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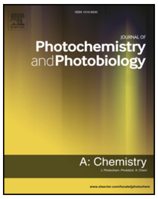

Feasibility of using UV/H_2O_2 process to degrade sulfamethazine in aqueous solutions in a large photoreactor

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ABSTRACT

This investigation evaluates the performance of a large photoreactor in degrading sulfamethazine (SMT) in aqueous solutions by the UV/H_2O_2 process. The effects of UV wavelength, initial H_2O_2 concentration, initial SMT concentration, and added anions on the efficiency of degradation of SMT were studied. The degradation of SMT proceeded more rapidly in the UV-254 nm/H_2O_2 process than in the UV-365 nm/H_2O_2 process. A higher initial H_2O_2 concentration was associated with more efficient degradation of SMT. However, an excessive initial H_2O_2 concentration limited the degradation of SMT. The efficiency of degradation of SMT increased with decreasing initial SMT concentration. The degradation of SMT by the UV/H_2O_2 process in a large photoreactor exhibited pseudo-first-order kinetics. Moreover, SO_4^{2-} and NO_3^- did not retard the degradation of SMT but Cl^- slightly inhibited the degradation of SMT. SMT was completely degraded in 10 min by the UV-254 nm/H_2O_2 process at an initial SMT concentration of 5 mg/L and an initial H_2O_2 concentration of 10 mM in the absence of anions. These results clearly reveal the potential of the UV/H_2O_2 process in a large photoreactor in the effective degradation of SMT in aqueous solutions.

1. Introduction

In recent years, the presence of residual antibiotics in aquatic environments has attracted increasing interest and become an important issue in relation to the function of aquatic ecosystems [1–3]. As a major sulfonamide antibiotic, sulfamethazine (SMT) is commonly utilized as a veterinary medicine to limit the spread of infectious diseases and promote animal growth, owing to its wide antimicrobial spectrum, excellent antibacterial activity, and low cost [3–6]. However, SMT cannot be completely metabolized after its uptake by animals, and up to 90% of SMT is discharged into aquatic environments in urine or feces [4–6]. Hence, SMT has often been detected in aquatic environments with concentrations ranging from ng/L to μg/L [3,5]. Furthermore, SMT cannot be effectively degraded by traditional biological wastewater treatment [4,6]. Therefore, many effective methods for degrading SMT have been developed, including the VUV/UV photo-Fenton process [3], the nanoscale zero-valent iron/persulfate process [4], photolysis and photocatalytic decomposition [6], combination of the electro/Fe^{3+}/peroxydisulfate process with a biological treatment [7], the heterogeneous Fenton process [8], catalytic ozonation [9], heat-activated persulfate oxidation [10], electrochemical degradation [11], the gamma irradiation/H_2O_2 process [12], sonolytic degradation [13], and ultraviolet (UV) light-activated persulfate oxidation [14].

Over the past few decades, a special class of oxidation methods, called advanced oxidation processes (AOPs), has been developed to degrade organic pollutants in aquatic environments [15]. Almost all AOPs produce reactive species, including hydroxyl radicals ($HO^{\cdot}$), which are extraordinarily reactive and attack most organic molecules with very high rate constants [15] and so can degrade rapidly and nonselectively a wide range of organic pollutants in aquatic environments [16]. A powerful oxidant (H_2O_2) can be used to generate $HO^{\cdot}$ to degrade organic pollutants in aquatic environments [15]. Among numerous methods of H_2O_2-based degradation, the combination of UV irradiation and the H_2O_2 process is gaining more attention. H_2O_2 can be activated to form two $HO^{\cdot}$ radicals under UV irradiation, in accordance with Eq. (1) [15]. Hence, the UV/H_2O_2 process has been confirmed to be effective in degrading organic pollutants in aquatic environments [17–20].

$$H_2O_2 + h\nu \rightarrow 2HO^{\cdot} \tag{1}$$

The UV/H_2O_2 process has exhibited great potential for degrading antibiotics in aquatic environments [21–30]. Efficiencies of degradation

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Table 1
Efficiencies of degradation of some antibiotics using UV/H_2O_2 process.

Antibiotics	Concentration	Operating conditions	Results	References
ofloxacin	10 mg/L	pH 3 0.27 g/L H_2O_2	97% degradation after 30 min	[21]
sulfapyridine	20 mg/L	circumneutral pH 0.7 g/L H_2O_2	99% degradation after 180 min	[22]
oxytetracycline	10 µM	0.5 mM H_2O_2	80% degradation at UV Fluence of 320 mJ/cm^2	[23]
norfloxacin	15 mg/L	pH 7 2.1 mM H_2O_2	100% degradation after 100 min	[24]
chloramphenicol	100 mg/L	pH 5.5 40 mM H_2O_2	100% degradation after 60 min	[25]
amoxicillin	100 µM	pH 7 10 mM H_2O_2	> 99% degradation after 20 min	[29]

