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# Removal of typical antibiotics in the advanced treatment process of productive drinking water

Jianguang Liu[a,*], Qiuyue Sun[a], Chunyang Zhang[c], Hao Li[d], Wuchang Song[b], Ni Zhang[a], Xiangfeng Jia[a]

[a]*School of Municipal and Environmental Engineering, Shandong Jianzhu University, Jinan 250101, China, emails: liujg@sdjzu.edu.cn (J. Liu), sunqiuyue2011@126.com (Q. Sun), zhangni@sdjzu.edu.cn (N. Zhang), jiaxf@sdjzu.edu.cn (X. Jia)*
[b]*Urban Water and Wastewater Monitoring Center of Shandong Province, Jinan 250021, China, email: songwuchang@163.com*
[c]*School of Thermal Engineering, Shandong Jianzhu University, Jinan 250101, China, email: zhangcy@sdjzu.edu.cn*
[d]*Jinan Quancheng Water Service Co. Ltd., Jinan 250118, China, email: lihaojn77@163.com*

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ABSTRACT

This study investigated the fate of six artificial antibiotics during treatment process of an industrial-scale drinking water treatment plant in China. The results showed that all the antibiotics can be effectively removed by the advanced treatment process. The average concentrations of the six antibiotics ranged from 1 to 43 ng/L in the influent while from non-detected to 6 ng/L in the effluent. The antibiotic removal efficiencies were 91% for total antibiotics, 85% for amoxicillin, 92% for tetracycline, 86% for oxytetracycline, and approximately 100% for sulfamethoxazole, sulfamethazine, and erythromycin in the integrated water treatment process. Of all treatment units in the plant, it was found that ozonation and biological activated carbon treatment were the most effective treatment to remove antibiotics.

*Keywords:* Drinking water; Water treatment plant; Antibiotics; Ozonation; Biological activated carbon

## 1. Introduction

Trace artificial antibiotics have been found in aquatic environments worldwide: 27 out of the 51 pharmaceuticals and hormones were detected in surface waters in France [1]; veterinary antibiotics including macrolides, sulfonamides, and trimethoprim were observed at 7–360 ng/L in Vietnam's Mekong Delta [2]; low concentrations of fluoroquinolones and macrolides were found in the ambient marine water of Victoria Harbour in Hong Kong, and antibiotics in the Pearl River of South China were detected higher than those in America and other western developed countries [3]. To identify the source and fate of antibiotics, recent research focused on the removal efficiency of different water treatment processes. Watkinson found that the lincosamide and sulfonamide presented low removals (11 and 25%, respectively) in conventional water treatment plant; however, MF/RO plant could eliminate majority of antibiotics from the effluent of the conventional plant [4]. Nakada investigated the removal efficiencies of 24 pharmaceutically active compounds in the sand filtration/ozonation process of a municipal sewage treatment plant, and more than

*Corresponding author.

80% of all the target compounds were removed except for carbamazepine and diethyltoluamide [5]. Gobel found that biological treatment process could reduce most sulfamethoxazole (SMX) [6]. However, little research reported the antibiotics removal in full-scale advanced treatment process (ozonation/biological activated carbon process) in China.

This study chose SMX, sulfamethazine (SMZ), amoxicillin (AM), tetracycline (TC), oxytetracycline (OTC), and erythromycin (ETM) as target antibiotics and focused on the fate of them in a full-scale conventional treatment processes (include: coagulation sedimentation, sand filtration, and chlorination) combined with advanced treatment process (ozonation/biological activated carbon process). The degradation law and collaborative removal mechanisms of antibiotics would be investigated.

## 2. Materials and methods

SMX, SMZ, ETM, OTC, TC, and AM were purchased from Dr. Ehrenstorfer GmbH (Germany). LC-grade methanol and formic acid were obtained from Tedia Company, Inc. (USA). Disodium ethylenediaminetetraacetate ($Na_2EDTA$) was of analytical grade (China). Ultrapure water was made by Molecular Lab Water Purifier (China). Agilent SampliQ 12- and 20-Position SPE Manifolds were purchased from Agilent Technologies Inc. (USA). Solid phase extraction cartridges (Oasis HLB, 200 mg/6 mL) were from Waters. Portable Waterproof pH meter (HI8424NEW) was purchased from HANNA. KL512 Nitrogen Evaporators were purchased from Beijing KangLin Science & Technology Co., Ltd (China). Individual stock standard solutions were prepared by adding 10 mg standard target compound in 10 mL methanol and stored in amber glass bottles at −20°C. External calibration standards for HPLC–MS/MS (0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 1, and 10 mg/L) were prepared by diluting the stock solution with ultrapure water/methanol mixture (70:30, v/v) before each test. These standards were temporarily stored at 4°C and used on the same day.

