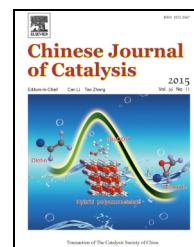


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Article

Kinetics and mechanism of thymine degradation by TiO₂ photocatalysis

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ABSTRACT

The advanced oxidation processes were examined toward the degradation of thymine (C₅H₆N₂O₂), a type of nucleic acid from the pyrimidine family. As observed, the photodegradation of thymine over TiO₂ photocatalyst was rapid and significant in aqueous solution under UV irradiation. Different parameters were studied, including the adsorption of thymine onto TiO₂ photocatalyst, the kinetics of degradation, and the effect of pH on the photocatalytic properties of thymine degradation. Additionally, the mineralization of the products obtained upon thymine photodegradation was studied. The disappearance and mineralization rates of thymine during the photocatalytic process were also compared and discussed. The mineralization of nitrogen was also investigated, and the identification of the intermediate products was established. Finally, electronic density calculations were used to propose possible chemical pathways for the photodegradation of thymine over TiO₂ photocatalyst under UV irradiation.

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1. Introduction

The photocatalytic degradation of the components of DNA was investigated in the presence of UV-irradiated TiO₂ aqueous suspensions. Compounds of DNA have received much attention as a chemical and pharmaceutical water treatment as it may be a potential target of photo-oxidative damage sensitized by TiO₂ [1–4]. Such processes may be directly involved in aquatic environments leading to the formation of intermediate species before final mineralization. Pyrimidine compounds are widely found in biomolecules and agrochemicals [5]. Their photocatalytic degradation has been examined in various studies [6–8], which mostly focus on the degradation mechanism of DNA bases (uracil, thymine, and cytosine) and ionic effects. These

studies are very relevant to water and cancer treatments. Pyrimidine bases, which are the products generated from the decomposition of nucleic acids, exist in natural waters and sediments [9]. These compounds are regarded as water pollutants that may be treated using photocatalysis processes [10,11]. The influence of different parameters, i.e., the concentration of pollutant, concentration of catalyst, pH, CdCl₂, concentration of oxygen, and presence of metallic ions, on the photodegradation of pyrimidine bases over TiO₂ catalyst, was studied by Jaussaud et al. [12] and Dhananjeyan et al. [8]. Horikoshi et al. [13] investigated the photomineralization pathways of pyrimidine and purine bases over TiO₂ photocatalyst under UVA/UVB illumination₂ and the associated rates of formation of NH₄⁺ and NO₃⁻ ions. Recently, Li et al. [14] established

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a combined photocatalytic and photo-electrochemical degradation mechanism of these nucleotide bases.

Singh et al. [15] reported a comprehensive photodegradation kinetics study of uracil and 5-bromouracil. The authors inferred that TiO_2 can efficiently catalyze the photomineralization of uracil and 5-bromouracil. Furthermore, they found that photocatalyst Degussa P25 displayed the highest photocatalytic activity and proposed that the addition of electron acceptors, such as hydrogen peroxide and potassium bromate, improved the decomposition process. The objective of our study is to determine the photocatalytic mechanism of the elimination of thymine, which is the simplest molecule present in the structure of microorganisms (DNA, proteins).

2. Experimental

Pure pyrimidine base thymine ($\text{C}_5\text{H}_6\text{N}_2\text{O}_2$, 99%) was purchased from Sigma-Aldrich and used as received. TiO_2 Degussa P25 (mainly anatase, 50 m^2/g , nonporous) was used as the photocatalyst. Ultrapure water used in all experiments was obtained using a Milli-Q PLUS 185 water system.

The photocatalytic experiments were carried out using a Pyrex cylindrical flask reactor, opened to the atmosphere with an optical area window of 19 cm^2 . An HPK 125 W Philips mercury lamp was used as the light source, and it was kept cooled with water circulation to prevent over heating during operation. The irradiation spectrum was cut-off below 340 nm using a Corning 0.52 filter. The radiant flux was measured using a VLX-3W radiometer equipped with a detector CX-365 (355–375 nm). The volume of the test solution was 20 mL, and the TiO_2 slurry concentration was set at 1.25 g/L to ensure absorption of all the photons [16]. Degradation was performed at room temperature ($T = 25\text{ }^\circ\text{C}$) and at natural pH (pH = 5).

