Applied Catalysis A: General 485 (2014) 207–213

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Titania-based photocatalytic degradation of two nucleotide bases, cytosine and uracil

L. Elsellami[a,b], K. Sahel[a,c], F. Dappozze[a], S. Horikoshi[d], A. Houas[b], C. Guillard[a,*]

[a] IRCELYON, CNRS UMR 5256/Université Lyon1, 2 av. Albert Einstein, Villeurbanne Cedex, 69626, France
[b] Unité de recherché Catalyse et Matériaux pour l'Environnement et les Procédés URCMEP (UR11ES85) Campus Universitaire Hatem BETTAHAR-Cité Erriadh, 6072 Gabes, Tunisia
[c] Laboratoire Physico-chimie des Matériaux, Catalyse et Environnement, Département de Chimie, Faculté des Sciences, Université des Sciences et de la Technologie d'Oran (USTO) , Oran, Algeria
[d] Sophia University, Faculty of Science and Technology, Department of Materials and Life Sciences, 7-1 Kioicho, Chiyodaku, Tokyo, Japan

ARTICLE INFO

Article history:
Received 23 March 2014
Received in revised form 22 July 2014
Accepted 30 July 2014
Available online 7 August 2014

Keywords:
Cytosine
Uracil
TiO_2
Photocatalysis
Reaction mechanism

ABSTRACT

The photocatalytic degradation of two components of DNA and RNA, cytosine ($C_4H_5N_3O$) and uracil ($C_4H_4N_2O_2$) differing only by the presence of an amine or a carbonyl group was investigated in the presence of UV-irradiated TiO_2 aqueous suspensions. The adsorption in the dark and under UV-A conditions, the photolysis, the kinetics of degradation, the fate of nitrogen and the identification of some intermediate products were investigated. The impact of pyrimidine cycles on the coverage of TiO_2 under UV-A, the effect of NH_2 substituent on the oxidation products and mineralization and the importance of carbonyl and amine groups on the fate of nitrogen atoms were evaluated. Electronic density was used to propose a possible chemical pathway. The comparison of the disappearance and mineralization rates in the photocatalytic process was discussed.

1. Introduction

Heterogeneous photocatalysis is an advanced oxidation process (AOT) allowing efficient production of hydroxyl radicals under appropriate conditions depending of the photocatalyst used. These radicals have an oxidizing power much greater than traditional oxidants. They are capable of partially or completely mineralizing most of organic compounds [1–4]. The most widely used catalyst is TiO_2 because of its relative high photocatalytic activity, its stability, its availability and its relative low cost [5–7]. Under UV-light, titanium dioxide is an extremely powerful oxidant able to break the carbon chains. The pollutants are mineralized into water and carbon dioxide.

Pyrimidine compounds are largely found in biomolecules and agrochemicals [8]. Several studies deal with the photocatalytic degradation of pyrimidine compounds [9–16]. They mainly focused on the degradation mechanism of DNA bases (uracil, thymine, and cytosine) and on ionic effects. Such studies are highly relevant to water and cancer treatments.

The pyrimidine bases, issued from the decomposition of nucleic acids, are present in natural waters and sediments [17]. All these compounds may be considered as water pollutants which can be eliminated by photocatalysis [12,14,16].

Jaussaud et al. [18] and Dhananjeyan et al. [11] have studied the influence of different parameters such as concentration of pollutant, concentration of catalyst, pH, $CdCl_2$, oxygen concentration, influence of metallic ions on the photodegradation of pyrimidine bases in the presence of titanium dioxide. Horikoshi et al. [16] have studied the photomineralization pathways of pyrimidine and purine bases by UVA/UVB illuminated TiO_2 and the respective rates of formation of NH_4^+ and NO_3^- ions. Recently, Li at al [15] have compared the photocatalytical and photo-electrochemical degradation mechanism of these nucleotide bases. Singh et al. [19] gave a detailed kinetic study of uracil and 5-bromouracil. They deduced that TiO_2 can efficiently catalyze the photomineralization of uracil and 5-bromouracil. They also found that photocatalyst Degussa P25 showed the highest photocatalytic activity and they suggested that the addition of electron acceptors such as hydrogen peroxide and potassium bromate can enhance the decomposition.