### 2.1. Water treatment process and sample collection

The full-scale drinking water treatment plant (DWTP) is designed with the processing capacity of 200,000 $m^3$/d. During the sampling period, the raw water of the plant was from the Yellow River reservoir with water quality of approximately 3.0 mg/L for TOC, approximately 8.0 for pH, and approximately 0.05 $cm^{-1}$ for $UV_{254}$. The treatment process consists of the high-density sedimentation tank, the ozone contact system, the upflow biological activated carbon (BAC) filter, and the V-sand filter. The ozone system contains two parallel three-stage fine bubble diffuser ozone contactors. The fine bubble diffusers are arranged at the bottom of chambers to produce ozone and water flowing in opposite directions. Designed maximum $O_3$ dose is 3 mg/L and the treatment detention time is approximately 15 min. The UBAC (29 m × 55 m × 8.55 m) is separated into two parallel parts receiving water from both ozone contractors, respectively. Each part is divided into six cells with effective area of 60.48 $m^2$ per cell. The active carbon layer is 3.0 m in depth and contact time is 15 min. To assess the removal efficiency of each process, samples were collected before and after each treatment unit as shown in Fig. 1.

### 2.2. Analytical methods

Antibiotics were extracted and analyzed by solid phase extraction using Oasis HLB cartridges and Agilent 1,200 module liquid chromatography/tandem mass spectrometry (HPLC–MS/MS). Five hundred milliliter samples were added with 0.1 g $Na_2EDTA$ and acidified to pH 3.0 with sulfuric acid. The cartridges were preconditioned with 5 mL methanol and 5 mL ultrapure water at the flow rate of 1 mL/min. Samples were loaded to the preconditioned cartridges at 5 mL/min and then dried by vacuum extraction column. Then, the analytes were eluted with 6 mL methanol and evaporated to dryness with nitrogen stream before reconstituting to 0.2 mL with 30% methanol. The final solutions were transferred into 1.5 mL amber glass bottles for HPLC–MS/MS analysis.

HPLC–MS/MS was operated in Analysis and Test Center of Shandong province, equipped with a ZORBAX Eclipse XDB-C18 column (50 mm × 2.1 mm, 1.8 μm). Ultrapure water containing 0.2% mixture of formic acid (A) and methanol (B) (70:30 (v/v)) were used as mobile phases through the column at a flow rate of 0.4 mL/min. The column was maintained at 15°C and the injection volume was 5 μL. The gradient were initiated by linearly increasing the concentration of B from 30 to 95% in 6 min and holding at 95% for 2 min before decreasing back to 30% in 0.1 min. Agilent 6410 triple quadrupole mass spectrometry was equipped with an ESI interface in positive ionization mode, and the flow rate of desolvation gas was set at 10 L/min held at 350°C; the nebulizer pressure was of 35 psi, the capillary voltage was set at 4,000 V, and the quantitative analysis was performed in multiple reaction monitoring (MRM) using two highest

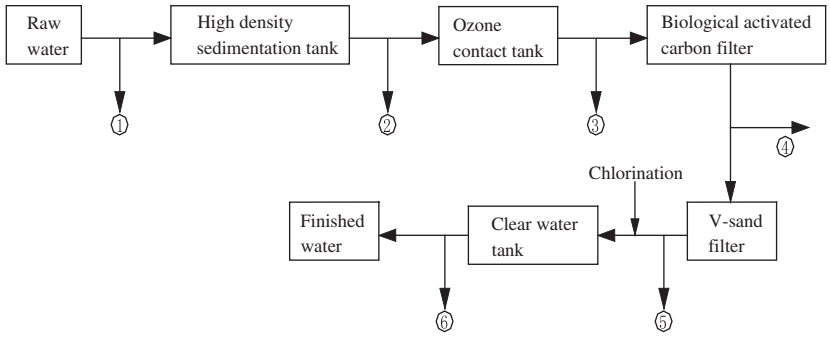


Fig. 1. Schematic diagram of the integrated process flow and sampling position.

characteristic precursor ion/product ion transition pairs, which are listed in Table 1.

Recovery experiments were performed with spiked ultrapure water (100 ng/L of target analysts). The standard calibration curve was constructed with the standard mixtures as mentioned above. The limits of detection and method detection limits were all listed in Table 1.

