Journal of Hazardous Materials 339 (2017) 174–181

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Interaction of ciprofloxacin chlorination products with bacteria in drinking water distribution systems

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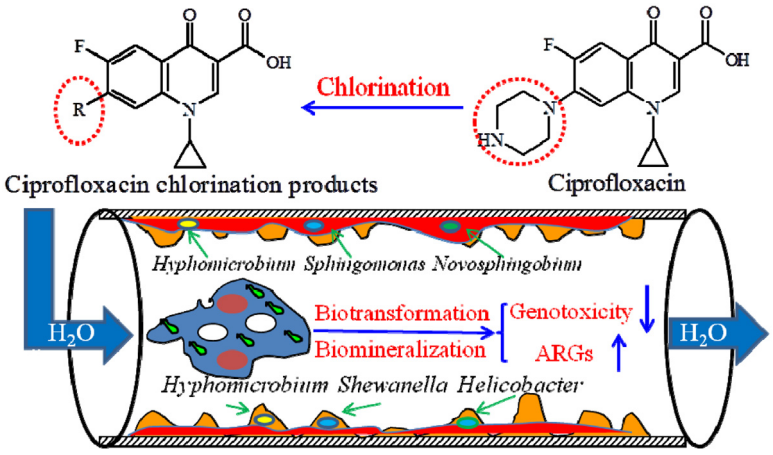
HIGHLIGHTS

- Interaction of ciprofloxacin chlorination products with bacteria was investigated.
- Chlorination can't mineralize ciprofloxacin, but can destroy the piperazine ring.
- Chlorination initiated biotranformation of ciprofloxacin chlorination products.
- Genotoxicity decreased clearly due to synergistic effect of chlorine and bacteria.
- Biotransformation of chlorination products increased antibiotic resistance genes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 April 2017
Received in revised form 14 June 2017
Accepted 15 June 2017
Available online 17 June 2017

Keywords:
Ciprofloxacin chlorination products
Biotransformation
Bacterial community
Antibiotic resistance genes
Genotoxicity

ABSTRACT

The interaction of ciprofloxacin chlorination products (CIP-CPs) with bacteria in drinking water distribution systems (DWDSs) was investigated. The piperazine ring of CIP was destroyed by chlorination. Among of CIP-CPs, by the bacterial role, 7.63% of the derivative with two carboxylic groups went through decarboxylation to form desethylene ciprofloxacin, and then loss of C_2H_5N group generated aniline compound. Furthermore, 12.3% of the aniline compound, 7.60% of chlorinated aniline compound and 1.35% of defluorinated product were bio-mineralized. Therefore, the chlorine and bacteria played synergistic effects on transformation of CIP-CPs in DWDSs, contributing to the obvious decrease of genotoxicity in effluents. Correspondingly, the $TEQ_{4\text{-}NQO}$ decreased from 667 μg/L to 9.41 μg/L. However, compared with DWDSs without CIP-CPs, the relative abundance of *mexA* and *qnrS* increased 1-fold in effluents and the relative abundance of *qnrA* and *qnrB* increased 3-fold in biofilms in DWDSs with CIP-CPs. *mexA* and *qnrS* positively correlated with *Hyphomicrobium*, *Sphingomonas* and *Novosphingobium* ($p < 0.05$), while *qnrA* and *qnrB* positively correlated with *Shewanella* and *Helicobacter* ($p < 0.05$), indicating

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http://dx.doi.org/10.1016/j.jhazmat.2017.06.033
0304-3894/

the increase of antibiotic resistance genes (ARGs) came from the growth of these bacterial genera by transformation of CIP-CPs in DWDSs. These results suggested that biotransformation of antibiotics might increase ARGs risk in DWDSs.

1. Introduction

Fluoroquinolones are a family of synthetic, broad-spectrum antibiotics, used to treat diseases in both humans and animals [1]. They are frequently detected in groundwater and surface water because of insufficient removal of these compounds by conventional wastewater treatment operations [2–4]. Fluoroquinolones contribute to the emergence and spread of antibiotic resistant bacteria (ARB) and antibiotic resistance genes (ARGs) [5,6]. Moreover, these antibiotics increase the toxicity of source water [3], and this will pose risks to human health.

A representative antibiotic of fluoroquinolone class is ciprofloxacin (CIP), which has been extensively used over the past 20 years [7]. The concentration of CIP in source water is generally low, typically in μg/L or ng/L level [3,8]. Ineffective removal of CIP by conventional water treatment technologies has caused the detection of CIP in drinking water in ng/L level [9,10]. However, the low concentration of CIP is toxic to some aquatic organisms [11], and it works against gram-negative and gram-positive bacteria through inhibition of bacterial DNA unwinding and duplicating [12]. CIP can also affect the bacterial community composition in aquatic environment [7,13], and its impact on microbial communities is selective [14]. Moreover, bacterial community shift drives antibiotic resistance promotion during drinking water chlorination [5]. Therefore, in order to control the water contamination by CIP, many studies have investigated the degradation of CIP by different water treatment technologies, including chlorination, ozonation and other advanced oxidation process [1,4,15,16]. CIP is degraded quickly during these treatments, however, its mineralization is very difficult and some intermediates containing quinolone ring were produced usually. The toxicity of CIP is slowly diminished due to its degradation, but in some cases the degradation products of ciprofloxacin appear to have a higher toxicity than the parent compounds [17].

