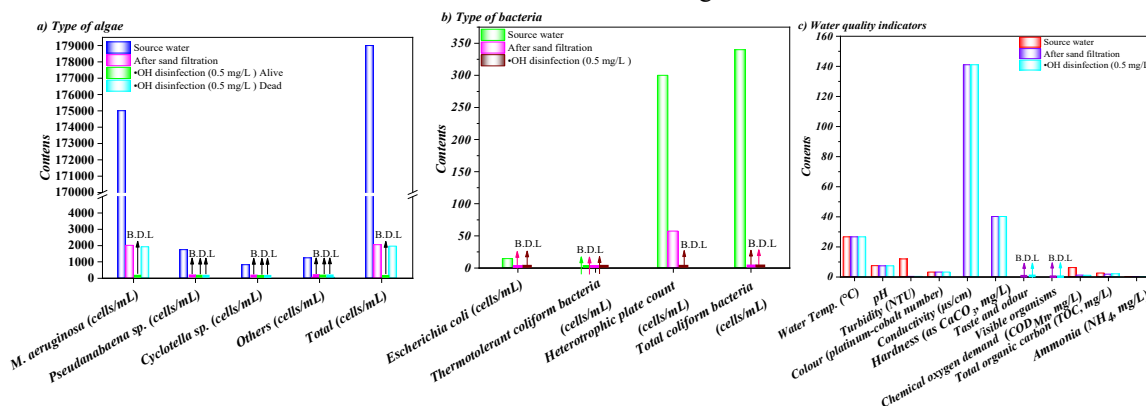


Figure 3: Data of inactivated algae, bacteria, and water quality indicators in the •OH DWTS (B.D.L =bellow detection limit).

3.3 Analysis of Possible DBPs

In DWTS of 500 m³/h, the same dose of •OH and 0.5 mg/L NaClO solution were injected into the main pipe for disinfection after 20 s of reaction. Table 1 shows that the DBP formed when TRO dosage (•OH/NaClO) was 0.5 mg/L. No halates, such as chlorite (ClO₂⁻), chlorate (ClO₃⁻) and BrO₃⁻ were detected during •OH disinfection. When the NaClO disinfection, ClO₂⁻ and BrO₃⁻ were not detected, but the concentration of ClO₃⁻ increased to 14 µg/L, lower than the national standard (GB5749). Notably, ClO₃⁻ in water can be taken up by cells and converted to more toxic ClO₂⁻ by nitrate reductase. According to the reports, aldehydes are mutagenic in mammalian cells and cause liver tumors in rodents. In the period of •OH disinfection, there was no formaldehyde and chloral detected. While, during NaClO disinfection, the content of chloral increased to 4.2 µg/L (below the limit of the Chinese Standard GB5749) because NaClO oxidizes alcohol functional groups, nitrogen

compounds, and amino acids to form chloral. At alkaline pH, chloral further decomposes to generate TCM, which is carcinogenic to human beings.

THM is potentially carcinogenic and genotoxic to humans. No TCM, DCBM, DBCM, TBM and total THM were detected during •OH disinfection. During NaClO disinfection, the contents of Trichloromethane, DCBM and DBCM reached to 5.2, 4.2 and 2.1 µg/L, respectively, which were all lower than the national standard (GB5749). The total THM content was up to 188 µg/L, which was 2.35 times higher than the limit set by EPA (80 µg/L) in the United States. This is because NaClO oxidizes a methyl hydrogen atom through a substitution reaction to form TCM. The OCl⁻ could re-oxidize existing Br⁻ through electron transfer reaction to form HOBr, and brominated THMs, such as DBCM and DCBM are generated by the substitution reaction.

Therefore, •OH did not produce DBPs after disinfection of algal bloom water, indicating that the treated drinking water after treatment is safe for human body.

Table 1: Formation of DBPs during •OH/NaClO disinfection.

(TOC = 1.65 mg/L, TRO = 0.5 mg/L, temperature = 26.5 °C, pH = 7.19).

Test items	Control (µg/L)	•OH disinfection (µg/L)	NaClO disinfection (µg/L)
ClO ₂ ⁻	B.D.L	B.D.L	B.D.L
ClO ₃ ⁻	B.D.L	B.D.L	13±2
BrO ₃ ⁻	B.D.L	B.D.L	B.D.L
Formaldehyde	B.D.L	B.D.L	B.D.L
Chloral	B.D.L	B.D.L	5±1
Trichloromethane	B.D.L	B.D.L	5.2±1
Bromodichloro methane	B.D.L	B.D.L	4.2±0.8
Dibromochloro methane	B.D.L	B.D.L	2.1±0.5
Tribromomethane	B.D.L	B.D.L	B.D.L
Trihalomethane	B.D.L	B.D.L	188±3

B.D.L = bellow detection limit

4 CONCLUSIONS

•OH equipment was installed after sand filtration in 500 m³/h DWTS during algal bloom outbreaks. During algal blooms, •OH equipment was installed after sand filtration in 500 m³/h DWTS.

To contrast with common oxidants, the •OH method possesses great practical application potential in antibiotic mineralization, algae inactivation, drinking water disinfection and other aspects. The main results suggest that:

(1) In the transporting of algal bloom water within 20 s, after coagulation precipitation and sand filtration by •OH degradation at 1.0 mg/L and 0.5 mg/L there is no SD detected. Compared with it, the corresponding degradation rates of SD by NaClO were 24% and 2%, respectively.

(2) In the main pipeline with a treatment capacity of 500 m³/h, •OH disinfection at 0.5 mg/L inactivated algae from 2040 cells/mL to 0 cells/mL in only 20 s. The 106 water quality indexes all meet the limit requirements of China Drinking Water Sanitation Standard (GB5749, China, 2006).

(3) DBPs, for example HAAs, aldehydes, THMs, and bromate, were not produced in the process of the •OH disinfection. During the disinfection by NaClO, the total THMs increased to 188µg/L, 2.35 times higher than 80 µg/L which is the limit that set by USEPA standards. This result showed that the •OH disinfection will lead no harm to human health potentially.

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