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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 (C₅H₈N₂O₂), 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 photocatalytical 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 ~5%. Computer simulations using MOPAC software were performed to calculate the frontier electron density, which was used to identify the position of $\text{OH}^\bullet$ 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 ~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.

trast, the low OH coverage value obtained could partially be explained by (i) considering the study by Tran et al. [20], who suggested that effective adsorption of thymine only occurs on basic terminal OH groups on the solid surface and (ii) the small concentration of thymine used in the present study.

As consistent with most studies involving organic compounds [21,22], the adsorption of thymine could be described by the Langmuir adsorption mechanism:

$$Q_e = \frac{K_{\text{ads}} Q_{\text{max}} C_{\text{eq}}}{1 + K_{\text{ads}} C_{\text{eq}}} \quad (1)$$

where Q_e ($\mu\text{mol/g}$) is the quantity of thymine adsorbed onto the photocatalyst at adsorption equilibrium, K_{ads} ($\text{L}/\mu\text{mol}$) is the adsorption constant, Q_{max} ($\mu\text{mol/g}$) is the maximum amount which can be adsorbed, and C_{eq} ($\mu\text{mol/L}$) is the concentration of thymine at equilibrium. The values of the Langmuir parameters for thymine were determined as $K_{\text{ads}} = 0.005 \text{ L}/\mu\text{mol}$ and $Q_{\text{max}} = 2.36 \mu\text{mol/L}$.

3.2. Photodegradation of thymine

The results of thymine photodegradation are discussed herein. More specifically, the effect of thymine concentration on the photocatalytic degradation was examined, and the results are shown in Fig. 2. To study the photocatalysis of thymine, we ensured that direct photolysis was negligible (less than 5%).

The initial rates of thymine disappearance as a function of the concentration of thymine in solution (C_{eq}) were examined, and the results are shown in Fig. 3. As deduced, the initial disappearance rate of thymine followed first order kinetics ($r = kK_{\text{ads(UV)}}C_{\text{eq}}$, where r ($\mu\text{mol L}^{-1} \text{ min}^{-1}$) is the rate of disappearance of thymine, k ($\mu\text{mol L}^{-1} \text{ min}^{-1}$) is the rate constant, and $K_{\text{ads(UV)}}$ ($\text{L}/\mu\text{mol}$) is the adsorption constant under UV conditions) at low concentrations of up to ~ 100 – $120 \mu\text{mol/L}$ [23]. At the higher concentrations, the initial rate was independent of thymine concentration. This phenomenon is consistent with the Langmuir-Hinshelwood-type kinetics [24,25], where $r = kK_{\text{ads(UV)}}C_{\text{eq}}/(1 + K_{\text{ads(UV)}}C_{\text{eq}})$. The least squares method was used to determine $K_{\text{ads(UV)}}$ (i.e., $0.011 \text{ L}/\mu\text{mol}$) and k (i.e., $16.06 \mu\text{mol L}^{-1} \text{ min}^{-1}$).

Fig. 2. Kinetics of thymine disappearance at different initial thymine concentrations.

Fig. 3. Variation in the initial rate of disappearance of thymine as a function of thymine equilibrium concentration.

The coverage rate ($\theta = K_{\text{ads(UV)}}C_{\text{eq}}/(1 + K_{\text{ads(UV)}}C_{\text{eq}})$) under UV conditions was determined from $K_{\text{ads(UV)}}$ (Fig. 4). This behavior can be explained by taking into consideration the electrical charge of the molecule. Thymine has a pK_{a} of 9.3 (Scheme 1). Thus, at natural pH ($\text{pH} = 5$), thymine is neutral at all obtained coverage. A higher amount of thymine was obtained on TiO_2 surface, thus leading to a higher disappearance rate.

3.3. Organic carbon mineralization

Variations in the TOC (measured TOC) and organic carbon content deriving from residual thymine in solution (thymine residual OC) as a function of irradiation time over P25 photocatalyst are represented in Fig. 5. As observed, the two plots were different, thereby suggesting the presence of several intermediate compounds formed during the photocatalysis process. Irradiation time of longer than 22 h was necessary to

Fig. 4. Thymine coverage rate under dark and UV conditions as a function of thymine equilibrium concentration.

Scheme 1. Ionization states of thymine as a function of pH.

