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Photodegradation of salicylic acid in aquatic environment: Effect of different forms of nitrogen

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ABSTRACT

Salicylic acid (SA), as an extensively used compound, can be detected in a great variety of environmental water samples. Photodegradation is important in many ways. The present study concerns the environmental behavior of SA under simulated sunlight. A kinetic model was used for SA degradation in water, and the variations of the photodegradation of SA in the presence of different initial concentrations, different oxygen levels, different forms of nitrogen and different pE values in the aquatic environment were determined. Experiments demonstrated that the photodegradation process had pseudo-first-order reaction kinetics. The photodegradation rate decreased with increasing initial concentration and increased with increasing oxygen level. The NO_3^- and NO_2^- ions promoted photodegradation of SA, but increases of NH_4^+ concentration had no effect. The form of nitrogen depends on pE, which therefore has a significant influence on the photodegradation of SA. When the pE value increased gradually, there was a transformation of NH_4^+ to NO_2^- and then to NO_3^-. The photodegradation rate of SA first increased, then decreased and finally increased again. When NO_2^- and NH_4^+ coexisted, the photodegradation rate was almost the same as it was in the presence of NO_2^- alone. When NO_2^- and NO_3^- coexisted, the promoting effect on the photodegradation SA was less than the sum of the partial promoting effects. The results indicated that NO_2^- had an obvious antagonistic action on NO_3^- when NO_3^- and NO_2^- coexisted in the aquatic environment.

1. Introduction

Pharmaceutical and personal care products (PPCPs) have been found polluting a wide range of aquatic environments, including surface water, ground water and drinking water (Xin et al., 2011). Most PPCPs are not regulated by existing water quality standards, and existing water treatment technology does not remove many PPCPs. These substances have caught the attention of environmental scientists (Panswad and Luangdilok, 2000; Stefan et al., 2002; Bound and Voulvoulis, 2004; Smital et al., 2004). Even though PPCPs have very low concentrations in the aquatic environment, long-term exposure could be a serious threat to human health. Therefore, it is important to study the environmental behavior of PPCPs (Daughton and Ternes, 1999; Boyd et al., 2004; Carballa et al., 2005; Jones et al., 2005).

Salicylic acid is used as a disinfecting antiseptic agent in the pharmaceutical industry. In the Guangzhou Pearl River Delta in China, SA was detected at a concentration of 2098 ng/L (Peng et al., 2008). Large quantities of SA can cause vomiting, abdominal pain, acidosis and other symptoms. Thus SA in the aquatic environment is a potential threat to human health. The transfer of SA in aquatic environments and its biological effects are important, but they are rarely reported. There are large amounts of nitrogen in natural waters. Inorganic nitrogen occurs mainly in the form of NH_4^+ and NO_3^- and sometimes also in the form of NO_2^-. These nitrogen-containing ions can produce hydroxyl radicals and other reactive groups under natural light conditions (Mack and Bolton, 1999; Nélieu et al., 2009), thereby promoting the oxidation of organic matter.

The objective of the present research was to investigate a kinetic model of SA degradation and to assess the effects of different forms of nitrogen and different pE values on the photodegradation of SA under simulated sunlight in the aquatic environment.

2. Materials and methods

Salicylic acid (99% purity), was purchased from J&K Chemical Co. Ltd. (Beijing, China). Sodium nitrate, sodium nitrite and ammonium sulfate were all obtained from Tianjin Guangfu Chemical Reagents Co. Ltd. (Tianjin, China). High performance liquid chromatography (HPLC) graded methanol, was obtained from Suqian Guoda Chemical Reagent Co. Ltd. (Jiangsu, China). Ammonium acetate was obtained from Tianjin Bodi Chemical Co. Ltd. (Tianjin, China). 500 W xenon lamp, was purchased from Beijing Tianmai Hang Fai light Electric

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Co., Ltd. (Beijing, China). All of the chemicals used were of analytical grade without further purification. Ultra-pure water from a Milli-Q apparatus (Millipore, USA) was used for preparing all aqueous solutions.

Photodegradation experiments were performed with a 250 mL hollow cylindrical quartz tube photoreactor (Fig. 1). The reaction liquid containing salicylic acid and other additives was stirred by a magnetic stirrer throughout the experiments in order to remain homogeneous in the quartz tube which was put vertically inside the reactor. A 500 W xenon lamp was put in the double walled quartz cooling jacket and temperature was controlled by a constant-temperature liquid-circulating apparatus. Salicylic acid and other additives were placed into the 250 mL volumetric flask and diluted with Milli-Q water, then the reaction solution was placed into the quartz tube. During experiments, 2 mL samples were taken out every 20 min, using a pipette and were immediately analyzed by reversed-phase high-performance liquid chromatography.

The concentrations of salicylic acid solutions were determined by reversed-phase high-performance liquid chromatography,which consisted of two Waters 1525 Binary HPLC pumps and Waters 2747 Fluorescence detector (Waters, Massachusetts,USA). Analytical column temperatures were controlled with a Model 1500 Column Heater (Waters, and Product of Singapore). The analytical column was a 150 mm × 4.6 mm Waters C18 column, (particle size 5 μm). A Waters guard column (C18, 4.6 mm × 20 mm, particle size 5 μm) was used to protect the analytical column. The injection volume was 20 μL. The mobile phase was a mixture of 20% HPLC-grade methanol and 80% ammonium acetate solution (0.02 mol/L) at a constant flow rate of 1.0 mL/min. The excitation wavelength was set at 300 nm and emission wavelength at 407 nm.

