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Effects of acetylacetone on the photoconversion of pharmaceuticals in natural and pure waters☆

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ABSTRACT

Acetylacetone (AcAc) has proven to be a potent photo-activator in the degradation of color compounds. The effects of AcAc on the photochemical conversion of five colorless pharmaceuticals were for the first time investigated in both pure and natural waters with the UV/H_2O_2 process as a reference. In most cases, AcAc played a similar role to H_2O_2. For example, AcAc accelerated the photodecomposition of carbamazepine, oxytetracycline, and tetracycline in pure water. Meanwhile, the toxicity of tetracyclines and carbamazepine were reduced to a similar extent to that in the UV/H_2O_2 process. However, AcAc worked in a way different from that of H_2O_2. Based on the degradation kinetics, solvent kinetic isotope effect, and the inhibiting effect of O_2, the underlying mechanisms for the degradation of pharmaceuticals in the UV/AcAc process were believed mainly to be direct energy transfer from excited AcAc to pharmaceuticals rather than reactive oxygen species-mediated reactions. In natural waters, dissolved organic matter (DOM) played a crucial role in the photoconversion of pharmaceuticals. The role of H_2O_2 became negligible due to the scavenging effects of DOM and inorganic ions. Interestingly, in natural waters, AcAc first accelerated the photodecomposition of pharmaceuticals and then led to a dramatic reduction with the depletion of dissolved oxygen. Considering the natural occurrence of diketones, the results here point out a possible pathway in the fate and transport of pharmaceuticals in aquatic ecosystems.

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1. Introduction

The widespread use of pharmaceuticals and personal care products (PPCPs) and their incomplete elimination by conventional water treatment have resulted in their undesirable accumulation in the environment (Gao et al., 2012; Zhang et al., 2014a). A significant number of PPCPs have been frequently detected in various water bodies (wastewater, surface water, drinking water, ground water) and solids (sludge, soil, and sediments) (Benotti et al., 2009; Musolff et al., 2009; Gobel et al., 2005; Kim and Carlson, 2007; Sun et al., 2016; Kuemmerer, 2009a, 2009b; Li et al., 2015; Li, 2014). Although the acute and chronic effects of PPCPs on the ecosystem and human health are not yet fully understood, long-term and low-dose exposure to PPCPs will inevitably induce irreversible adversity by increasing the drug resistance of bacteria, and subsequently threatening the health of human beings (Andreozzi et al., 2006; Costanzo et al., 2005; Dodgen et al., 2013; Schmitt et al., 2004). Considering the risks of PPCPs in the ecosystem, the study of their occurrence, toxicity, distribution, and fate becomes necessary.

Photolysis under solar irradiation has been considered as one of the most important ways for the degradation of PPCPs in the natural aquatic environment (Boreen et al., 2003; Bohn et al., 2013). The UV/H_2O_2 process is one of the most intensively investigated processes in water treatment because of the efficient formation of strongly oxidative hydroxyl radicals (Kim et al., 2009). Small molecular diketones are natural products of biofermentation. Some of them exist in all brewery sewage (White and Wainwright, 1975). Among the diketones, acetylacetone (2,4-pentanedione, AcAc) has been widely used in organic synthesis as precursors or catalysts (metal complexes) and in chemical analysis due to its strong chelating ability (Zhou et al., 2008). AcAc is also an additive in gasoline, lubricants, inks, and dyes (Budavari et al., 2001). It is reported that the content of AcAc in one printing ink was as high as 6% (*w/w*) (Rastogi, 1991). AcAc could be directly released into the environment from various waste streams. Furthermore, AcAc is also a possible semi-oxidation product in water treatment, such as the ozonation of sludge-press liquors (Boyle and McCullough, 1996).

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Therefore, the coexistence of diketones and pharmaceuticals in the environment is highly possible.

AcAc has been reported as an excellent alternative to H_2O_2 in the photobleaching of dyes (Liu et al., 2014; Wang et al., 2013). In terms of decolorization, the UV/AcAc process was much more efficient than the UV/H_2O_2 process because of the formation of dye-AcAc exciplexes (Zhang et al., 2014b). Therefore, the strong light absorbing ability of dyes, which usually reduces the efficiency of the UV/H_2O_2 process due to the inner filter effect, became a useful characteristic in the UV/AcAc process. Unlike dyes, pharmaceuticals are usually colorless. We were curious whether the good target-selectivity of the UV/AcAc process still works for pharmaceuticals. Therefore, in the present work, the photodegradation of several pharmaceuticals were systematically investigated side-by-side with the UV/AcAc and UV/H_2O_2 processes.

The main objectives of this study are: (i) to compare the efficiency of the two processes in degradation of PPCPs, (ii) to explore the effect of AcAc and oxygen on the photolysis mechanism, (iii) to investigate the influence of water matrices on the photochemical behavior of PPCPs in the UV/AcAc and UV/H_2O_2 processes, and (iv) to assess the toxicity evolution in the photochemical processes.

2. Materials and methods

2.1. Chemicals

AcAc, 2,3-butanedione (denoted as BD), and H_2O_2 of analytical grade were purchased from Shanghai Reagent Station, China. NaOH and HCl of analytical grade were obtained from Nanjing Reagent Station, China. Methanol, acetonitrile, and formic acid of chromatographical grade were purchased from Sigma-Aldrich and were used as received. LB-broth was supplied from Qingdao Hope Bio-Technology Co., Ltd., China. Catalase (2000–5000 u/mg), tetracycline hydrochloride (TC) (95%, CAS number: 64-75-5) and rose bengal (RB) were purchased from Sigma-Aldrich. Oxytetracycline hydrochloride (OTC) (97%, CAS number: 2058-46-0) was obtained from J&K, China. Carbamazepine (CBZ) (98%, CAS number: 298-46-4), ciprofloxacin hydrochloride (CIP) (98%, CAS number: 86393-32-0), and chloramphenicol (CHL) (98%, CAS number: 56-75-7) were purchased from Aladdin, China. More detailed information about the tested PPCPs is listed in Table S1.