Fig. 5. Kinetics of the total organic carbon (TOC) disappearance and organic content (OC) in solution during thymine degradation. The initial thymine concentration was 200 $\mu\text{mol/L}$.

mineralize > 99% of organic carbon. Based on the TOC profile at the early stages of the process, the presence of methyl groups appeared to decrease the rate of decarboxylation and therefore the opening of the aromatic ring in thymine. Based on the radical frontier density (Table 1), before opening of the aromatic ring, the occurrence of several ring hydroxylations is expected, mainly at carbon C5, which has the highest electronic density and also at C6, on nitrogen N1, and finally at C4 (Scheme 1). Hydroxylation on C4 is expected to enable ring opening of thymine.

Additionally, Fig. 5 shows that only 34% of TOC had been mineralized following the disappearance of thymine (95%). Thus, the initial disappearance rates of the parent molecule (thymine in this case) are insufficient to determine whether the photocatalytic process is efficient. In fact, the degradation rates of the parent molecule are not always consistent with the removal rates of TOC.

3.4. Nitrogen mineralization

The kinetics of NH_4^+ and NO_3^- release in water are shown in Fig. 6. NH_4^+ and NO_3^- ions were detected at the early stage of the degradation process, then ammonium and nitrate ions are primary oxidation.

The nitrogen mass balance, obtained by adding both ion concentrations, was nearly comparable to the final expected stoichiometric value. After an irradiation time of 20 h, ~98% of

Fig. 6. Evolution of nitrate and ammonium as a function of irradiation time during the degradation of thymine. The initial concentration of thymine was 200 $\mu\text{mol/L}$.

nitrogen mineralization was observed.

Fig. 6 shows the evolution of NH_4^+ ions and NO_3^- ions as a function of the percentage of thymine concentrations disappearance. As observed, NH_4^+ ions formed rapidly from the early stages of the degradation process, and hydroxylation of C4 in thymine is the first step of the degradation process. This result is in agreement with the electronic density results and the increased formation of nitrates after total disappearance of thymine. The most important formation of NO_3^- ions is in agreement with the work of Horikoshi et al. [13] and Pelizzetti et al [26]. Actually, the latter authors suggested that the presence of a carbonyl group near the amine group (in the case of urea or of form amide) favors the formation of nitrate ions.

3.5. Organic intermediate compounds formation

The formation of organic intermediate compounds was monitored during the photocatalytic degradation of thymine to understand the various steps involved in the degradation of the pyrimidine compound. Fig. 7 shows the chromatogram obtained after 60 min of the degradation of the molecule.

Five peaks (labeled as A, B, C, D, and E) were detected. However, only three of the peaks could be identified as oxalic

Fig. 7. Chromatogram of intermediate compounds formed after 60 min of degradation of thymine.

Table 1

Frontier electron densities and point charge calculations of thymine using the CAChe (MOPAC) system.

Atom	Frontier electron density	Point charge
N1	0.25289	0.2973
C2	0.11434	0.6345
N3	0.06287	0.2781
C4	0.19101	0.5051
C5	0.53874	0.0100
C6	0.49477	0.0754
O7	0.13746	-0.6474
O8	0.08429	-0.6604
C9	0.03488	-0.0809

acid (peak A), pyruvic acid ($\text{CH}_3\text{-CO-COOH}$, peak B), and lactic acid (HOOC-CH(OH)-CH_3 , peak D). The corresponding formation kinetics of the compounds are shown in Fig. 8. In addition to these compounds, formic acid was detected, however, in very low concentrations. Its formation was potentially attributed to the degradation of the carbonyl portion of urea (-NH-C(=O)-N) in thymine. In contrast, lactic, pyruvic, and oxalic acids were detected from the start of the degradation process, and their contents increased to a maximum that corresponded to the time required for the complete disappearance of thymine in solution. The acid compounds obtained were primary products. It should be noted that after the total disappearance of thymine, ~80% of the detected organic matter originated from the acid compounds.

3.6. Photodegradation mechanism

Based on experimental observation, we propose that the first step of the degradation process involves hydroxylation of C6 because of the presence of methyl group. And the photo-oxidative transformation of thymine involves two major processes: (i) the adsorption of thymine onto the TiO_2 particle surface through two carbonyl oxygens and (ii) the opening of the thymine ring structure by cleavage of the $\text{=C6}\pm\text{N1}\pm$ bond after attack by $\text{OH}\cdot$ radicals on the $\pm\text{C5}=\text{C6}\pm\text{N1}\pm$ positions as evidenced by the temporal changes observed in the UV spectral data (not shown) during 60 min. Scheme 2 illustrates potential pathways of the disappearance of thymine.

