Feasibility of using UV and persulfate in degrading ofloxacin in a large reactor

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ABSTRACT
Ofloxacin (OFL) was degraded by ultraviolet (UV) and persulfate (PS) in a large reactor. The effects of pH and PS concentration on the UV/PS process were examined. The degradation rate and efficiency of OFL at pH 3 markedly exceeded those at pH 11. The degradation rate and efficiency of OFL increased with PS concentration. However, a higher PS concentration disfavored the OFL degradation. The optimal PS concentrations at pH 3, 7, and 11 were 1.00, 0.50 and 0.50 mmol/L, respectively. The OFL degradation by the UV/PS process initially exhibited pseudo-first-order kinetics. At pH 3 and a PS concentration of 1.00 mmol/L, 82% of OFL was degraded after 30 min. Therefore, the UV/PS process effectively degrades OFL.

Keywords: Degradation; Antibiotic, Ofloxacin; UV; Persulfate

1. Introduction
An innovative method, involving sulfate radical-based advanced oxidation processes (SR-AOPs), has gained considerable attention as an efficient solution for degrading recalcitrant organic compounds in water [1–3]. In the SR-AOPs, the sulfate radical (SO4•−) with the high reactivity degrades organic compounds to CO2 and H2O [1–3]. Usually, SO4•− is formed by the activation of persulfate (S2O82−, PS) [1–4]. Many approaches for the activation of PS have been proposed, including activation by ultraviolet (UV) light, heat, ultra-sonication, iron, minerals, base, and an electrochemical mechanism [1–4].

In the UV/PS process, two SO4•− radicals can be formed by the activation of one PS molecule as a result of UV irradiation, according to Eq. (1) [3]. SO4•− is a strong oxidant (E° = 2.5–3.1 V) [5,6], and the UV/PS process has been verified to be effective to degrade organic compounds in water [3,7–16]. For example, Lin and Wu [14] adopted the UV/PS process to degrade ciprofloxacin (10 mg/L) in water and achieved the result that the degradation efficiency of ciprofloxacin was 95% after 30 min at an Na2S2O8 concentration of 1.92 g/L. Lin et al. [15] utilized the UV/PS process to degrade polyvinyl alcohol (20 mg/L) in water and obtained the result that 97% of polyvinyl alcohol was degraded within 10 min at an Na2S2O8 concentration of 1 mmol/L.

SO4•− + hν → 2SO4•−

In recent years, the presence and risks of residual antibiotics in water and wastewater have become emerging issues [14,17,18]. Among frequently used antibiotics, fluoroquinolones (FQs) are a major group of broad-spectrum synthetic antibiotics that have been extensively utilized in human, veterinary, and aquaculture medicines since they were introduced in the 1980s [14,17,18]. Ofloxacin (OFL) is one of the most extensively utilized FQs globally [19] and is widely adopted to treat diverse bacterial infections in humans and animals [18,20]. Most OFL cannot be metabolized following its uptake by humans and animals, and a large amount of OFL is excreted to the environment through feces and urine.

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Thus, OFL has been detected in the aquatic environment [21]. Due to its appearance and toxicity, OFL may present a significant risk to aquatic species [18,22]. Therefore, different approaches to removing OFL have been developed, such as the UV/H₂O₂ process [18], adsorption [19], ozonation [22], photocatalytic degradation [23], the heterogeneous Fenton process [24], the solar Fenton process [25] and sonophotocatalytic degradation [26]. To the best of the authors’ knowledge, very little research has been done on the OFL degradation by the UV/PS process. A large reactor must be used to elucidate the effectiveness of this process before it can be industrially applied. Hence, the main purpose of this work is to evaluate the feasibility of the UV/PS process in degrading OFL in a large reactor. The effects of the main operating parameters, which are pH and PS concentration, on the OFL degradation are also determined.

