

PHOTODEGRADATION OF BERBERINE HYDROCHLORIDE UNDER SIMULATED SUNLIGHT IRRADIATION****Chengbin Xu¹, Jiajia He¹, Ying Wang¹, Zien Xu¹, Xiping Ma^{1*}, Xuelian Meng^{2*}**

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Berberine hydrochloride (BH) is a frequently detected antibiotic in environmental waters. The objective of this study was to investigate the photodegradation of the problematic antibiotic in pure water under simulated sunlight (290–800 nm) using a photodegradation chamber. The effects of irradiation time, pH, and the presence of the matrix (nitrate, humic acid, copper, and hydrogen peroxide) were investigated in this study. The results showed that the BH degradation follows pseudo-first-order kinetics, with the degradation of BH decreasing slightly with increasing irradiation time. The rate of BH photolysis was more efficient in the near-neutral condition than in alkaline or acidic solutions and increased in the presence of nitrate and copper. Hydrogen peroxide and humic acid accelerated or inhibited degradation of BH depending on their concentration. The rapid photodegradation of BH under simulated sunlight suggested that photolytic disinfection could also be effective for degradation of the target antibiotics in water.

Keywords: berberine hydrochloride, photodegradation, simulated solar radiation, antibiotics.

ФОТОДЕГРАДАЦИЯ ГИДРОХЛОРИДА БЕРБЕРИНА ПРИ ОБЛУЧЕНИИ ИСКУССТВЕННЫМ СОЛНЕЧНЫМ ИЗЛУЧЕНИЕМ**Ch. Xu¹, J. He¹, Y. Wang¹, Z. Xu¹, X. Ma^{1*}, X. Meng^{2*}**

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Исследована фотодегградация гидрохлорида берберина (ГБ) в чистой воде под действием искусственного солнечного излучения (290–800 нм) с помощью фотодегградационной камеры. Изучено влияние времени облучения, pH и наличия матрицы (нитрат, гуминовая кислота, медь и перекись водорода). Показано, что дегградация ГБ соответствует кинетике псевдопервого порядка и незначительно уменьшается с увеличением времени облучения. Скорость фотолиза ГБ в практически нейтральной среде более высокая, чем в щелочных или кислых растворах, и увеличивается в присутствии нитрата и меди. Перекись водорода и гуминовая кислота ускоряют или ингибируют дегградацию ГБ в зависимости от их концентрации. Быстрая фотодегградация ГБ под действием искусственного солнечного света позволяет предположить, что фотолитическое обеззараживание может быть эффективным средством для дегградации целевых антибиотиков в воде.

Ключевые слова: гидрохлорид берберина, фотодегградация, искусственное солнечное излучение, антибиотики.

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Introduction. The presence of antibiotics in environmental water is of particular ecological concern [1–6]. Antibiotics are considered to be emergent pollutants because they are bioactive, polar, and persistent, which may cause adverse effects on aquatic life and humans [7, 8]. Moreover, antibiotics and their transformation products may induce the development of bacterial resistance [9]. Unfortunately, antibiotics are not completely removed by conventional processes such as sewage treatment, hydrolysis, biodegradation, and sorption [10].

Large amounts of antibiotics are constantly discharged into the environment from many sources including household sewer system, agricultural runoffs, and so on [11–15]. Another important pathway of antibiotics into the environment is the antibiotic pharmaceutical industry. Antibiotics were detected at concentrations between 0.1 and 90.2 $\mu\text{g/L}$ of antibiotics in the pharmaceutical wastewaters [16, 17]. It is reported that approximately half of the pharmaceutical wastewaters in the world were discharged without specific treatment [18]. Hence, it is necessary to investigate a new and effective water treatment system to remove antibiotics from wastewater.

Berberine hydrochloride (BH), a quaternary ammonium chloride, is a broad-spectrum antibiotic widely used in medicine. However, BH is poisonous for microorganisms and difficult to decompose [19]. It has been demonstrated that BH cannot be eliminated by conventional biological water treatment such as activated sludge treatment [20]. In recent years, the photodegradation of antibiotics was studied using different light sources including UV light [21], solar simulation [22], and natural sunlight [23] in various water matrices including pure water, fresh water (from rivers and lakes), and saltwater [24]. It indicates that the effectiveness of photodegradation depends on the integrative effects of photon flux, the structure of the molecule, and the composition of water matrix. For example, Jieqiong Wang showed that seawater dissolved organic matter (DOM) exhibits higher rates of light absorption and higher reactivity on photodegradation of the sulfonamide antibiotics compared to freshwater lake DOM [25]. The photodegradation rate of organic compounds can be hindered or facilitated by the presence of dissolved organic matter in natural waters [26]. Salma reported that the removal rates of ciprofloxacin strongly depended on pH [27]. However, there is little information on the photodegradation of BH.