Deuteroxide (D_2O) was purchased from the Sigma Chemical Corporation. 2,2,6,6-Tetramethylpiperidine (TEMP) (98%) was obtained from J&K Co., China. KO_2 (96.5%) was purchased from Alfa Aesar, USA. Nitro blue tetrazolium chloride (NBT) was purchased from Aladdin, China. High purity N_2 (99.999%) and N_2O (99.95%) were used to purge the solutions whenever needed. All experiments were carried out under ambient conditions unless otherwise stated.

2.2. Water quality measurements

Natural waters were sampled from three local water bodies: Yangtze River, Jiuxiang River, and Xuanwu Lake, China. The sampling locations are available in our previous work (Zhou et al., 2015). After sampling, the waters were immediately filtered through a 0.45 μm cellulose nitrate filter (Shimadzu, Japan) and stored at 4 °C until use. The total organic carbon (TOC), total carbon (Tot C), total nitrogen (Tot N) were determined with a Multi N/C TOC apparatus (TOC-L, Shimadzu, Japan). The pH, electronic conductivity (EC), dissolved oxygen (DO), oxidation-reduction potential (ORP) were determined with an HQ30d apparatus (HACH, United States). The water quality parameters were measured in duplicate or triplicate and are listed in Table S2.

2.3. Photoirradiation experiments

The UV irradiation experiments were carried out in a rotating disk photoreactor (Nanjing StoneTech Electric Equipment, China), which is shown in Fig. S1a. A medium pressure mercury (UV) lamp (300 W) with a maximum light emission at 365 nm or a Xenon (Xe) lamp (350 W) was vertically placed in a cooling water jacket. Sample solutions containing 80 μM target compound and 0.5 mM AcAc or H_2O_2 were parallelly arranged in a quartz tube around the lamp. The distance between the sample tube and the lamp was 5 cm. The sample holder revolves around the lamp and the tubes self-rotate. The light intensity reaching the solution was measured using a radiometer (Photoelectric Instrument Factory of Beijing Normal University, China), equipped with a sensor with peak sensitivity at 365 nm (Fig. S1b). Considering that the pH of natural waters is usually in range of 6–9 (Brezonik and Arnold, 2011), the initial solution pH was adjusted to 7.0 with HCl or NaOH in pure water unless otherwise stated. As for the natural water matrices, there was no pH adjustment during the irradiation.

2.4. Analytical methods

The UV-Vis spectra were analyzed with a double beam spectrophotometer (UV-2700, Shimadzu, Japan). The concentrations of pharmaceuticals were determined with a high performance liquid chromatography (HPLC) system (Dionex U3000, United States) equipped with an Agilent C18 reversed phase column (100 mm × 4.6 mm, 3.5 μm) at 25 °C. The detailed HPLC conditions are listed in Table S1. The concentration of AcAc was determined by the HPLC equipped with a C8 reversed phase column (150 mm × 4.6 mm, 5 μm) at a flow rate of 0.6 mL/min at 274 nm. The mobile phase (60/40, *v/v* %) was methanol/1 mM $CuCl_2$ solution adjusted with CH_3COOH to pH 4.0.

Reaction intermediates and products were identified with a liquid chromatography-mass spectrometer (LC-MS) equipped with a ThermoFinnigan LCQ Advantage MAX mass spectrometer with an electrospray ionization (ESI) interface source. The LC system was equipped with an Agilent 4.6 × 150 mm, 5 μm ZORBAX Eclipse Plus C18 column, and the flow rate was 0.2 mL min^{-1}. A sample volume of 10 μL was injected by using an auto sampler. MS settings were as follows: capillary temperature: 300 °C, spray voltage: 4.5 kV, sheath gas flow: 35 and auxiliary gas: 5 (arbitrary units), capillary voltage: 25 V, and tube lens offset: 100 V. The mass spectral data were obtained in the negative ion mode between *m/z* 50 and 800.

Electron paramagnetic resonance (EPR) experiments were performed with a Bruker EMX-10/12 spectrometer. The settings for the EPR spectrometer were as follow: center field: 3480 G; sweep width: 200.0 G; microwave frequency: 9.785 GHz; temperature 296 K, microwave power: 20 mW, field modulation: 0.1 mT at 100 kHz, scan time: 83.8 s. The light source for EPR determination was a 180 W mercury lamp. Quartz capillary tubes with an inner diameter of 1 mm were used in the UV irradiation experiments.

2.5. Toxicity assay

The antimicrobial activities of the two tetracyclines and CBZ during the photodegradation process in pure water were evaluated by the bacterial growth assay. The standard test bacterial species, *Bacillus subtilis*, was grown in LB broth. The assays were conducted in a 96 well microtiter plate. Each well contained 60 μL bacterial suspension (10^3 CFU/well), 40 μL samples, and 200 μL LB medium with a final volume of 300 μL. The plates were incubated at 32 °C. The optical density at 550 nm (O.D. 550 nm) was measured using a microtiter reader (Synergy H1M microplate reader). At the selected photoreaction time, a specific amount of reaction solution was

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