In a typical photocatalysis test procedure, the test suspension was first stirred in the dark until equilibrium adsorption was achieved. Then, the solution was irradiated at $\lambda > 340\text{ nm}$ and a radiant flux of 3.5 mW/cm^2 . Aliquots were withdrawn at different times of the irradiation process and filtered through 0.45- μm pore size Waters filters to remove the TiO_2 particles before analysis of the filtrate.

The degradation of thymine was monitored by high-performance liquid chromatography conducted on a Varian System equipped with a Varian Prostar 230 isocratic pump and a Varian Prostar 330 Diode Area 29 Detector adjusted at 254 nm. A Hypersil BDS C18 reverse phase column (length = 125 mm, diameter = 4 mm) was used. The mobile phase constituted of 90% ultrapure water containing H_3PO_4 (62 μL) at pH = 3 and 10% methanol. The flow rate was 0.8 mL/min.

The mineralization of the pyrimidine base was monitored by determining the total organic carbon (TOC) concentration by direct injection of the filtered samples into a TOC-VCSH Shimadzu apparatus equipped with an ASI-V Shimadzu sampler.

The intermediate products formed upon degradation of thymine were analyzed by liquid chromatography conducted on an Agilent 1100 equipped with a Varian Prostar 230 pump, a Varian Prostar 325 UV detector (detection at 210 nm), and a

Transgenomic Icsep Coregel 87H column (length = 300 mm, diameter = 4.6 mm). The injection volume was 100 μL and the mobile phase was H_2SO_4 (5 mmol/L). The flow rate was 0.7 mL/min.

The formation of nitrate ions (as a result of thymine photodegradation) was monitored using ionic chromatography conducted on a DX-120 equipped with a Dionex DX-120 pump and conductivity detector, and an Ion Pac AS14A column (length = 250 mm, diameter = 4 mm). The flow rate was 1 mL/min and the mobile phase was an alkaline buffer (NaHCO_3 (1.0 mmol/L) + Na_2CO_3 (8.0 mmol/L)). The formation of ammonium ions (as a result of thymine photodegradation) was also monitored using ionic chromatography; a CS 12A column (length = 250 mm, diameter = 4 mm) was used. The flow rate was 1 mL/min and the mobile phase was based on H_2SO_4 -based solutions containing 610 $\mu\text{L}/\text{L}$ of pure sulfuric acid.

For all analyses, the error bars were $\sim 5\%$. Computer simulations using MOPAC software were performed to calculate the frontier electron density, which was used to identify the position of OH^\bullet radical attack in thymine.

3. Results and discussion

3.1. Adsorption

To determine the effect of the initial concentration of thymine on the adsorption kinetics, solutions of thymine at different concentrations (85, 162, 218, 253, 326, and 481 $\mu\text{mol}/\text{L}$) were stirred in the dark for 60 min until equilibrium was reached. The plot of the amount ($\mu\text{mol}/\text{g}$) of thymine adsorbed per gram of TiO_2 as a function of the thymine equilibrium concentration (C_{eq}) is shown in Fig. 1. As observed, the amount of thymine adsorbed onto TiO_2 surface (Q_{ads}) increased gradually until a plateau was obtained with equilibrium concentration. The calculated maximum coverage of thymine was ~ 0.03 molecule/ nm^2 , which represents $\sim 0.6\%$ of the maximum coverage of OH surface groups (5 OH/ nm^2) [17]. The maximum coverage of thymine obtained herein was consistent with maximum coverage values obtained for molecules containing aromatic rings such as tryptophan and phenylalanine [18,19]. In con-

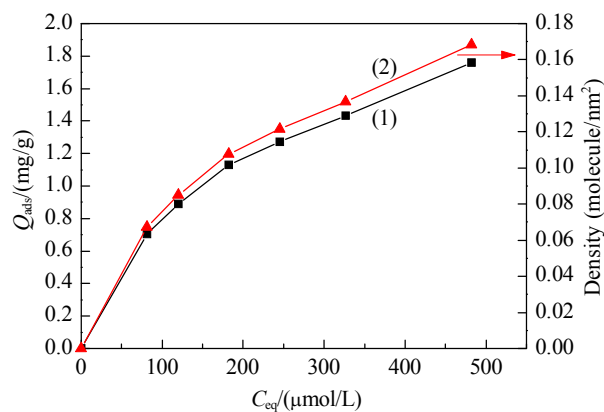


Fig. 1. Amount of thymine adsorbed onto TiO_2 Degussa P25 (1.25 g/L) (1) and area density of adsorbed thymine (2) as a function of equilibrium concentration.

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