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Effects of NOM on the degradation of chloramphenicol by UV/H_2O_2 and the characteristics of degradation products

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ABSTRACT

Effects of natural organic matter (NOM) on the degradation of chloramphenicol (CAP) by UV/H_2O_2 and the characteristics of degradation products were investigated. With initial concentration of 5 mg L^{-1} CAP, UV and 0.5 mM H_2O_2 process induced the degradation rate constant increased to $3.75 \times 10^{-3}\ s^{-1}$, which was about 1.6 times of that treated with UV alone. The excitation-emission matrix (EEM) fluorescence spectra showed that the degradation products included many humic acid-like compounds (HA). Therefore, addition of 5 mg/L HA to the solution decreased the degradation rate constant to $1.78 \times 10^{-3}\ s^{-1}$, because they would compete for the oxidizing reaction of CAP with $^{\cdot}OH$. However, the degradation rate constant and removal efficiency of CAP were influenced not only by the initial concentration of HA but also by the ratio of $[HA]_0/[CAP]_0$. When the initial concentration of CAP decreased to 0.1 mg/L, the ratio of $[HA]_0/[CAP]_0$ increased to 50. The degradation rate constant increased to $2.32 \times 10^{-3}\ s^{-1}$. Moreover, the results of ultra high-performance liquid chromatography & quadrupole time-of-flight mass spectrometer (UPLC-Q-TOF-MS) suggested that the main degradation products were dichloroacetic acid (*m/z* 129) and aromatics 4-nitro-benzoic acid (*m/z* 167). These products were induced by the radical reaction during the UV/H_2O_2 treatment process. Meanwhile, Fourier transform infrared spectroscopy (FTIR) indicated that UV/H_2O_2 could destroy the aromatic ring of CAP and initiating the mineralization of CAP. $TEQ_{4\text{-}NQO}$ decreased to 0.20 μg L^{-1} after the treatment with UV dose 2000 mJ cm^{-2} and 0.5 mM H_2O_2. Therefore, the radical reaction and mineralization of CAP also decreased the genotoxicity obviously.

1. Introduction

Antibiotics are widely used to treat bacterial diseases in both humans and animals [1]. Chlorampenicol (CAP) is a kind of broad-spectrum antibiotic, and it has been used to inhibit both Gram-positive and Gram-negative bacteria since the 1950s [2,3]. Because CAP can cause numerous serious side effects on human health, such as aplastic anemia, bone marrow suppression and neonatal gray syndrome, it has been banned by many countries for use in food-producing animals in the European Union and the United States of America in the 1990s [4,5]. However, CAP is still widely used in many low-income countries because of its low cost and high availability [6].

According to previous studies, CAP is partially metabolized after intake and about 16% and 38% of them finally discharged to environment in the form of original compound through urine or feces [7]. In addition, CAP is ineffectively removed through conventional processes [8]. Therefore, CAP is always present in various aquatic environments [9], and it is reported that CAP in concentration of 4.2–28.4 ng L^{-1} has been detected in Shanghai water supply network in China [10]. The presence of CAP in aquatic environments may threaten the ecosystem and human health even at trace levels. Therefore, the development of innovative technologies that can effectively remove CAP is important.

Advanced oxidation processes (AOPs), which are based on the generation of hydroxyl radical (·OH) and other free radicals, have been reported as potentially powerful methods in water treatment [11,12]. Several studies have used Fenton, photo-Fenton, and persulfate activated by Fe^{2+} and zerovalent iron to investigate the degradation of CAP [1,13,14]. These methods are more effective to remove CAP than conventional treatment processes. However, their economic effectiveness and applicability to real situations have not been fully assessed. UV/H_2O_2 is also one of the certain processes of AOPs, and reactive specie ·OH can be produced from UV/H_2O_2 treatment process, which can degrade a wide range of antibiotics with no selectivity [15–17].

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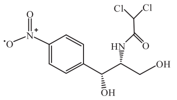
Table 1
Characteristics of chloramphenicol (CAP).

Name	Molecular formula	Chemical structure
Chloramphenicol (CAP)	$C_{11}H_{12}Cl_2N_2O_5$	

