Degradation of ofloxacin using UV/H$_2$O$_2$ process in a large photoreactor

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ABSTRACT

This study evaluates the effectiveness of the UV/H$_2$O$_2$ process in degrading ofloxacin in aqueous solution using a large photoreactor. The effects of UV wavelength, H$_2$O$_2$ dosage, and pH on the efficiency of degradation of ofloxacin were investigated. The UV/H$_2$O$_2$ process exhibited pseudo-first-order kinetics. The observed degradation rate constant (k) was determined under various operating conditions. The k value under UV-254 nm was 10.3 times that under UV-365 nm at an H$_2$O$_2$ dosage of 0.07 g/L and pH 3. The k value at pH 3 was 12.7 times that at pH 11 when the H$_2$O$_2$ dosage was 0.47 g/L. A larger H$_2$O$_2$ dosage was associated with a greater efficiency of degradation of ofloxacin. However, an excessive H$_2$O$_2$ dosage inhibited the degradation of ofloxacin. The efficiency of degradation of ofloxacin was 97% within 30 min at pH 3 using an H$_2$O$_2$ dosage of 0.27 g/L under UV-254 nm. Under the same conditions, the efficiency of mineralization of ofloxacin was 89% after 180 min. These promising results clearly demonstrate the potential of the UV/H$_2$O$_2$ process for the effective degradation of ofloxacin.

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1. Introduction

Antibiotics are administered in large amounts in both human medicine and veterinary medicine [1]. Therefore, the presence, fate and risks of residual antibiotics in the natural environment have become a growing concern [2]. Moreover, the presence of antibiotics in wastewater has increased in recent years, and their elimination will be a substantial challenge in the near future [1]. Among commonly used antibiotics, fluoroquinolones are a major group of broad-spectrum synthetic antibacterial agents [2]. Ofloxacin, a fluoroquinolone antibiotic, is extensively utilized to treat various bacterial infections in humans and animals [3]. In fact, ofloxacin has often been detected in water and wastewater [4,5]. Owing to its occurrence and toxicity, ofloxacin may pose a considerable risk to aquatic organisms [5]. Hence, many works have proposed several methods for removing ofloxacin, such as adsorption [6], ozonation [7], photocatalytic degradation [8], the solar Fenton method [9], and sonophotocatalytic degradation [10].

Over the last few years, a novel set of methods, called advanced oxidation processes (AOPs), for degrading organic contaminants in wastewater, have attracted considerable research interest [11]. Almost all AOPs are based on the formation of reactive species, such as the hydroxyl radical (HO·), that can degrade rapidly and non-selectively a wide range of organic contaminants [12]. A combined UV irradiation and H$_2$O$_2$ process, specified by Eq. (1), is cur-

rently attracting more interest because the UV/H$_2$O$_2$ process has been provided to be effective for degrading organic contaminants [13–17].

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

Moreover, the UV/H$_2$O$_2$ process has great potential for degrading antibiotics in water and wastewater [18–22]. However, very little work, if any, has been carried out on the degradation of ofloxacin by the UV/H$_2$O$_2$ process. Additionally, a large photoreactor is utilized to broaden the industrial application of the UV/H$_2$O$_2$ process. Accordingly, the main objective of this study is to investigate the feasibility of using the UV/H$_2$O$_2$ process to degrade ofloxacin in a large photoreactor. Also, the relationships between the efficiency of degradation of ofloxacin and the main operating variables, which are UV wavelength, H$_2$O$_2$ dosage, and pH, were elucidated. The findings of this study may be helpful in the treatment of wastewater that is contaminated with ofloxacin.

2. Experimental

Ofloxacin (C$_{18}$H$_{20}$FN$_3$O$_4$, 99.5%) was obtained from Sigma-Aldrich. Its chemical structure is shown in Fig. 1. Hydrogen peroxide (H$_2$O$_2$, 30%) was purchased from Showa. Hydrochloric acid (HCl, 37%) was supplied by Scharlau and sodium hydroxide (NaOH, 99%) was obtained from Mallinckrodt. All stock and working solutions were prepared in deionized water with a resistivity of 18.2 MΩ cm, which was obtained using a Direct-Q 3 UV-R Tap to Pure & Ultrapure water purification system (Merck Millipore).

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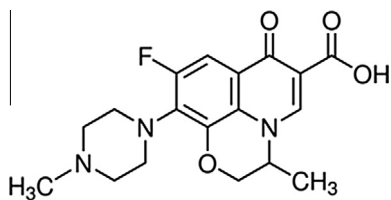 *E-mail address:* higee@mail.cgu.edu.tw (C.-C. Lin).

Fig. 1. Chemical structure of ofloxacin.

The degradation of ofloxacin by the UV/H₂O₂ process was conducted in a Pyrex batch cylindrical photoreactor. Two quartz tubes were installed vertically within the photoreactor; each tube contained a low-pressure mercury lamp (8 W, Philips) as the source of UV irradiation. The wavelength of the maximum emission that was obtained from the lamps was 365 or 254 nm. Nitrogen was fed continuously to the photoreactor from the bottom at a flow rate of 0.4 L/min to ensure that no oxygen influenced the process. The volume of the aqueous ofloxacin in the photoreactor was 3 L. The initial concentration of ofloxacin in the aqueous solution was 10 mg/L. The reactor was immersed in a temperature-controlled water bath to keep the temperature of the aqueous ofloxacin at 25 °C. An agitator in the center of the photoreactor ensured homogeneity of the solution. The pH of the aqueous ofloxacin was adjusted by adding concentrated aqueous HCl and NaOH. When the pH and temperature of the aqueous ofloxacin had reached constant values, a known amount of H_2O_2 was added. Then, two lamps were turned on and degradation proceeded for 30 min. Analytic samples of 10 mL were withdrawn at known intervals and the remaining ofloxacin was analyzed thereafter. The amount of ofloxacin in each sample was measured at a maximum absorption wavelength of 288 nm using a UV–vis spectrophotometer (Jasco, V-630) with reference to previously prepared calibration curves that were obtained at various pH. The mineralization of ofloxacin was identified by the reduction in total organic carbon (TOC), which was determined using a TOC analyzer (O.I. analytical, model 1010).