2. Experimental setup

Aqueous OFL (10 mg/L) was prepared by dissolving OFL powder (99.5%, Sigma-Aldrich, USA) in deionized water. All degradation experiments were carried out in a batch system with a Pyrex cylindrical reactor. Three liters of the aqueous OFL was put in the cylindrical reactor. Two quartz sleeves were placed vertically in the cylindrical reactor. Each quartz sleeve held a low-pressure mercury lamp (8 W, 365 nm). An agitator that was set in the center of the cylindrical reactor assured great mixing. Nitrogen was continuously introduced into the aqueous OFL from the bottom of the cylindrical reactor at a flow rate of 0.4 L/min to assure that no oxygen influenced the OFL degradation. A temperature-controlled water bath was employed to maintain the temperature of the aqueous OFL at 25°C. The pH of the aqueous OFL was adjusted to a designated value by adding concentrated aqueous NaOH (99%, Mallinckrodt, Ireland) or HCl (37%, Scharlau, Spain). A given amount of Na₂SO₄ (99%, Sigma-Aldrich, USA) was added to the aqueous OFL in the cylindrical reactor after the pH and temperature of the aqueous OFL had reached constant values. When UV was adopted to activate PS, two UV lamps were switched on immediately as PS was added. Subsequently, degradation was performed for 30 min. During the course of the degradation, the pH of the aqueous OFL was maintained to the designated value by adding concentrated aqueous NaOH or HCl.

At specified sampling intervals, the samples (10 mL) were taken from the cylindrical reactor, and the amount of remaining OFL was measured. A UV-Vis spectrophotometer (Jasco, V-630, Japan) was utilized to determine concentration of OFL in each sample by measuring the absorbance of the sample at 288 nm. The linearity of the dependence between absorbance and concentration was assessed using aqueous OFL at various concentrations in the range 0–20 mg/L and at various pH values. The linearity was obtained over the whole range of concentrations at these pH values. The degradation efficiency of OFL (E) is given by

\[ E(\%) = \frac{C_0 - C}{C_0} \times 100 \]  

where \( C_0 \) represents the concentration of OFL at the beginning of degradation and \( C \) represents the concentration of OFL at time \( t \). A higher \( E \) value exhibits a higher degradation efficiency of OFL. To evaluate the effectiveness of the UV/PS process in degrading OFL in water, the effects of pH and PS concentration on the degradation efficiency of OFL are studied.

3. Results and discussion

To elucidate the performance of the UV/PS process, experiments on the OFL degradation were performed by three processes, (1) UV, (2) PS, and (3) UV/PS. These experiments were carried out at pH 3. The PS concentration in the PS and UV/PS processes was 1.00 mmol/L. Fig. 1 indicates the results of the OFL degradation by the three processes. The OFL degradation by UV was low as the UV process achieved only 11% degradation after 30 min. In the PS process, the concentration of OFL remained almost constant for 30 min, suggesting that PS alone did not degrade OFL. During degradation by the UV/PS process, the degradation efficiency of OFL rapidly increased with time, reaching 82% after 30 min. A similar finding was achieved in the florfenicol degradation by the UV/PS process [11]. The florfenicol degradation by the PS process was negligible [11]. The degradation efficiencies of florfenicol by the UV and UV/PS processes were about 25% and 98%, respectively, in 60 min [11].

These findings demonstrate that the UV/PS process degraded OFL with high efficiency, owing to the following mechanism. Two \( \text{SO}_4^- \) radicals were produced by the activation of one PS molecule using UV radiation, consistent with Eq. (1), and several radical chain reactions were initiated by \( \text{SO}_4^- \) to degrade OFL (Eq. (3)). Thus, in the UV/PS process, high amounts of \( \text{SO}_4^- \) were formed, leading to great degradation of OFL, as indicated in Fig. 1.

\[ \text{SO}_4^- + \text{ofloxacin} \rightarrow \text{degradation product} \]  

Fig. 1. OFL degradation by UV/PS process.
To investigate the effect of pH on the OFL degradation in water by the UV/PS process, degradation was carried out at pH 3, 7, and 11. Fig. 2a displays the results that were achieved at a PS concentration of 0.06 mmol/L. The E values in 30 min at pH 3, 7, and 11 were 80%, 48%, and 15%, respectively; obviously, the degradation efficiency of OFL decreased as the pH was increased. As displayed in Fig. 2b, as the PS concentration was increased to 0.13 mmol/L, the degradation efficiency of OFL also declined as the pH was increased. At higher PS concentrations (0.25, 0.50, 1.00, and 2.00 mmol/L), as shown in Figs. 3 and 4, the degradation efficiencies of OFL also followed the order pH 3 > pH 7 > pH 11.