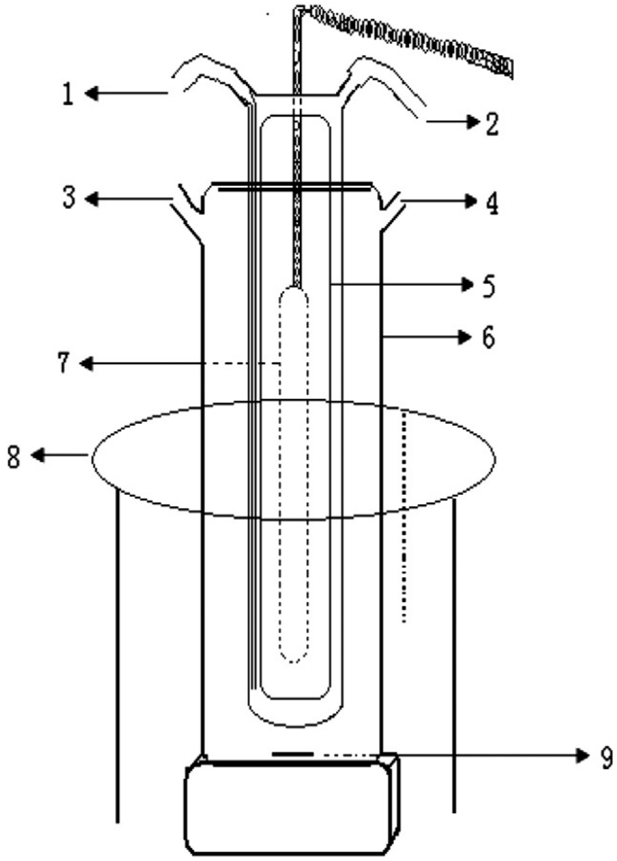

Fig. 1. Scheme of the photoreactor. 1. Cooling water inlet. 2. Cooling water outlet. 3. Sampling ports. 4. Vent 5. Quartz cooling device 6. Quartz reactor. 7. 500 W xenon lamp 8. Tripod 9. magneton.

3. Results and discussions

3.1. Effect of initial salicylic acid concentration on the photodegradation of SA

In Fig. 2, it can be seen that as the initial concentration increased, the degradation rate decreased. This result can be explained by considering the competition for absorption of the limited quantity of available photons by the SA. Because the initial concentration of SA increased but the number of available photons did not change, the number of photons available per molecule of SA decreased, so the degradation rate of SA decreased.

3.2. Effect of oxygen concentration on the photodegradation of SA

The photodegradation of SA was studied under three conditions: (1) natural conditions (limited dissolved oxygen in the water), (2) enrichment of oxygen (dissolved oxygen in the water saturated) and (3) continued access to nitrogen (oxygen-free water).

In Fig. 3, it can be seen that with light, enrichment of oxygen, the fastest degradation of SA occurs; when it under continued access to nitrogen, the SA degradation is the slowest; under natural conditions, the SA degradation rate is between the two extremes.

In some reports, two forms of photodegradation are recognized: direct photodegradation, and self-sensitized photodegradation (Chin et al., 2004; Engel et al., 2008; Ge et al., 2010).

The photodegradation of SA may have one of two forms: (1) SA absorbs actinic photons and forms an excited SA, followed by direct photodegradation; (2) SA is degraded by sensitized photodegradation, mainly resulting from self-sensitized photo-oxidation reactions. That is, an excited state of SA forms after absorption of photons, and there is then an energy transfer to other substances, thereby generating reactive oxygen species. The reactive oxygen species then cause oxidative degradation of SA.

When N_2 is present, direct photodegradation of SA can occur under anaerobic conditions; the direct photodegradation rate constant is 0.0021. In the natural environment, with access to oxygen, the degradation rate of SA is greater than that of N_2. When oxygen is saturated, the photodegradation rate of SA is at a maximum. The presence of oxygen promoted the photodegradation of SA. Clearly, degradation of SA can occur not only by direct photodegradation, but also by self-sensitized photodegradation.

The self-sensitized photodegradation of SA may be caused by oxygen in the water reacting with other substances to produce a number of active groups under the prevailing light conditions; the SA

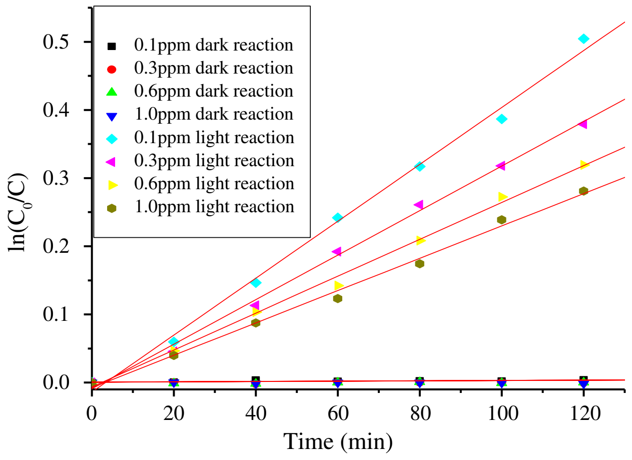

Fig. 2. Four different initial concentrations under simulated sunlight photodegradation kinetics of SA.