## 3. Results and discussion

### 3.1. Antibiotics concentrations in the water treatment process

The technological process of the DWTP as shown in Fig. 1 combined with the arrangement of sample points, between the two sampling points for a processing unit, that is, coagulation sedimentation (between sampling point 1 and 2), ozonation (between sampling points 2 and 3), biological activated carbon (between sampling point 3 and 4), sand filtration (between sampling points 4 and 5), chlorination (between sampling points 5 and 6), and studied the removal performance of target antibiotics in the treatment processes. The residual concentrations of target antibiotics at all the sampling sites are shown in Fig. 2.

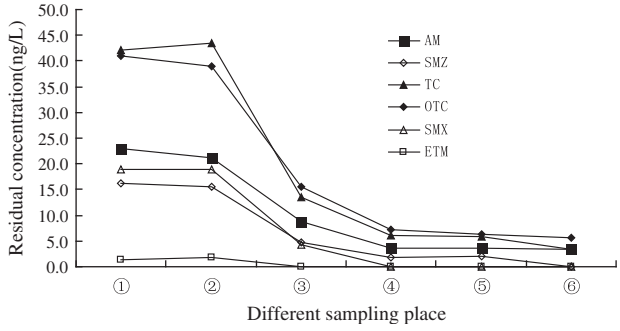


Fig. 2. The residual concentration of target antibiotics at each sampling place.

It was found that all antibiotics were decreased to different extents through the water treatment process. In the influent, the concentrations of the six antibiotics in raw water ranged from 1 to 43 ng/L, in which ETM was the lowest and TC was the highest. All the six antibiotics were reduced to non-detected (ND) ~6 ng/L in the effluent. The concentrations were at relatively lower level for both sampling point position 5 and 6, indicating that the advanced treatment process "ozonation → biological activated carbon" played the key role in removing antibiotics.

Table 1
Quality parameters of six target antibiotics

| Target compounds | MRM | Recovery (%) | Limits of detection (ng/mL) | Method detection limits (ng/L) |
|---|---|---|---|---|
| SMX | 254.1/92.0 | 89.0 | 0.5 | 0.2 |
| SMZ | 279.1/124.0 | 84.4 | 2.0 | 0.8 |
| AM | 366.1/113.9 | 68.4 | 0.5 | 0.2 |
| TC | 445.2/410.0 | 78.6 | 2.0 | 0.8 |
| OTC | 461.2/426.0 | 81.2 | 2.0 | 0.8 |
| ETM | 734.5/158.1 | 83.4 | 0.5 | 0.2 |

### 3.2. The removal of target antibiotics in the water treatment process

The relative removal efficiency (the relative removal efficiency is the ratio of target antibiotics concentration differences between influent and effluent of a process unit to the influent concentration of this process unit) of each target antibiotic and total antibiotics in treatment processes is shown in Fig. 3.

As seen in Fig. 3, the target antibiotics removal efficiency of coagulation sedimentation process unit was limited. The relative removal efficiencies of the total antibiotics of ozonation and biological activated carbon process unit were 66 and 60%, respectively, meanwhile the numbers were less than 5% during the sand filtration and approximately 31% during the chlorination.

The absolute removal efficiencies (The absolute removal efficiency is the ratio of target antibiotics concentration differences between influent and effluent of a process unit to target antibiotics concentration in the raw water.) of target antibiotics in the treatment process units and overall process are shown in Fig. 4.

As seen from Fig. 4, ozonation and biological activated carbon process units are the major steps to remove antibiotics with absolute removal efficiency of total antibiotics of approximately 65 and 20%, respectively. The removal efficiency of the six target antibiotics was more than 85% in the overall process (91% of total antibiotics, 85% of AM, 92% of TC, 86% of OTC, and approximately 100% of SMX, SMZ, and ETM). The possible removal mechanism for each step was listed as following:

