



# Trimethoprim degradation by Fenton and Fe(II)-activated persulfate processes



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## HIGHLIGHTS

- Fe(II)-activated persulfate and Fenton process can degrade trimethoprim.
- Fe(II)-activated persulfate was more efficient for actual wastewater.
- The degradation pathway of trimethoprim was different for two processes.

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## ABSTRACT

Trimethoprim is a pollutant ubiquitous in the environment due to its extensive application, and it cannot be effectively removed by conventional wastewater treatment processes. In this study, the Fenton and the Fe(II)-activated persulfate processes were employed to degrade trimethoprim in an aqueous solution. The results showed that the concentration of persulfate, H<sub>2</sub>O<sub>2</sub> and Fe(II) had a significant influence on the degradation of trimethoprim in both processes. De-ionized water spiked with trimethoprim resulted in the complete degradation of trimethoprim (0.05 mM) by the mineralization of 54.9% of Fenton's reagent when the concentrations of H<sub>2</sub>O<sub>2</sub> and Fe(II) were 1 mM and 0.05 mM, respectively. In contrast, 73.4% of trimethoprim was degraded by the mineralization of 40.5% of the Fe(II)-activated persulfate process when the concentration of persulfate and Fe(II) were each 4 mM. Intermediate compounds with different *m/z* were detected for the Fenton and the Fe(II)-activated persulfate processes, indicating alternative degradation pathways. In the actual wastewater spiked with trimethoprim, the removal efficiency of trimethoprim decreased to 35.8% and 43.6%, respectively, for the Fenton and the Fe(II)-activated persulfate processes. In addition, the decomposition efficiencies for hydrogen peroxide and persulfate were 43.8% and 92.5%, respectively, which was lower than those in the de-ionized water system. These results demonstrated that wastewater components had a negative influence on trimethoprim degradation and the decomposition of the oxidants (persulfate and H<sub>2</sub>O<sub>2</sub>). In summary, the Fe(II)-activated persulfate process could be used as an alternative technology for treating trimethoprim-containing wastewater.

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## 1. Introduction

Antibiotics have been widely used by humans and the aquaculture and livestock industries for preventing or treating microbial infections (Sarmah et al., 2006). Considerable amounts of antibiotics used by humans and animals are excreted through their feces (Kim and Carlson, 2007; Zhou et al., 2013a,b; Wang and Wang,

2017) and enter the environment, affecting surface water, ground water and soil (Wang and Wang, 2016). The presence of antibiotics in the environment, especially in water bodies, has caused adverse effects, including bacteria that are resistant to antibiotics as a result of developing a resistance gene (Baquero et al., 2008; Rodriguez-Mozaz et al., 2015). Therefore, it is necessary to remove antibiotics from water bodies (Wang and Chu, 2016).

Trimethoprim is one of most commonly used antibiotics in the world and has been frequently detected in wastewater (Göbel et al., 2007; Mceneff et al., 2014), indicating that conventional wastewater treatment processes do not effectively remove trimethoprim.

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Advanced oxidation processes (AOPs) are capable of removing recalcitrant compounds (Wang and Xu, 2012; Wang and Bai, 2017). Hydroxyl radicals produced during AOPs are primarily responsible for the removal of recalcitrant compounds (Bai et al., 2016). Fenton is one of the most effective advanced oxidation processes with respect to the removal of recalcitrant compounds. In the presence of Fe(II), hydrogen peroxide can be decomposed rapidly into hydroxyl radicals. The Fenton process is typically used as a pretreatment process to improve the biodegradability of recalcitrant compounds (Ramteke and Gogate, 2016) or as a polishing process to further enhance the removal of recalcitrant compounds (Gupta et al., 2014). For the removal of trimethoprim by advanced oxidation processes, studies have primarily focused on the photo-Fenton (Dias et al., 2014) and the photoelectron-Fenton processes (Moreira et al., 2015; Zhang et al., 2016). Li et al. (2012) reported the complete removal of 1 µg/L of trimethoprim with 20 mg/L Fe(II) and 30.4 mg/L hydrogen peroxide (molar ratio of Fe(II)/H<sub>2</sub>O<sub>2</sub> of 2.5) in real wastewater.

Although the Fenton process is efficient for the removal of organic contaminants, there are disadvantages to using Fenton's agent, such as sludge formation, excess consumption of chemicals and a pH dependency. Similar to hydrogen peroxide, persulfate can be decomposed into sulfate radicals in the presence of Fe(II). In comparison with hydroxyl radicals, sulfate radicals have a similar or even higher redox potential (2.6–3.1 V), depending on the method used for activation (Ghauch and Tuqan, 2012). Sulfate radicals can effectively oxidize recalcitrant pollutants (Matzek and Carter, 2016). In addition, they can persist for a greater amount of time in the groundwater and soil than hydrogen peroxide (Deng and Ezyske, 2011), which aids in the removal of recalcitrant compounds to some degree. In addition, sulfate radicals have a greater selectivity than hydroxyl radicals (Ahmed et al., 2012), which can reduce the consumption of radicals by natural organic matter and other untargeted compounds. Finally, sulfate radicals are more stable than hydroxyl radicals (Devi et al., 2009). Thus, it is expected that the activated persulfate process has similar or even better performance in the removal of recalcitrant compounds compared with the Fenton process. To date, only a few studies have been conducted to investigate the removal of trimethoprim by the Fe(II)-activated persulfate process and to compare its performance with the Fenton process.

