Radiation Physics and Chemistry 145 (2018) 34–38

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

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

Degradation kinetics and mechanism of penicillin G in aqueous matrices by ionizing radiation

Libing Chu[a,b], Shuting Zhuang[a], Jianlong Wang[a,b,*]

[a] Collaborative Innovation Center for Advanced Nuclear Energy Technology, INET, Tsinghua University, Beijing 100084, PR China
[b] Beijing Key Laboratory of Radioactive Waste Treatment, INET, Tsinghua University, Beijing 100084, PR China

ARTICLE INFO

Keywords:
Antibiotic
PPCPs
Ionizing radiation
Advanced oxidation processes
Antibiotics production wastewater

ABSTRACT

The gamma radiation induced-degradation of a β-lactam antibiotic, penicillin G was investigated in aqueous solution. Special attention was paid to the effects of the organic substances such as peptone and glucose on penicillin G degradation, which can be found in the wastewater of the factories producing antibiotics. Results showed that gamma radiation was effective to degrade and deactivate penicillin G in pure water. With the initial concentrations of 0.27 mM, 1.34 mM and 2.68 mM, a complete removal of penicillin G could be achieved at the adsorbed doses of 2.5 kGy, 10 kGy and 20 kGy, respectively. Penicilloic acid from the β-lactam ring cleavage and a series of fragment compounds such as thiazolidine and penicillic acid were identified during gamma irradiation-induced degradation of penicillin G. Addition of Fe^{2+} was efficient to enhance the mineralization. The TOC removal efficiency of penicillin G was 21.7% using gamma irradiation alone at 10 kGy, which increased to 56.4% with 1.0 mM Fe^{2+} addition. The gamma radiation-induced degradation of penicillin G was inhibited in the presence of peptone and glucose and the inhibitive effect increased with increasing their concentrations. The rate constant, k of the pseudo first-order kinetics decreased by 74% and 64% in the presence of 1.0 g/L of peptone and glucose, respectively, and by 96% and 89% in the presence of 10 g/L of peptone and glucose, respectively. The ratio of k/k_0 was increased by 1.3 times with H_2O_2 addition and by 3 times with Fe^{2+} addition, in the presence of 10 g/L of glucose. Adding Fe^{2+} was effective to improve the ionizing radiation induced degradation of penicillin G antibiotic in the glucose-containing wastewater.

1. Introduction

Antibiotics are one of the most commonly used pharmaceuticals for human medicine to treat bacterial infection and as veterinary drugs to prevent diseases and promote growth (Kümmerer, 2009a). Penicillin G belonging to the β-lactam antibiotic group, was one of the most widely used antibiotics for human, animals and agriculture owing to its high antibacterial activity, low cost and toxicity (Aldeek et al., 2016). The penicillin antibiotics such as penicillin G, ampicillin and amoxicillin have been detected in different waters involving secondary effluent, groundwater and surface water (Kümmerer, 2009b; Li et al., 2008; Peterson et al., 2012). β-lactam antibiotics were among the most prevalent antibiotics detected in both the hospital effluent and wastewater treatment plants influent (Watkinson et al., 2009). These antibiotics emitted to the environment e.g. with treated wastewater, even at trace levels, promote the development and spread of antibiotic-resistance genes and antibiotic-resistance bacteria, which present a potential threat to human health and ecological safety (Guo et al., 2014; Pruden et al., 2006).

The advanced oxidation processes (AOPs), involving photolysis, Fenton oxidation, ozonation and ionizing irradiation, etc. as separate techniques or combined processes (such as UV-ozonation and photo-Fenton) were shown to be effective to decompose the recalcitrant antibiotics in aqueous solution (Wang and Wang, 2007; Homem and Santos, 2011; Wang and Lim, 2012; Wang and Xu, 2012; Wang et al., 2013; Liu et al., 2014a; Almasi et al., 2016; Wang and Wang, 2016; Wang and Bai, 2017). He et al. (2014) revealed that the reaction mechanism of ampicillin by UV_{254} photochemical oxidation coupled with H_2O_2 and $S_2O_8^{2-}$ activation involve the hydrolysis of the β-lactam ring opening and decarboxylation, the hydroxylation of the benzene ring or the sulfur, and the oxidation of the amine groups. Ionizing radiation, including both gamma and electron irradiations, has shown to be effective to degrade various pharmaceuticals, such as anti-inflammatory drug, endocrine disrupting compounds and antibiotics in aqueous solution (Reinholds et al., 2017; Szabó et al., 2016b, d; Wang and Chu, 2016; Yu et al., 2010a, b). It has the advantages such as in-situ generation of the oxidative species •OH and reductive species e_{aq}^- by water radiolysis, good penetration in water matrix and no residuals generated,