Our objective is a better understanding of the photocatalytic mechanism of the elimination of uracil and cytosine, which are the simplest molecules constituting the microorganisms (DNA, RNA, proteins, etc.).

* Corresponding author at: 2 avenue Albert Einstein, F-69626 Villeurbanne, France. Tel.: +33 472445316; fax: +33 472445399.
E-mail address: chantal.guillard@ircelyon.univ-lyon1.fr (C. Guillard).

http://dx.doi.org/10.1016/j.apcata.2014.07.043
0926-860X/

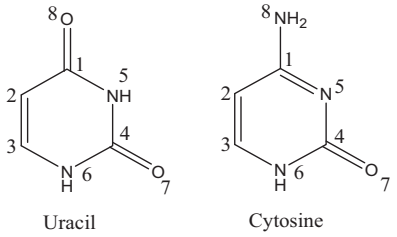

Fig. 1. Structural formulas of uracil and cytosine.

2. Experimental

2.1. Reagents and chemicals

Pyrimidine bases uracil (Ura: $C_4H_4N_2O_2$) and cytosine (Cyt: $C_4H_5N_3O$) (99% purity) were purchased from SIGMA-Aldrich and used as received. Their formulae are given in Fig. 1. Water used for preparation of samples was ultra-pure water, filtered through a milli-Q PLUS 185 water system. The photocatalyst was titanium dioxide Degussa P-25 (particle size, 20–30 nm; crystal structure, 80% anatase and 20% rutile; surface area, 50 $m^2\,g^{-1}$).

2.2. Reactor and light source

The aqueous suspensions were irradiated in a 100 mL open cylindrical reactor whose base contained an optical window with a surface area of about 12.6 cm^2. The output of a Philips HPK 125 W high mercury lamp was filtered through a circulating water cell (thickness = 2.2 cm), avoiding the solution warming by IR, and a Corning 0.52 mW/cm^2 filter to remove radiation with wavelength below 340 nm. The radiant flux was measured using a VLX-3 W radiometer with a detector CX-365 (355–375 nm).

2.3. Photocatalytic experiments

A volume of 20 mL of uracil and cytosine solution with different concentrations containing a concentration of 1.25 $g\,L^{-1}$ of TiO_2, sufficient to absorb all photons entering the photoreactor was used [20]. The degradation was carried out at room temperature (T = 25 °C) and at natural pH (pH 5). The suspension was first stirred in the dark until equilibrium adsorption was achieved. Then, the solution was irradiated at $\lambda > 340$ nm and a radiant flux equal to 3.5 mW/cm^2. Samples taken at different times of irradiation were filtered through 0.45 μm Waters filters to remove TiO_2 particles before analyses.

2.4. Methods of analysis

The degradation of uracil and cytosine were followed by HPLC with a Varian System equipped with a Varian Prostar 230 isocratic pump and a Varian Prostar 330 Diode Area Detector adjusted at 254 nm. A Hypersil BDS C18 reverse phase column (125 mm long, 4 mm diameter) was used. The mobile phase was constituted by 90% of ultra-pure water containing 62 μL H_3PO_4 at pH 3 and 10% of methanol. The flow rate was 0.8 mL min^{-1}.

Mineralization of pyrimidine bases was monitored by determination of Total Organic Carbon (TOC) concentrations by direct injection of the filtered samples using TOC-VCSH Shimadzu and ASI-V Shimadzu sampler.