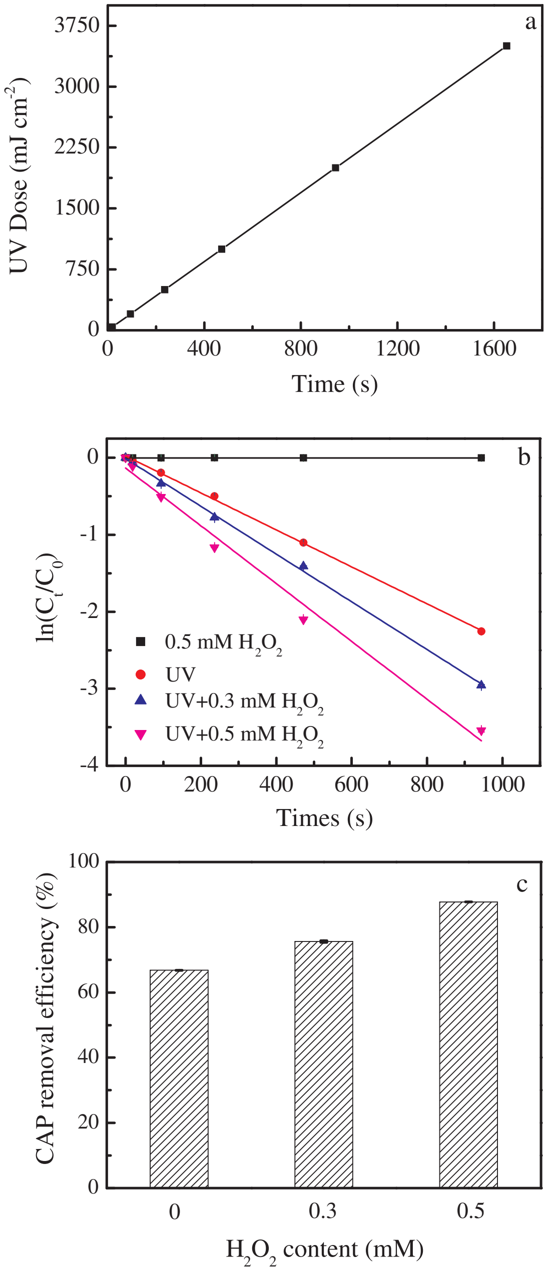


Fig. 1. The relationship between UV dose (mJ cm^{-2}) and irradiation time (s) (a), and effects of UV, H_2O_2 and UV/H_2O_2 on degradation of CAP with initial concentration 5 mg L^{-1} (b), and the removal efficiency of CAP in UV and UV/H_2O_2 process when UV dose was 1000 mJ cm^{-2} with irradiation time of 472 s (c).

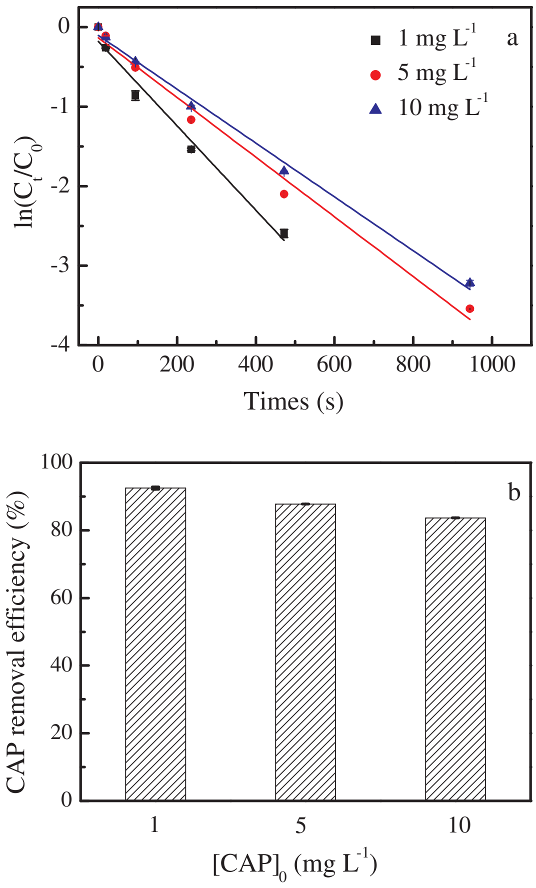


Fig. 2. Effects of initial CAP concentration (1 mg L^{-1}, 5 mg L^{-1} and 10 mg L^{-1}) on the degradation of CAP by UV/H_2O_2 treatment process (a), and the removal efficiency of CAP in UV/H_2O_2 process when UV dose was 1000 mJ cm^{-2} with irradiation time of 472 s (b). The initial concentration of H_2O_2 was 0.5 mM.

Zuorro et al. have reported the degradation and antibiotic activity reduction of CAP in aqueous solution by UV/H_2O_2 process, however, the study is about the wastewater treatment with high initial CAP concentration (50–100 mg L^{-1}) [5]. In drinking water treatment process, CAP concentration in source water is always at the level of μg L^{-1} and ng L^{-1} [10,14]. In source water, the concentration of natural organic matter (NOM) is usually at the level of mg L^{-1}, which is much higher than that of CAP. Therefore, the higher concentration of NOM will influence the degradation of CAP during UV/H_2O_2 treatment process. The question is that whether UV/H_2O_2 treatment process will only oxide the NOM but not CAP, when initial CAP concentration is very low. Until now, little is known about the effects of different ratio of NOM and CAP on the CAP degradation, especially in low concentration of CAP. Moreover, the chemical structure of antibiotics will change and some new organic matters will appear during UV/H_2O_2 treatment process. In some cases the degradation products of antibiotics have a higher toxicity than the parent compounds [18]. There is little information of the toxicity changes after the CAP degradation by UV/H_2O_2 treatment.

The objective of this study is to (1) evaluate the efficacy of the UV/H_2O_2 treatment process to degrade CAP, (2) investigate the effects of different ratio of NOM and CAP on the CAP degradation during UV/H_2O_2 treatment process, and (3) characterize the degradation products of CAP, give the degradation pathways and analyze the genotoxicity changes of CAP during UV/H_2O_2 treatment process.

2. Experimental

2.1. Reagents

Chloramphenicol (CAP, 99%) was bought from J & K Chemical Ltd. (Shanghai, China). Its molecular structure was shown in Table 1. Hydrogen peroxide (H_2O_2, 30% w/w) was supplied by Sinopharm Chemical Reagent Co., Ltd (Beijing, China). Humic acid (HA) and fulvic