of some antibiotics by the UV/H_2O_2 process are shown in Table 1, implying that the UV/H_2O_2 process is effective in degrading antibiotics. However, very little work, if any, has been done on the degradation of SMT by the UV/H_2O_2 process. The use of a large photoreactor increases the industrial usefulness of the UV/H_2O_2 process. Therefore, the main purpose of this investigation is to assess the feasibility of using the UV/H_2O_2 process to degrade SMT in a large photoreactor. The relationships between the efficiency of degradation of SMT and the main operating variables, which are UV wavelength, initial H_2O_2 concentration, and initial SMT concentration, are elucidated. The effects of added anions on the efficiency of degradation of SMT are also considered. The findings of this investigation are helpful in treating wastewater that has been contaminated with SMT.

2. Experimental

Sulfamethazine ($C_{12}H_{14}N_4O_2S$, 99%) was obtained from Sigma-Aldrich. Its chemical properties are listed in Table 2. Hydrogen peroxide (H_2O_2, 30%), methanol (CH_3OH, 99%), and sodium nitrate ($NaNO_3$, 99.5%) were supplied by Sigma-Aldrich. Acetonitrile (CH_3CN, 99.9%), sodium sulfate (Na_2SO_4, 99%), and sodium chloride (NaCl, 99.7%) were purchased from J.T. Baker. Deionized water with a resistivity of 18.2 MΩ·cm was obtained using a Direct-Q 3 UV-R Tap to Pure & Ultrapure water purification system (Merck Millipore).

Aqueous SMT was prepared by dissolving sulfamethazine powder in deionized water. All of the experiments were performed with a Pyrex cylindrical photoreactor in batch mode. In each experiment, the photoreactor was filled with 3 L of aqueous SMT. The UV light source was two 8 W low-pressure mercury lamps, which were housed in two quartz sleeves with an axial orientation inside the photoreactor. The wavelength of the maximum emission that was obtained from the different lamps was 365 or 254 nm. An agitator was placed in the middle of the photoreactor to mix the aqueous SMT completely. Aeration with nitrogen during the degradation removed the dissolved oxygen from the aqueous SMT. The temperature of the aqueous SMT was maintained at 25 °C using a temperature-controlled water bath. The original pH of the aqueous SMT was approximately 6. When the pH and temperature of the aqueous SMT had reached constant values, a specified amount of H_2O_2 was added. Then, the two UV lamps were switched on and the degradation proceeded for 30 min. In all experiments, the pH of the aqueous SMT varied during the degradation.

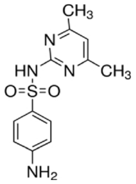
In sampling interval, a 1 mL sample was extracted from a sampling port on the cover of the photoreactor and quenched immediately with 1 mL of methanol, which is a well-known quenching agent for reactive radicals. The concentration of SMT in the analytic sample was measured using a high-performance liquid chromatography (HPLC) system (Jasco) that was equipped with a UV–vis detector and a Shimadzu VP-ODS column (250 mm × 4.6 mm). The mobile phase was a mixture of acetonitrile and deionized water in a ratio of 35%/65% (v/v) [4]. The flow rate of the mobile phase was maintained at 1 mL/min [4]. The injection volume of all samples was 50 µL, and spectrophotometric detection was conducted at 266 nm for SMT [4]. Total organic carbon (TOC) analysis was performed using a Torch Combustion TOC analyzer (Teledyne Tekmar).

3. Results and discussion

To assess the effectiveness of the UV/H_2O_2 process, control experiments on the degradation of SMT were carried out by the following processes; (1) UV, (2) H_2O_2, and (3) UV/H_2O_2. These experiments were performed using an initial SMT concentration of 10 mg/L. The UV wavelength was 254 nm in the UV and UV/H_2O_2 processes. The initial H_2O_2 concentration was 10 mM in the H_2O_2 and UV/H_2O_2 processes. Fig. 1 presents the results of degrading SMT by the three processes. The UV process degraded 79% of the SMT after 30 min. During degradation by the H_2O_2 process, the concentration of SMT was almost 10 mg/L for 30 min (data not shown here), indicating that H_2O_2 alone did not degrade SMT. In the UV/H_2O_2 process, the efficiency of degradation of SMT rapidly increased over time, and was observed to reach 100% in 15 min.

The above observations suggest that the UV/H_2O_2 process was associated with more efficient degradation of SMT than other two processes because it involves the following mechanism. $HO^{\cdot}$ was produced by the photolytic decomposition of H_2O_2 (Eq. (1)), and can directly

Table 2
Chemical properties of SMT.

Chemical formula	Chemical structure	Molecular weight (g/mol)	λ_{max} (nm)[a]	pK$_a$[a]	Solubility in water (g/L)[a]
$C_{12}H_{14}N_4O_2S$		278.33	260	2.65, 7.65	1.5

[a] Ref. [7].