* Corresponding author at: Collaborative Innovation Center for Advanced Nuclear Energy Technology, INET, Tsinghua University, Beijing 100084, PR China.
E-mail address: wangjl@tsinghua.edu.cn (J. Wang).

https://doi.org/10.1016/j.radphyschem.2017.12.009
Received 20 September 2017; Received in revised form 24 November 2017; Accepted 10 December 2017
Available online 11 December 2017
0969-806X/

which has been used for degradation of various pollutants, such as chlorophenols, triclosan, carbamazepine, sulfamethazine and the like (Hu and Wang, 2007; Liu and Wang, 2013; Chu et al., 2015; Yin et al., 2016; Zhang et al., 2016; Wang et al., 2017). It was documented that the reaction rate constants of the β-lactam antibiotics involving penicillin G with •OH radicals and e_{aq}^- were 6.9–8.8 × 10^9 L/mol s and 3.5–5.8 × 10^9 L/mol s, respectively (Dail and Mezyk, 2010; Song et al., 2008).

Song et al. (2008) reported that more than 90% of β-lactam antibiotics involving penicillin V, penicillin G, and amoxicillin with the concentration of 1.0 mmol/L was removed at the absorbed dose of around 12 kGy using ^{137}Cs gamma irradiation. Szabó et al. (2016c) reported that •OH radicals and e_{aq}^- destroy the β-lactam ring of amoxicillin with ~ 55% and ~ 88% efficiency, respectively. The antibacterial potency was decreased and finally lost after ionizing irradiation treatment (Szabó et al., 2017, 2016a). In addition, to improve the degradation efficiency especially the mineralization and decline the cost, the additives of H_2O_2 and Fe^{2+} are often applied to enhance the production of hydroxyl radicals during irradiation by ionizing radiation (Guo et al., 2012; Liu et al., 2014b).

For treating the realistic waters, it has been reported that the presence of the dissolved organic carbon and some inorganic anions such as HCO_3^-, CO_3^{2-}, NO_3^- and Cl^- compete the reactive species produced by water radiolysis and decrease the degradation efficiency of the target pollutants (Abdel daiem et al., 2013; Kubesch et al., 2005; Ocampo-Perez et al., 2011). Limited studies are available to investigate the effect of the bio-macromolecular substance such as protein and carbohydrate glucose on antibiotics removal during ionizing irradiation. Those substances are commonly used by the antibiotics production plants as fermentative medium components and currently found in the antibiotics production wastewater and hospital wastewater.

In the present work, the gamma radiation induced degradation of penicillin G was investigated at various initial concentrations. The effect of various additives such as peptone, glucose, H_2O_2 and Fe^{2+} were also studied. The mechanism of gamma irradiation-induced degradation of penicillin G was proposed through identification of the intermediates by LC-MS and GC-MS. The results would provide an insight into understanding the mechanism and parameters that affect the ionizing radiation induced degradation of penicillin G.

2. Materials and methods

2.1. Chemicals

Penicillin G potassium salt (98% purity) was purchased from Aladdin. Hydrogen peroxide (30%), ferrous ($FeSO_4{\cdot}7H_2O$), peptone and glucose were all analytical grade. Acetonitrile and formic acid were HPLC grade. The molecular formula of the examined antibiotic, penicillin G is $C_{16}H_{18}N_2O_4S$ and the molecular weight is 334.4. The chemical structure of penicillin G is as follows.