3.7. Influence of pH

The pH influences both the surface state of TiO_2 and the ionized state of thymine. At pHs higher than the point of zero charge of titania, which is ~6.5 for TiO_2 Degussa P25, the surface of TiO_2 is negatively charged. In contrast, at pHs lower than the point of zero charge of TiO_2 , the surface of TiO_2 is positively charged according to the respective equilibrium equations:

The influence of pH on the photocatalytic degradation of

Fig. 8. Formation of oxalic, lactic, pyruvic, and formic acids during the photocatalytic degradation of thymine.

Scheme 2. Proposed photocatalytic degradation pathways of thymine.

thymine rate was studied at acidic, neutral, and alkaline pH values of 2, 6.3, and 10, respectively (Fig. 9). For pH values below 6, the initial rate of degradation increased with increasing pH. It should be noted that the lower concentration of OH^- ions and $\text{OH}\cdot$ radicals in acidic medium caused a reduction in the photocatalysis performance. The increase in the initial photo-degradation rate of thymine at pH = 6 was due to an increased in the extent of surface coverage by OH^- ions, which in turn could be converted into $\text{OH}\cdot$ that could participate in the degradation of thymine. Similar results of the effect of reaction pH

Fig. 9. Kinetics of thymine disappearance at pH = 2, 6.3, and 10. The inset shows the variations in the initial disappearance rate of thymine as a function of pH.

on the degradation of thymine were reported previously by Dhananjeyan et al. [27]. In our case, thymine ($pK_a = 9.3$) is deprotonated and negatively charged under basic pH conditions [28]. TiO_2 is also negatively charged under basic pH conditions [29]; thus, repulsion between the thymine anion and negatively charged TiO_2 particle surface led to a reduced rate of initial disappearance of thymine. By maintaining the pH at 6.3, a balance between these two above-mentioned effects could be achieved, thus leading to optimal photodegradation efficiency of thymine.

4. Conclusions

Herein, we examined the photodegradation of thymine over TiO_2 photocatalyst under UV irradiation. The adsorption constants of thymine as calculated from the Langmuir and Langmuir-Hinshelwood models were comparable regardless of the mode of irradiation (i.e., in the absence of irradiation (dark conditions) or under UV-A). However, a low mineralization rate of thymine was observed, indicating that the disappearance rate was insufficient to estimate the efficiency of the photocatalytic process. Furthermore, we found that the formation of NH_4^+ and NO_3^- ions was dependent of the presence of carbonyl and amine groups on the pyrimidine rings. The formation of NO_3^- ions was more significant in the presence of carbonyl groups. The electronic density, nitrogen mineralization, and study of the organic intermediates enabled us to suggest chemical pathways for the photodegradation of thymine. Because of their high electronic density, the two carbon atoms of the double bond were susceptible to attack by $OH^\bullet$. Attack by $OH^\bullet$ radicals on the carbon atom bearing the methyl substituent led to the formation of five intermediate products during thymine degradation, some of which were identified as oxalic, glycolic, pyruvic, and formic acids. The study of the influence of pH on the degradation of thymine revealed that the initial degradation rate was maximum at pH 6.3. Additionally, the analysis revealed that the formation of $OH^\bullet$ by reaction between OH^- and H^+ , at basic pH, was not the origin of the increased photocatalytic efficiency, as typically observed for most organic

compounds studied in the literature. Thus, the present study is important to understanding the possible applications of photocatalysis in the “bioworld” including disinfection, sterilization, and degradation of biomolecules such as DNA, RNA, and undesirable organic aqueous pollutants.

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Graphical Abstract

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Kinetics and mechanism of thymine degradation by TiO_2 photocatalysis

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A degradation mechanism is proposed for the mineralization of thymine using TiO_2 . The organic molecules and acids formed upon degradation are predominantly photoconverted into CO_2 and H_2O .

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TiO₂光催化降解胸腺嘧啶的动力学和机理

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摘要: 考察了用于降解来自嘧啶家族的一种核酸—胸腺嘧啶(C₅H₆N₂O₂)的高级氧化过程. 结果发现, 在光催化剂TiO₂作用下, 胸腺嘧啶的光降解进行得很快, 且在紫外光照射和水溶液中时更为明显. 研究了胸腺嘧啶在TiO₂催化剂上的吸附、降解动力学、以及pH值对光催化降解胸腺嘧啶性能的影响. 另外, 考察了胸腺嘧啶降解产物的矿化; 比较和讨论了在光催化过程中胸腺嘧啶的消失和矿化速率. 同时还研究了氮的矿化, 确立了中间产物的识别方法. 最后, 采用电子密度计算提出了在紫外光照射下TiO₂催化剂上胸腺嘧啶降解的可能化学途径.

关键词: 二氧化钛; 光催化; 胸腺嘧啶; 光矿化; 前沿电子密度

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