(1) Coagulation sedimentation: polymeric aluminum ferric chloride was used as coagulants with the dosage of 2 mg/L in the DWTP. As Fig. 4 showing, coagulation sedimentation contributed little on the antibiotic removal (approximately 8% of AM, 4% of SMZ, 5% of OTC, 1% of SMX, and 0% to TC and ETM). The considerable amount of dissolved organics in the raw water could decrease the antibiotics removal efficiency by competing in the coagulation [7].
(2) Ozonation: ozone dosage was 1 mg/L in the water plant. As seen from Fig. 4, ozonation removed 65% of total antibiotics and 54% of AM (absolute removal efficiency), 67% of SMZ, 71% of TC, 57% of OTC, 76% of SMX, and ETM reached approximately 100%. Numerous studies have found that ozonation could degrade 90% of pharmaceuticals, endocrine disruptors, and personal care products [8–10].
(3) Biological activated carbon filtration: as seen from Fig. 4, biological activated carbon contributes to remove total antibiotics up to 20% and 23% of AM (absolute removal efficiency), 19% of SMZ, 17% of TC, 20% of OTC, and 23% of SMX. The degradation of antibiotics by biological activated carbon may result from three reasons: (i) The micro-organisms fixed more antibiotics because they form bacteria colonies on the surface of the activated carbon when adsorbing [11]; (ii) The biological film can also degrade antibiotics; (iii) Dissolving $O_3$ in the water can generate a certain amount of hydroxyl radical (·OH) by reacting with the basic surface groups of the activated carbon, which could remove some antibiotics [12].
(4) Sand filtration: sand filtration only removed 1% of total antibiotics. As shown in Fig. 2, the

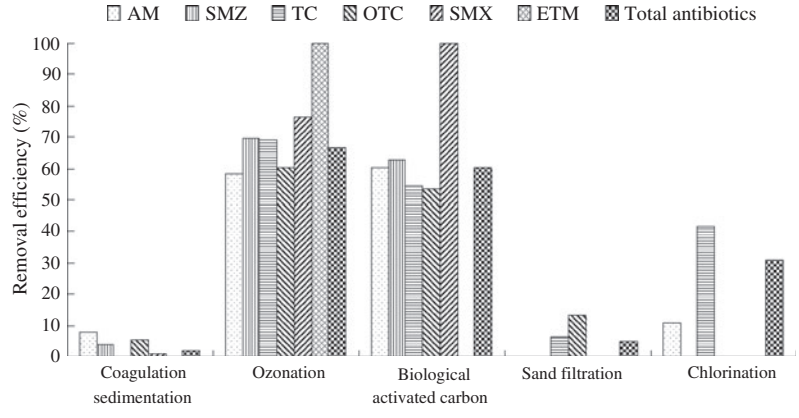


Fig. 3. Relative removal efficiency of antibiotics in treatment processes.

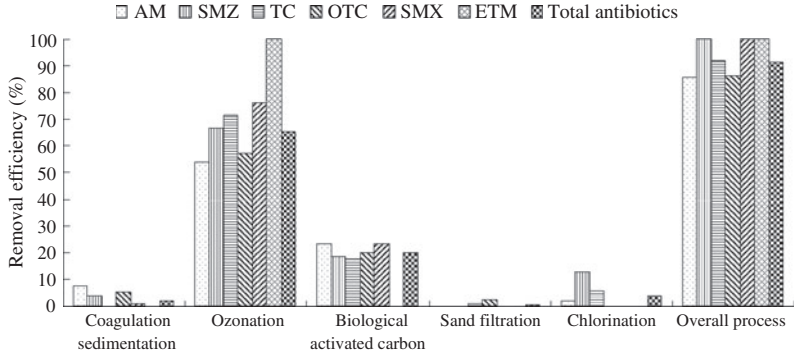


Fig. 4. Absolute removal efficiency of antibiotics in the treatment processes.

influent antibiotics concentration of sand filter were less than 10 ng/L, resulting in the inefficient removal of the antibiotics [5].

(5) Chlorination: chlorination removed 4% of the total antibiotics. Previous studies found that the antibiotics can be removed by chlorination (with HOCl and $ClO_2$) [13,14]. In this project, the low removal efficiency may due to low dosage of chlorine and the low concentration of antibiotics in the influent.

## 4. Conclusions

(1) The advanced treatment process "ozonation → biological activated carbon" played the key role in removing the target antibiotics in the DWTP. The concentrations of the six antibiotics in effluent ranged from ND to 6 ng/L. The removal efficiency of total antibiotics reached 91% and 85% of AM, 92% of TC, 86% of OTC, and approximately 100% of SMX, SMZ, and ETM in the overall process of the DWTP.

(2) The conventional treatment processes including coagulation sedimentation, sand filtration, and chlorination showed relative low removal efficiencies of antibiotics (2%, 1%, and 4%, respectively).

(3) "Ozonation/biological activated carbon" advanced treatment process was the major step for removing antibiotics in the DWTP and removed 65 and 20% of total antibiotics, respectively.

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