The carboxylic acids formed were analyzed by LC using a Varian Prostar 230 pump, a Varian Prostar 325 UV detector (detection at 210 nm), and a Transgenomic Icsep Coregel 87H (300 mm × 4.6 mm) column. The flow rate was 0.7 mL min^{-1}. The injection volume was 100 μL and the mobile phase was H_2SO_4 (5×10^{-3} mol L^{-1}).

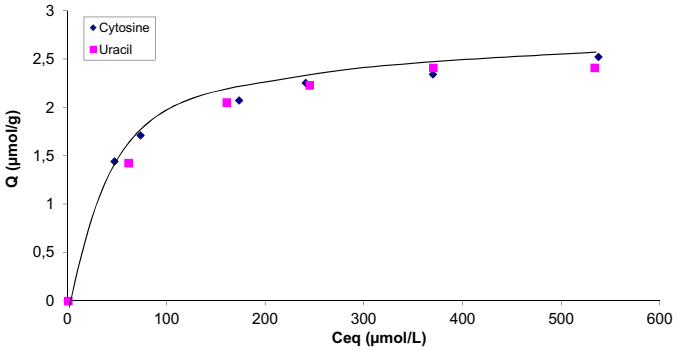

Fig. 2. Amounts of cytosine and of uracil adsorbed per gram of TiO_2 as a function of the equilibrium concentration C_{eq} on TiO_2 Degussa P25 (1.25 $g\,L^{-1}$).

The formation of nitrate ions was monitored using ionic chromatography with a Dionex DX-120 pump and conductivity detector, and an IonPac AS14A (250mm × 4 mm) column. The flow rate was 1 mL min^{-1} and the mobile phase was an alkaline buffer ($NaHCO_3$ (1.0 mmol L^{-1}) + Na_2CO_3 (8.0 mmol L^{-1})).

The formation of ammonium ions was also followed using ionic chromatography with a Dionex DX-120 pump and conductivity detector. The column was a CS 12A (250 mm × 4 mm). The flow rate was 1 mL min^{-1} and the mobile phase was H_2SO_4 solutions containing 610 μL L^{-1} of pure sulfuric acid.

For all analyses the error bars are about 5%.

Computer simulations with MOPAC allowed to calculate the frontier electron density used to determine the positions of •OH radical attack in uracil and cytosine.

3. Results and discussion

3.1. Adsorption

In order to ensure that the adsorption process reached equilibrium, different concentrations of uracil and cytosine were stirred in the dark in the presence of TiO_2 and analysed as a function of time. In both cases, the uracil and cytosine adsorptions reached equilibrium after about 60 min.

Fig. 2(a) represents the amounts (μmol g^{-1}) of cytosine and uracil adsorbed per gram of TiO_2 as a function of the cytosine and uracil equilibrium concentration (C_{eq}). In dark conditions, the amounts of cytosine and uracil adsorbed on the TiO_2 surface (Q_{eq}) increase with the equilibrium concentration until reaching a plateau. The amounts of cytosine and of uracil adsorbed are identical, probably because of their similar formulae. The maximum coverage of cytosine and uracil is about 0.03 molecule nm^{-2}. This represents about 0.6% of the maximum coverage in OH surface groups equal to 5 OH/nm^2 [21]. This value is similar to values found for molecules containing aromatic cycles such as tryptophan, phenylalanine [22,23].

As for the majority of organic compounds [22–27], the adsorption isotherms of cytosine and uracil can be modelled using the Langmuir approach:

$$Q_{eq} = K_{ads} Q_{max} C_{eq} (1 + K_{ads} C_{eq})$$

Q_{eq} is the adsorbed quantity of pollutant on the photocatalyst at the equilibrium (μmol g^{-1}), K_{ads} is the adsorption constant (L μmol^{-1}), Q_{max} is the maximum amount to be adsorbed (μmol g^{-1}), and C_{eq} is the concentration of the compound at the adsorption equilibrium (μmol L^{-1}). The values of the Langmuir parameters for cytosine and uracil are presented in Table 1.