As proposed elsewhere [14,15] and presented in Figs. 2–4, the OFL degradation by the UV/PS process in the initial period (0–7 min) is consistent with a pseudo-first-order kinetic model, as follows.

\[
\frac{dC}{dt} = -kC
\]  

(4)

where \( C \) is the concentration of OFL at time \( t \) and \( k \) is the observed degradation rate constant (k). Integrating Eq. (4) gives Eq. (5), as follows. The slope of the plot of \( \ln(C/C_0) \) versus time gives \( k \), where \( C_0 \) is the initial concentration of OFL.
To investigate the effect of the main operating parameters on the OFL degradation by the UV/PS process, the \( k \) values were estimated at diverse pH and PS concentrations, and are listed in Table 1. The agreement between the experimental data and the results that were estimated using the model (Eq. (5)) was obtained by coefficients of determination (\( R^2 \)). Therefore, the high \( R^2 \) values at all pH and PS concentrations demonstrated that the OFL degradation by the UV/PS process corresponded to pseudo-first-order kinetics under all considered conditions. As listed in Table 1, \( k \) increased as the pH was decreased at all PS concentrations. For example, at a PS concentration of 0.06 mmol/L, the \( k \) value at pH 3 was about 1.4 times that at pH 7 and about 27.1 times that at pH 11.

As described in previous studies [12,15,16], when PS was present in the acidic water, acid-catalyzation produced more \( \text{SO}_4^{•–} \), which reacted with OFL, promoting the OFL degradation. \( \text{SO}_4^{•–} \) reacted with \( \text{OH}^- \) to form \( \text{HO}^{•} \) in alkaline conditions, as described by Eq. (6) [9,12,15]. \( \text{HO}^{•} \) predominated owing to the base-convertion of \( \text{SO}_4^{•–} \) to \( \text{HO}^{•} \) at pH > 7. \( \text{HO}^{•} \) exhibited a lower reactivity with OFL than did \( \text{SO}_4^{•–} \). Thus, in alkaline conditions, \( \text{OH}^- \) served as a scavenger of \( \text{SO}_4^{•–} \), inhibiting the OFL degradation. Additionally, in alkaline conditions, carbon oxide that was generated in the OFL degradation formed carbonate and bicarbonate ions [15], inhibiting the OFL degradation. The pKa values of OFL are 5.97 and 8.28 [27], suggesting that protonation of OFL occurred at pH 3 and deprotonation of OFL occurred at pH 11. At pH 3, electrostatic interaction between positively charged OFL and \( \text{SO}_4^{•–} \) enhanced the degradation efficiency of OFL. However, at pH 11, electrostatic repulsion between negatively charged OFL and \( \text{SO}_4^{•–} \) further reduced the degradation efficiency of OFL. The findings that were achieved in this work were consistent with previous results that the degradation of diethyl phthalate [7], the degradation of chloramphenicol [8], the degradation of methyl salicylate [10], the degradation of carbamazepine [12], the degradation of polyvinyl alcohol [15], and the degradation

\[
\ln \left( \frac{C_0}{C} \right) = kt
\]

(5)

Fig. 4. Effect of pH on OFL degradation at PS concentrations of (a) 1.00 mmol/L and (b) 2.00 mmol/L.

### Table 1

<table>
<thead>
<tr>
<th>PS (mmol/L)</th>
<th>pH 3</th>
<th>pH 7</th>
<th>pH 11</th>
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<tr>
<td></td>
<td>( E ) (%)</td>
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<td>50</td>
<td>80</td>
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<tr>
<td>0.50</td>
<td>67</td>
<td>81</td>
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</tr>
<tr>
<td>1.00</td>
<td>74</td>
<td>82</td>
<td>58</td>
</tr>
<tr>
<td>2.00</td>
<td>71</td>
<td>84</td>
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of 1,1,1-trichloroethane [16] by the UV/PS process were enhanced by acidic conditions.

$$\text{SO}_4^{2-} + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{HO}^+$$  \hspace{1cm} (6)