This study was focused on investigating the effects of the conditions (irradiation time and pH) and water constituents (nitrate, humic acid, copper, and hydrogen peroxide) on BH photodegradation. The photodegradation of BH was conducted in pure water by simulated sunlight (290–800 nm) using a photodegradation chamber under various conditions.

Chemicals and materials. The standard of berberine hydrochloride (purify >99%) was purchased from Northeast Pharmaceutical Co., Ltd (Shenyang, China). Humic acid was obtained from Sigma Aldrich (St. Louis, MO, USA). Copper(II) chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and furfuryl alcohol (FFA) were provided by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Sodium nitrate (NaNO_3) was purchased from Xinxing Chemical Reagent Co., Ltd (Shenyang, China), while hydrogen peroxide (H_2O_2) was from Dongling Fine Chemical Reagent Co., Ltd (Shenyang, China). Other chemicals were of guaranteed grade and were used as received, without further purification. Ultrapure water was produced in the laboratory using a GW-RO system from Purkinje General (Beijing, China).

Photodegradation experiments. The photochemical experiments were conducted using a photochemical chamber with two Xenon lamps separated by 60 mm on the top of the chamber shown in Fig. 1. The Xenon lamps produced a continuum of wavelengths from 290 to 800 nm as a substitute for natural sunlight. The solution of BH was placed into a beaker fixed in the groove of the photodegradation chamber. The groo-

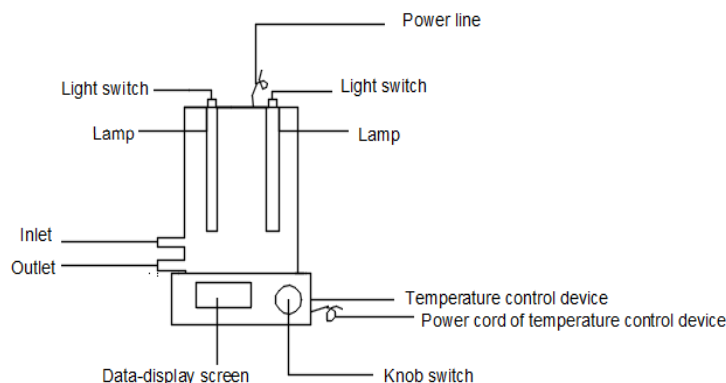


Fig. 1. The diagram of the photoreaction apparatus.

ve was filled with water controlled by a circulator bath to maintain a constant temperature (25°C). After stabilizing the lamp and controlling the temperature, the photoreactor was turned on and aliquots were withdrawn from the glass beaker at different time intervals. The concentration of BH was determined by a Varian Cary 50 Scan UV-Vis spectrophotometer.

The photodegradation experiments were conducted to investigate the influence of irradiation time and initial pH values of the solution on the degradation of BH in pure water. The effects of the composition of the water matrix (nitrate ion, humic acid, Cu^{2+} , and H_2O_2) on the photodegradation of BH were also studied.

Quantitative analysis and statistical evaluation. The concentration of BH was determined using an UV-Vis spectrophotometer (Varian Cary 50, USA). The UV-Vis spectra were acquired between 200–800 nm, and the absorbance at 344 nm was taken as the quantification wavelength for BH. The standard curve method was employed for quantification in the study.

All experiments were performed in triplicate. The data were statistically analyzed using a Statistical Package for the Social Sciences 13.0 for windows (SPSS Inc, Chicago, Illinois). At the given experimental condition, plots of the degradation rate of BH versus the value of pH and the concentration of nitrate, copper iron, humic acid, and hydrogen peroxide were constructed. The least significant difference (LSD) test was used to evaluate the statistical significance of differences between mean values.