The efficiency of degradation of ofloxacin (E) by the UV/H₂O₂ process is defined as

$$E(\%) = \frac{C_0 - C}{C_0} \times 100 \tag{2}$$

where C_0 is the initial concentration of ofloxacin and C is the concentration of ofloxacin at time t. A higher E value represents a higher degradation efficiency of ofloxacin. To evaluate the performance of the UV/H₂O₂ process in degrading ofloxacin in aqueous solution, the efficiency of degradation of ofloxacin is presented as a function of the main operating variables, which are UV wavelength, H₂O₂ dosage, and pH.

3. Results and discussion

3.1. Performance of UV/H₂O₂ process

To evaluate the performance of the UV/H₂O₂ process, control experiments on the degradation of ofloxacin were conducted using various processes: (1) UV, (2) H₂O₂, and (3) UV/H₂O₂. These experiments were carried out at pH 3 and an initial ofloxacin concentration of 10 mg/L. The UV wavelength was 254 nm in the UV and UV/H₂O₂ processes. The H₂O₂ dosage was 0.07 g/L in the H₂O₂ and UV/H₂O₂ processes. Fig. 2 reveals that the self-photolytic degradation of ofloxacin was not very significant. After 30 min, the efficiency of degradation of ofloxacin was 30%. When H₂O₂ was added, significant degradation of ofloxacin was observed. In the UV/H₂O₂ process, the efficiency of degradation of ofloxacin drastically
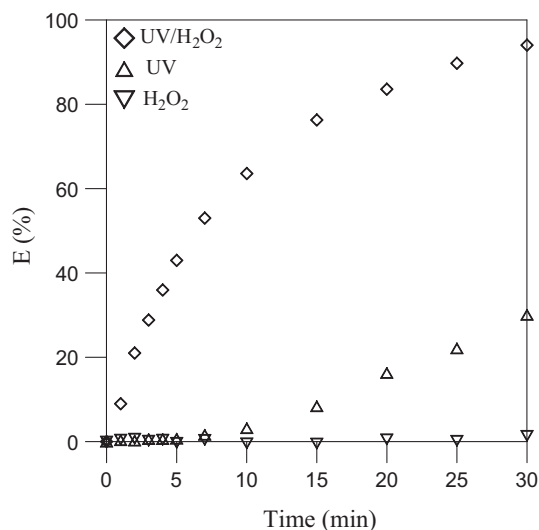

Fig. 2. Efficiency of UV/H₂O₂ process in degrading ofloxacin.

increased over time, and was observed to be 94% after 30 min. However, the degradation of ofloxacin by the H₂O₂ process was negligible; the efficiency of degradation of ofloxacin (1%) was much lower than that by the UV/H₂O₂ process, as measured after 30 min.

These observations imply that the UV/H₂O₂ process was associated with a high efficiency of degradation of ofloxacin, on account of the following mechanism.

$$HO^{\cdot} + \text{ofloxacin} \rightarrow \text{degradation product} \tag{3}$$
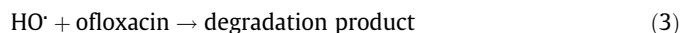
where $HO^{\cdot}$ denotes the hydroxyl radical. $HO^{\cdot}$ was formed from photolytic decomposition of H₂O₂ (Eq. (1)), and it can directly degrade ofloxacin in aqueous solution (Eq. (3)). Therefore, in the presence of both H₂O₂ and UV irradiation, large amounts of $HO^{\cdot}$ were formed, significantly degrading ofloxacin, as displayed in Fig. 2.

3.2. Degradation of ofloxacin

The degradation of ofloxacin by the UV/H₂O₂ process is described by a pseudo-first-order kinetic model, as follows.

$$\frac{dC}{dt} = -kC \tag{4}$$

where C represents the concentration of ofloxacin at time t and k is the observed degradation rate constant (k). Integrating Eq. (4) yields Eq. (5), as follows.

$$\ln\left(\frac{C_0}{C}\right) = kt \tag{5}$$

The slope of the plot of $\ln(C_0/C)$ against time yields the k values, where C_0 is the initial concentration of ofloxacin. To elucidate the effect of the operating variables on the degradation of ofloxacin by the UV/H₂O₂ process, the k values were obtained under various operating conditions.

3.2.1. Effect of UV wavelength

To investigate the effect of UV wavelength on the efficiency of degradation of ofloxacin, an experiment was performed at pH 3 with an H₂O₂ dosage of 0.07 g/L. As presented in Fig. 3, after 30 min, the efficiencies of degradation of ofloxacin using UV-365 nm and UV-254 nm were 26% and 94%, respectively, revealing that the UV wavelength strongly influenced the efficiency of degradation of ofloxacin. According to Eq. (5), the k values that were