As presented in Figs. 2–4, at pH 3 in 5 min, the $E$ values at PS concentrations of 0.06, 0.13, 0.25, 0.50, 1.00, and 2.00 mmol/L were 50%, 58%, 65%, 67%, 74%, and 71%, respectively. These results indicate that the degradation efficiency of OFL increased with PS concentration from 0.06 to 1.00 mmol/L, mainly because more PS produced more SO$_4^{2-}$ (Eq. (1)). However, the degradation efficiency of OFL fell slightly as the PS concentration was increased to 2.00 mmol/L, indicating that excess PS disfavored the OFL degradation. The same result was observed at pH 7 and pH 11, as indicated in Table 1. The effect of PS concentration on $k$ is displayed in Fig. 5. The OFL degradation by the UV/PS process was optimized at a particular PS concentration. This optimal concentration maximized the degradation rate of OFL. As displayed in Fig. 5, the optimal PS concentration was 1.00 mmol/L at pH 3. When the pH was increased to 7 or 11, the optimal PS concentration was 0.50 mmol/L.

At higher PS concentrations, SO$_4^{2-}$ reacted with PS, according to Eq. (7) [13–15], leading to the saturation of the concentration of SO$_4^{2-}$. Moreover, the experimental results indicated that S$_2$O$_8^{2-}$ was less effective than SO$_4^{2-}$ in degrading OFL. Therefore, excess PS inhibited the OFL degradation by the UV/PS process. Similar results were obtained in the degradation of isopropyl alcohol [3], the degradation of tetramethylammonium hydroxide [13], the degradation of ciprofloxacin [14], and the degradation of polyvinyl alcohol [15] by the UV/PS process.

$$\text{SO}_4^{2-} + S_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{2-} + S_2\text{O}_8^{2-}$$  \hspace{1cm} (7)

As indicated in Table 1, at pH 3, the $k$ value at a PS concentration of 0.50 mmol/L was about 1.6 times that at a PS concentration of 0.06 mmol/L. This difference was greater in alkaline conditions. At pH 11, the $k$ value at a PS concentration of 0.50 mmol/L was about 5.2 times that at a PS concentration of 0.06 mmol/L. The obtained $k$ values demonstrate that alkaline conditions reduced the inhibitive effect of PS (Eq. (7)).

Table 2 summarizes the variation in performance of the three methods in the OFL degradation. Photocatalytic degradation requires a long operating time, increasing the operating cost. The UV-based process has the advantage of reduced operating time because it degrades OFL faster than the other methods. The UV/PS process has a lower degradation efficiency of OFL than the UV/H$_2$O$_2$ process because the latter uses a UV wavelength of 254 nm. When the UV wavelength of 254 nm is adopted, the UV/PS process degrades OFL more efficiently than does the UV/H$_2$O$_2$ process. However, light with a wavelength of 254 nm is not environmentally suitable because relatively little light with wavelengths of less than 290 nm reaches the earth [28]. As proposed by Goslich et al. [29], the sun emits 0.2–0.3 mol photons per square meter per hour in a wavelength range of 300–400 nm close to the surface of the earth with a UV flux of 20–30 W/m$^2$ [28]. When the light source is the sun, the capital and operating costs of artificial light sources are saved [29]. According to the results in this work, using UV with a wavelength of 365 nm in the OFL degradation by the UV/PS process is ideal and sunlight can also be used.
4. Conclusions

This work investigates the effectiveness of the UV/PS process in degrading OFL in water in a large reactor. The effects of pH and PS concentration on the OFL degradation were elucidated. The UV/PS process initially exhibited pseudo-first-order kinetics in the OFL degradation. The observed degradation rate constants ($k$) were estimated at various pH and PS concentrations. The $k$ value at pH 3 was about 27.1 times that at pH 11 when the PS concentration was 0.06 mmol/L. A higher PS concentration was associated with more efficient degradation of OFL. However, excess PS limited the OFL degradation. The degradation efficiency of OFL was 82% in 30 min at pH 3 with a PS concentration of 1.00 mmol/L. These results show the potential of the UV/PS process to degrade OFL effectively.

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References