Results and discussion. *The effect of irradiation time.* The initial concentration of BH in the experimental solution used was 400 mg/L, and the aqueous solution was at pH 7 without any nitrate, humic acid, copper and hydrogen peroxide. The absorption spectra under different irradiation times for BH are shown in Fig. 2a. In general, the solution gives four absorption peaks in the range of 200–800 nm corresponding to the benzene ring in the BH molecule at any pH values. The absorption peaks after different irradiation times declined more or less in comparison with the original BH solution. This indicates that the benzene ring in the BH molecule was destroyed simultaneously with increasing irradiation time.

Figure 2b shows that photodegradation of BH is fit to pseudo-first-order kinetics. The pseudo-first-order kinetics form is

$$-\ln(C_t/C_0) = kt,$$

where C_t is the substrate concentration at any given point of time; C_0 is the initial substrate concentration; k is the first-order rate constant.

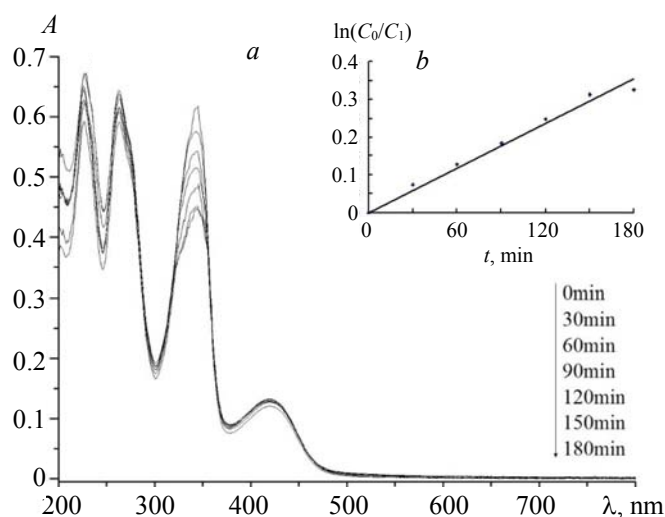


Fig. 2. UV-vis spectra of BH solutions under different irradiation time (a); degradation kinetic of BH in the presence of oxygen (b).

Half-life, $t_{1/2}$, was calculated using an equation derived from Eq. (1) by replacing C_t with $C_0/2$

$$t_{1/2} = \ln 2/k = 0.6931/k.$$

The slope was used to obtain the pseudo-first-order rate constant k . The pseudo-first-order rate constants k and half-life $t_{1/2}$ were 0.002 min^{-1} and 346.55 min, respectively.

The effect of pH. Figure 3 depicts the influence of the solution pH on the degradation of BH. The photodegradation rate of BH in aqueous solutions significantly increased when the pH increased from 5 to 7. When the value of pH was greater than 7, the degradation rate started to decrease. Therefore, the photodegradation of BH was more efficient in the near-neutral condition than in alkaline or acidic solutions. This phenomenon may indicate that both cationic and anionic species of BH are resistant to photodegradation compared to zwitterionic species. This is probably due to the interaction of lone pair of electrons on nitrogen atoms of the molecules with the media. The photodegradation of different ionic species of BH depends on pH and therefore the quantum yields of their excited triplet states in a particular environment [28]. Hence, the photodegradation of BH was enhanced in near-neutral conditions but decreased at acidic or alkaline conditions [29–32].

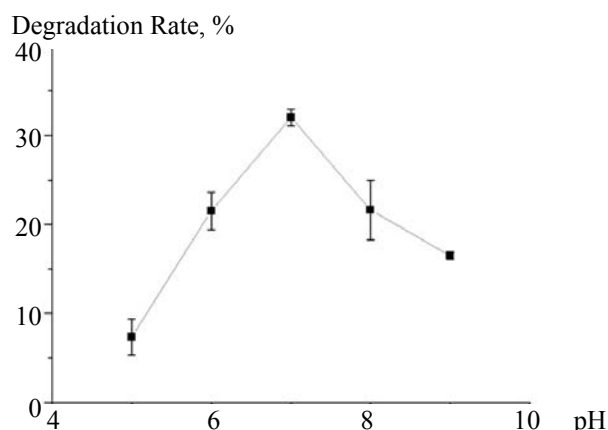
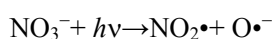
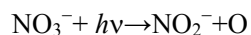
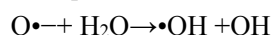


Fig. 3. The photodegradation of BH at different pH, $[BH]_0 = 400$ mg/L.