The drinking water usually goes through the drinking water distribution systems (DWDSs) before reaching the user points. DWDSs are an important component in the provision of safe drinking water to consumers, although often overlooked [18]. Maintaining chlorine residual is widely used for controlling microbial contamination in DWDSs. During water chlorination, the piperazine ring of CIP can quickly react with chlorine to form other degradation products including quinolone ring [1,19]. Therefore, the micropollutants were CIP chlorination products (CIP-CPs) rather than CIP in finished drinking water [5,8]. CIP-CPs with quinolone ring will affect the bacterial community in DWDSs, because the antibacterial activity of CIP is mainly caused by the quinolone moiety [20]. Moreover, biotransformation of CIP by bacteria and fungus in water have been found in some other studies, although this process is very slowly [21,22]. Therefore, CIP-CPs may also go through biotransformation by the bacteria in DWDSs, which can affect the water quality in DWDSs. It has been reported that the genotoxicity of tap water was higher than that of finished drinking water in some conditions [23], however, there is little known about the interaction of CIP-CPs and the bacterial community composition, and its effect on the genotoxicity of water in DWDSs.

The aims of this study were (1) to investigate the CIP chlorination process and the biotransformation of CIP-CPs, and their effects on genotoxicity changes in DWDSs; (2) to analyze the bacterial community and ARGs shift, and reveal the interaction between the CIP-CPs and bacteria in DWDSs.

2. Materials and methods

2.1. Materials

Sodium hypochlorite (NaClO) solution, analytical grade, was purchased from Sinopharm Chemical Reagent Co., Ltd (China). Ciprofloxacin (CIP), high performance liquid chromatography (HPLC) grade, was obtained from Sigma-Aldrich Fluka (USA).

The tested raw water was collected from a drinking water treatment plant in north of China, which was treated by coagulation, flocculation, sedimentation, sand filtration, and biologically-activated carbon filtration (prior to entering the chlorine contact tanks). All water samples were stored at 4 °C before using. Water quality parameters were measured according to standard methods [24] (Table S1). Dissolved organic carbon (DOC) was analyzed via a total organic carbon analyzer (TOC-V_{CPH}, SHIMADZU, Japan). Differences of water quality were measured using analysis of variance (ANOVA) with a significance threshold of $\alpha = 0.05$.

2.2. Experiments design

Firstly, in order to know the reaction of CIP with chlorine, three 1.5 L glass fiber-reinforced plastic bottles were used in this study. One was filled with 1 L raw water with addition of 1 mg/L chlorine, the other one was filled with 1 L raw water with addition of 1.6 mg/L CIP and 1 mg/L chlorine, the third one was filled with 1 L ultrapure water with addition of 1.6 mg/L CIP (DOC 1 mg/L) and 1 mg/L chlorine. Each experiment was done in triplicate. After 2 and 50 h, the DOC, chlorine residual and CIP concentration of different waters were analyzed, and the CIP-CPs were also analyzed.

Secondly, the transformation of CIP-CPs in DWDSs was studied. Ten cast iron coupons were immersed in covered 1.5 L glass fiber-reinforced plastic bottles to simulate the DWDSs. The information of cast iron coupons was described in the Supplementary Material (Text S1). Before this study, six simulated DWDSs have been run at the same conditions for more than two years, and the stable corrosion scales have been formed on the surface of the cast iron coupons. In one experiment, after 1 L raw water was chlorinated for 2 h with 1 mg/L chlorine, it was added into one DWDS. In the other experiment, after 1 L raw water with addition of 1.6 mg/L CIP was chlorinated for 2 h with 1 mg/L chlorine, it was also added into one DWDS. The water in each DWDS was displaced with fresh water at 48 h intervals and gently agitated by a magnetic rotor to mix the water, reflecting dead zones or worst case conditions in actual water distribution systems according to the reported methods [25,26]. The bulk water was also sampled at 48 h intervals to measure the DOC and CIP-CPs concentrations. The two experiments were run in triplicate for 250 days, respectively, and the experiment without CIP was performed as a control. Moreover, in order to know the biotransformation of CIP-CPs in DWDSs, from 40 to 60 days, after 1 L ultrapure water with addition of 1.6 mg/L CIP was chlorinated for 2 h with 1 mg/L chlorine, it was also added into one DWDS after the water, and DOC was analyzed.