



Photocatalytic degradation of the antiviral drug Tamiflu by UV-A/TiO₂: Kinetics and mechanisms



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HIGHLIGHTS

- Degussa P25 was highly active for OP photocatalytic degradation.
- P25 loading, OP concentration, and pH value affect OP's photocatalytic degradation.
- Hydroxyl radical was the major radical for OP photocatalytic degradation by P25.
- Photocatalytic degradation pathway of OP by P25 was proposed.

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ABSTRACT

The photocatalytic degradation of the antiviral drug Tamiflu (oseltamivir phosphate, OP) by TiO₂ – P25, ST-01 and ATO was investigated in aqueous solution under ultraviolet (UV-A) irradiation. The photocatalysis of OP is well described by pseudo-first-order kinetics with $r^2 > 98.0\%$ for all cases. The kinetic constant of P25 with 80% anatase and 20% rutile (0.040 min^{-1}) is 4 and 10 times higher than that of ATO and ST-01 with 100% purity of anatase, respectively. We examined the effects of the catalyst loading and initial OP concentration on the photodegradation of OP, and used potassium iodine, isopropanol, and calcium fluoride as radical quenchers to evaluate the contributions of the hydroxyl radical ($\cdot\text{OH}$) and photo hole (h^+) in the photodegradation. Results confirmed that 80% of the contribution came from the $\cdot\text{OH}$ species. Although more than 95% of the OP ($21 \mu\text{M}$) was removed after 80 min of UV-A irradiation with 20 and 100 mg L^{-1} P25, the removal efficiencies of total organic carbon (TOC) were only 45.6% and 67.0%, respectively, after 360 min UV-A irradiation. Based on an intermediate analysis by HPLC coupled with a triple quadrupole spectrometer and an ion trap mass spectrometer, typical intermediate species such as hydration derivatives, hydroxyl substitutes and keto-derivatives were identified and possible degradation pathways of OP by P25 were proposed.

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1. Introduction

Tamiflu, the commercial medicine name of oseltamivir phosphate (OP), is recommended by the World Health Organization (WHO) as a prophylactic and therapeutic treatment drug for avian influenza outbreaks (Ward et al., 2005). OP is transformed into an

oseltamivir carboxylate (OC) metabolite in the human body, which is an inhibitor of influenza virus neuraminidase and the release of viral particles (Ghosh et al., 2010a). Concerns about OP and OC contaminations of water environments have been raised because of the outbreaks of avian influenzas in recent years and the routine use of Tamiflu in pandemic seasons. Contaminations of OP and OC have been detected frequently in the influent and effluent of wastewater treatment plants (WWTPs) in the range of $17\text{--}800 \text{ ng L}^{-1}$ (Straub, 2009; Prasse et al., 2010; Ghosh et al., 2010b; Leknes et al., 2012). However, recent investigations reported that less than 20% of the OP and OC were removed by conventional active sludge treatment (Prasse et al., 2010; Azuma et al., 2012).

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The presence of OP and OC in aquatic environments can induce the evolution of antiviral drug resistant genes and viruses (Fick et al., 2007; Singer et al., 2007; Ghosh et al., 2010a). Thus, the removal of OP and OC contamination at WWTPs and in aquatic environments is of critical importance. Previous investigations have indicated that the photolysis (direct photodecomposition without catalysts) of OP could be affected by the aquatic environment and the light source. The OP photodecomposition half-life times in ultrapure water without using photocatalysts were found to be 4.1 h under simulated sunlight irradiation ($\lambda > 290$ nm) (Gonçalves et al., 2011), and 3.3 min under UV light ($\lambda_{\text{max}} = 254$ nm) with a very high light intensity (15.7 mW cm^{-2}) (Tong et al., 2011). The significant difference in OP's photofate under different light sources indicated that the photolysis of OP is wavelength dependent. To date, no reports have addressed the photolysis of OP by UV-A light, which is commonly used as the light source in photocatalytic reactions.

Titanium dioxide (TiO_2) is a well-known photocatalyst with high activity, good stability, low cost, and low toxicity in aqueous solution (Grabowska et al., 2012). TiO_2 has been widely used in the photodegradation of various organic pollutants such as phenol, chlorinated phenol, and many types of antibiotics and pesticides (Ohko et al., 2001; Elmolla and Chaudhuri, 2010; Lambropoulou et al., 2011). However, the kinetics and mechanisms of the photocatalytic degradation of OP by TiO_2 have never been investigated. In this study, we used three kinds of typical titania samples to examine the photocatalytic process of OP under UV-A. The effects of the operation parameters, the determining radical species, and the possible intermediates were investigated. We found that the photocatalytic decomposition of OP under UV-A is a very fast but much more complex process than the direct photolysis of OP under simulated sunlight and UV-254 nm. To the best of our knowledge, this is the first study of photocatalytic degradation of the newly evolved antiviral OP pollutant.