The effects of nitrate ion and copper ion. Nitrate ions are generally present in natural surface water at various concentrations depending on the agricultural and geographic location [33]. The effect of the nitrate ion from 0 to 2 mmol/L is shown in Fig. 4a. It shows that the degradation efficiency was enhanced markedly as the concentration of nitrate ions increased. This is probably because the nitrate ion produces OH^\bullet when excited by simulated sunlight. The mechanism of the photochemical reaction is represented by the following equations:



and the generation of OH^\bullet is illustrated by the equation



BH can react with hydroxyl radicals and other active substances, causing self-sensitized reactions that promote degradation. To sum up, nitrate ions play an important role in the photodegradation of BH.

Although the concentration of copper ion is not high in natural water or slightly polluted water, copper ion can be added in the production of BH during the chemical synthesis process [34, 35]. Figure 4b indicates that the photodegradation of BH was enhanced in the presence of Cu(II). It has been documented that irradiation can induce Fenton-like reaction in the presence of Cu(II) [36]. These reactions are as follows:



When Cu(II) in the solution absorbs photons, Cu(II) will be transformed into Cu(I); see Eq. (1). The transient Cu(I) is reoxidized to Cu(II) by a superoxide radical (Eq. (2)) [29, 30]. Then the formed HO_2^\bullet was transformed into H_2O_2 by a disproportionation reaction (Eq. (3)). Accordingly, the system containing Cu(I) and H_2O_2 is able to perform a Fenton-like reaction [37, 38] to generate $\bullet OH$ (Eq. (4)), which explains the enhancement of the photodegradation of BH.

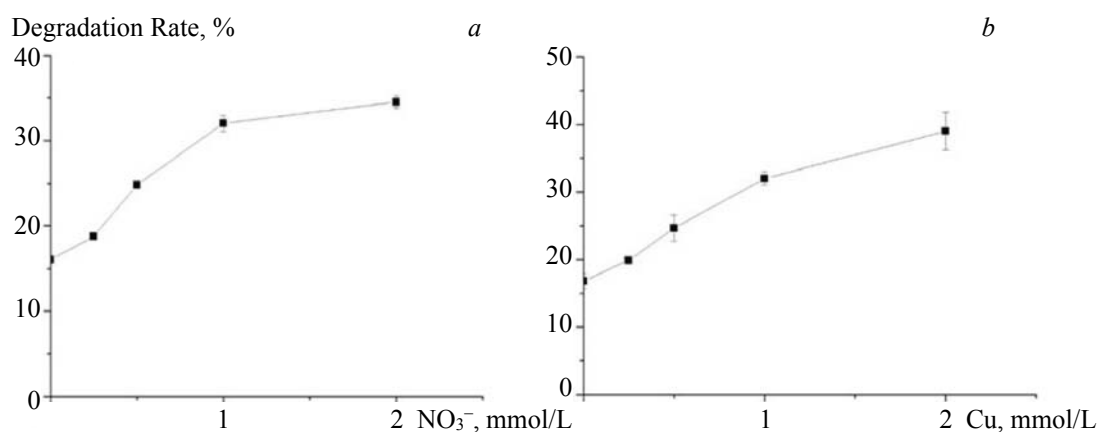
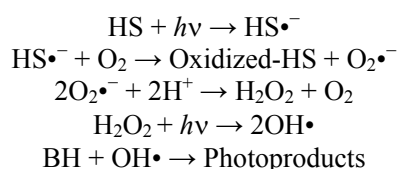


Fig. 4. Effects of nitrate ion (a) and copper ion (b) on the photodegradation of BH in an aqueous solution, $[BH]_0 = 400$ mg/L, pH 7.

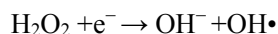
The effects of humic acid and H₂O₂. Humic substances (HS), the largest fraction of DOM, are ubiquitous in the aquatic environment. They are formed during the abiotic and microbiological transformations of plant and animal materials and can be categorized as humic and fulvic acids and humin depending on their solubility [39, 40]. Humic acid with an average molecular weight of 2000–5000 g/mol is the dominant constituent in HS and contains a lot of oxygen-containing functional groups (e.g., phenolic hydroxyl, carboxyl groups, and carbonyl-type chromophores). The chromophoric HS absorbs solar radiation mostly between 300 and 500 nm to reach an excited state and generate free radicals (e.g., hydroxyl radicals OH•, peroxy radicals ROO•, and singlet oxygen ¹O₂) that cause photooxidation of organic contaminants [41, 42]. Since the presence of humic acid plays a key role in natural aquatic environments, it is very important to study the influence of humic acid on the photodegradation of BH to predict the transport and fate of organic contaminants in natural water.