In addition, the concentrations of oxidants (persulfate and H<sub>2</sub>O<sub>2</sub>) have a significant effect on the performance of the Fenton and Fe(II)-activated persulfate processes in the removal of organic contaminants. Hydrogen peroxide can scavenge hydroxyl radicals, and persulfate can scavenge sulfate radicals (Yang et al., 2014). If excess oxidants exist, a quenching reaction of radicals caused by oxidants might occur, which increases the consumption of oxidants for a given concentration of organic contaminants. Similarly, the concentration of Fe(II) has an important effect on performance. Excess Fe(II) can scavenge hydroxyl radicals and sulfate radicals (Rastogi et al., 2009). Therefore, it is imperative to optimize the dosage of oxidants and Fe(II) to maximize the performance of the Fenton and Fe(II)-activated persulfate processes while reducing the number of oxidants and Fe(II) required.

The objective of this study was to investigate the degradation and mineralization of trimethoprim by Fenton and Fe(II)-activated persulfate processes in synthetic and actual wastewater. The intermediate products of the degradation of trimethoprim were detected, and a possible degradation pathway was tentatively proposed.

## 2. Materials and methods

### 2.1. Chemicals

Trimethoprim was obtained from the Aladdin Company (China)

with a purity of higher than 98%. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and persulfate were purchased from the Tianjin Yongda Chemical Reagent Co., LTD (China). Ferrous sulfate, sodium bicarbonate, potassium iodide and sodium nitrite were provided by Xilong Scientific (China). Methanol, acetonitrile and formic acid were obtained from Thermo Fisher. Potassium titanium oxalate was purchased from the Aladdin Company (China). De-ionized water was provided by the Wahaha Company (Hangzhou, China).

### 2.2. Trimethoprim degradation experiments

A stock solution of trimethoprim was prepared using de-ionized water (1 L) at room temperature (25 °C). The concentration of the trimethoprim stock solution was 1 mM. The initial concentration of trimethoprim used in this study was 0.05 mM. The concentration of the persulfate and the ferrous stock solution was 20 mM. For the preparation of the ferrous stock solution, small amounts of sulfuric acid were added to prevent the precipitation of Fe(II). During the experiments, the quantified ferrous stock solution was added into the glass bottle (150 mL).

All experiments were conducted at a constant temperature (25 °C). Based on the previous study, the shaker speed was 160 rpm (Huang et al., 2001; Yu et al., 2005). The initial pH was adjusted to 3, which is the optimal pH for the Fenton process. To provide a reasonable comparison between the Fenton process and the Fe(II)-activated persulfate process, the same pH was used in the Fe(II)-activated persulfate process. The pH was not adjusted during the experiments. The trimethoprim stock solution and oxidants (hydrogen peroxide or persulfate) were added into the reactor (150 mL) to achieve the desired concentration, and then Fe(II) was added to initiate the degradation experiment. The final volume was 100 mL. The time of reaction was 6 h, and samples were collected at a prescribed interval. Methanol (100 µL) was added to the samples to quench the radicals (hydroxyl radicals and sulfate radicals). To measure the TOC, a 5-mL sample was taken at the end of the experiments. Then, 200 µL of saturated sodium nitrite was immediately added into this sample to terminate the Fenton reaction and the ferrous ion-activated persulfate oxidation reaction (Rastogi et al., 2009). The sample was then passed through a 0.45-µm filter membrane and stored at 4 °C pending analysis.

For the analysis of trimethoprim degradation in actual wastewater, a stock solution of trimethoprim was prepared using actual wastewater from the secondary effluent of a wastewater treatment plant in Beijing. All experiments were conducted in triplicate. Other experimental conditions followed the previously described procedure.

### 2.3. Analytical methods

Trimethoprim concentrations were measured using high-performance liquid chromatography (HPLC) (Agilent 1200 Series, Agilent, USA) coupled to a C18 reversed-phase column (5 µm, 4.6 × 150 mm) and a diode array detector (DAD) with a wavelength of 237 nm. The column temperature was maintained at 20 °C. The flow rate was 0.6 mL/min. The initial mobile phase contained 30% acetonitrile (A) and 70% water with 0.1% (v:v) formic acid (B). The level of solvent A increased to 90% within 4 min, remained at this level for 2 min, and then returned to the initial conditions within 4 min.

The intermediates formed during the experiment were identified by HPLC coupled to a Shimadzu 2010 EV mass spectrometer. The analytical approach followed the previously stated method.

The mineralization of trimethoprim was measured with a TOC analyzer (Multi N/C 2100, Jena, Germany). The concentrations of hydrogen peroxide and persulfate were determined using the

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