2. Experimental

2.1. Materials and chemicals

OP with a purity of >95% was purchased from Medchemexpress Co., Ltd., China. Three kinds of powdered TiO_2 samples: P25 (80% anatase and 20% rutile), ST-01 (anatase type) and ATO (anatase type, Aldrich titanium oxide nano powder) were purchased from Degussa (Germany), Ishihara Sangyo (Japan) and Sigma-Aldrich (Germany), respectively. Table S1 summarizes the general characteristics of the TiO_2 . Acetonitrile and formic acid of HPLC grades, and special grades of potassium iodide (KI), sodium fluoride (NaF), and isopropanol (ISO) were purchased from Wako Pure Chemical Industries, Ltd., Japan. All solutions were prepared with ultra-pure water ($18.25 \text{ M}\Omega$) from a Milli-Q purification system (Millipore, Watford, UK).

2.2. Photocatalytic reaction experiments

We conducted the photocatalytic experiments at 298 K in a thermostatic reactor equipped with a UV-A irradiation system. Initial OP concentrations higher than the environmental level (usually in the range of $10\text{--}100 \mu\text{g L}^{-1}$) were used to investigate the removal efficiencies and mechanisms of OP by TiO_2 for the easiness of analysis. First, we added solutions (100 mL, without buffers) containing $2.6\text{--}53 \mu\text{M}$ OP and $5\text{--}200 \text{ mg L}^{-1}$ TiO_2 to 120 mL beakers, which were then placed in the reactor with the solution surface 10 cm below the UV-A lamps. The measured inherent solution pH was 5.8 ± 0.1 and the solution pH after photoreaction decreased slightly to ~ 5.6 . The dominant wavelength

of the UV-A light was 365 nm and, using a UV power meter (Hamamatsu Photonics K.K. C9536-01), we determined the irradiation intensity on the surface of solution to be 1.8 mW cm^{-2} . The effects of the radical species were studied by using KI, NaF, and ISO as scavengers. Further details on our photocatalytic reaction experiments are provided in the Supplementary Data.

2.3. Analysis methods

2.3.1. Analysis of OP concentration and total organic carbon

We determined the concentration of OP in the samples using an HPLC system (Shimadzu Co., Japan) equipped with LC-20AD pumps, an SPD-M20A photo-diode array (PDA) detector, and a VP-ODS C18 reverse column (150×4.6 mm, $4.6 \pm 0.3 \mu\text{m}$, Shimadzu). The mobile phase was a mixture of acetonitrile and a 0.4 M formic acid solution in Milli-Q water (pH was adjusted by NaOH to 3) at a ratio of 30%:70% (v:v) at a flow rate of 1 mL min^{-1} . The absorbance at 215 nm was chosen to trace the OP concentrations with a detection limit of $0.2 \mu\text{M}$.

The amount of total organic carbon (TOC) was measured with a Shimadzu VCPH-type TOC analyzer. The mineralization efficiency was discussed from the changes in the TOC amounts before and after photocatalysis.

2.3.2. Identification of intermediate species

The photocatalytic intermediate species of OP were identified with an HPLC system tandem with a triple quadrupole mass spectrometer (APCI 3200, Applied Biosystems, Canada) with electro-spray ionization (ESI) source. The HPLC system consisted of LC-20AD pumps and an Atlantis[®] T3 C18 column (100×2.1 mm, $3 \mu\text{m}$, Waters Co.). The mobile phase was a mixture of acetonitrile (A) and a 0.1% formic acid solution (B) according to the following process (in volume): 0–0.5 min 20% A; 0.5–1.5 min 20–80% A; 1.5–6.0 min 80% A; 6.0–7.0 min 80–20% A. Another ion trap MS/MS spectrometer (Amazon SL, Bruker Co., Germany) working in ESI(+) mode was also used to identify the structure of intermediate species.

3. Results and discussion

3.1. Preliminary screening of photocatalysts

As the photodecomposition properties of OP may possibly be influenced by its adsorptivity onto the photocatalysts, we employed and compared three kinds of photocatalysts with various specific surface areas but high photoactivity (pure or mixed anatase type). Fig. 1 shows the time course of OP concentrations by direct photolysis, adsorption onto the TiO_2 , and UV-A driven photocatalytic degradation by TiO_2 . We carried out the experiments at an initial OP concentration of $24.4 \mu\text{M}$, a photocatalyst loading of 20 mg L^{-1} , and an inherent pH of 5.8 ± 0.1 . In the absence of a catalyst, the direct photolysis of OP under UV-A irradiation can be neglected (less than 5% within 80 min) because of the weak light energy. In dark conditions, the three catalysts adsorbed only a small amount of OP. The ST-01, having the largest specific surface area, showed the largest adsorption (Fig. 1), indicating little affinity by the TiO_2 surface toward OP, similar to the cases of the antibacterial norfloxacin (Haque and Muneer, 2007) and the pain reliever paracetamol (Yang et al., 2008).

On the other hand, OP was significantly decomposed by irradiation of UV-A in the presence of photocatalysts. We analyzed the kinetics of OP photocatalytic degradation by the three kinds of TiO_2 and found the pseudo-first-order kinetic model to best fit the concentration decay curves for all the cases (Figs. S1 and S7). Among the three kinds of TiO_2 , P25 showed the highest

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