The degradation rate of BH in the presence of humic acid under simulated sunlight is shown in Fig. 5a. It depicts that humic acid at a concentration of 5 mg/L was more efficient in the photodegradation of BH. This is due to photooxidation:

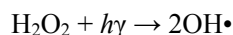


When the concentration of humic acid was greater than 10 mg/L, the degradation of BH was inhibited, resulting from the scavenging of reactive oxygen species as well as increased light attenuation with increasing humic acid concentration [43–47].

Hydrogen peroxide can inhibit or enhance the rate of photolysis of BH, depending on its concentration and nature of reductants [48]. The effect of H₂O₂ in the range of 0–20 mg/L on the degradation of BH is shown in Fig. 5b. The photodegradation rate of BH was increased in the presence of H₂O₂. This is because H₂O₂ at an optimal concentration can increase the formation rate of hydroxyl radicals in two pathways. Firstly, H₂O₂ can generate additional hydroxyl radicals by trapping of photogenerated electrons [49]:



Secondly, the self-decomposition by irradiation would also produce hydroxyl radicals [50]:



However, H₂O₂ at high concentrations can act as a powerful scavenger •OH:



The results show that reactions such as Eqs. (5) and (6) become predominant in water when the concentration of H₂O₂ was above 10 mg/L (Fig. 5b).

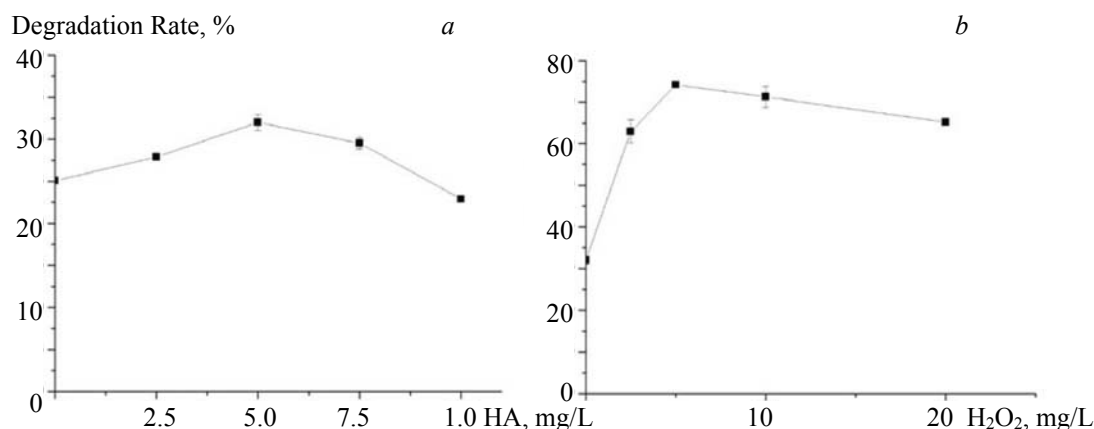


Fig. 5. Effects of humic acid (a) and H_2O_2 (b) on the photodegradation of BH in an aqueous solution, $[\text{BH}]_0 = 400 \text{ mg/L}$, pH 7.

Therefore, the proper concentration of hydrogen peroxide can accelerate the photodegradation of BH. In order to maintain the efficiency of the added hydrogen peroxide, it was necessary to choose the proper concentration of hydrogen peroxide according to the kinds and concentrations of the pollutants.

Conclusions. Antibiotics are highly water soluble and generally resistant to biodegradation. The presence of antibiotics in natural water bodies is a serious problem because of their potential biological activity. Our studies on the photolysis of berberine hydrochloride demonstrate that photochemical degradation plays an important role in the environmental fate of antibiotics. The extent of photodegradation largely depends on the irradiation time, pH, and the presence of water constituents. The BH degradation follows pseudo-first-order kinetics, with the degradation of BH decreasing slightly with increasing irradiation time. It was observed that the degradation rate was higher under near-neutral conditions than in alkaline or acidic media and increased in the presence of nitrate and copper. The results obtained show that humic acid and hydrogen peroxide at appropriate concentrations can accelerate the BH degradation by generating additional free radicals.

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