2.2. Irradiation of the samples

The gamma irradiation experiments were carried out using ^{60}Co source of 3.6 × 10^{14} Bq located in the campus of our institute. Around 20 mL of water samples were irradiated in quartz tubes close to the source with the dose rate of around 240 Gy/min at ambient temperature of 23–25 °C. The absorbed doses, 0.5 kGy, 1.0 kGy, 2.5 kGy, 5 kGy and 10 kGy were obtained by regulating the irradiation time. The irradiation experiments were performed at least in duplicate.

The penicillin G solution with different concentrations of 2.68 mM, 1.34 mM and 0.27 mM were prepared in the same day by dissolving penicillin G potassium salt in deionized water. For studying the effects of peptone and glucose addition, the initial penicillin G concentration was set at 0.27 mM. The natural pH of 0.27 mM penicillin G was 6.52. The applied doses of peptone and glucose were 10 g/L and 1.0 g/L. To study the enhanced degradation of penicillin G, Fe^{2+} (0.5 mM, 1.0 mM) and H_2O_2 (0.5 mM, 1.0 mM, 5.0 mM) were added to the penicillin G solution before irradiation.

2.3. Analytical methods

The samples after irradiation were filtered through 0.45 μm filter and introduced into a high-performance liquid chromatography (HPLC) system for penicillin G quantification using an Agilent 1200 HPLC with a XDB-C18 reversed-phase column and a photo-diode array detector. The mobile phase was composed of acetonitrile and 0.1% formic acid (50:50) with a flow rate of 1.0 mL/min. The oven temperature was 30 °C and the detected wavelength was 220 nm. At such conditions, the retention time of penicillin G was around 2.26 min.

The degradation intermediates were identified by LC-MS and GC-MS. For LC-MS analysis, the instrument used was Shimazu 2010EV LC-MS analyzer equipped with a photo-diode array and an MS detector of an atmospheric pressure chemical ionization (APCI) source. The LC was operated as the same conditions as HPLC involving the eluent, flow rate, oven temperature and the column applied.

For GC-MS analysis, the aqueous samples were pre-treated by Oasis HLB solid phase extraction following the protocol briefly including activation by 3 mL methanol and 3 mL water, rinse with 5 mL pure water, elution with 3 mL methanol, drying under N_2 gas, reconstitution with 2 mL acetonitrile and 0.45 μm membrane filtration. An Agilent 7890 A/5975 C GC-MS analyzer was applied with an OV-101 GC capillary column and an injection temperature of 250 °C. Helium was used as carrier gas at a flow rate of 0.6 mL/min. The electron ionization of the MS detector was 70 eV and the ion source temperature was 200 °C.

The evolution of Total Organic Carbon content (TOC) was measured by a multi N/C 2100 TOC analyzer (Analytik Jena). Potassium phthalate was used as calibration standard. pH was measured by a pH meter (8103BN, Thermo Orion). Protein was detected using the Lowry protein assay. The concentrations of glucose and volatile fatty acids were evaluated by a HPLC (Shimadzu LC-20AD) equipped with differential refraction detector.

3. Results and discussion

3.1. Influence of initial penicillin G concentrations and degradation intermediates

Fig. 1 illustrates the effect of initial concentrations on penicillin G removal as exposed to gamma irradiation. Penicillin G was successfully removed using gamma irradiation from pure water. With the initial concentrations of 0.27 mM, 1.34 mM and 2.68 mM, a complete removal

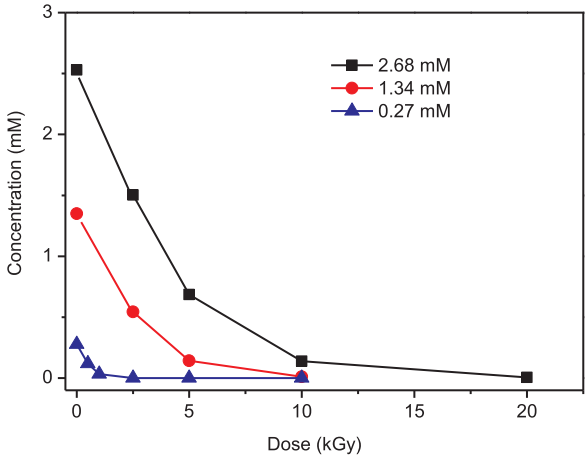

Fig. 1. Effect of initial concentrations on penicillin G removal during gamma irradiation.