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Photodegradation of propranolol by Fe(III)–citrate complexes: Kinetics, mechanism and effect of environmental media

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ABSTRACT

Photogeneration of HO• was optimized in Fe(III)–citrate solution within the pH range of 3.0–9.0 to investigate its photoreactivity at neutral pH without the addition of H_2O_2 under simulated sunlight. The generation of HO• decreased with increasing pH within the range of 6.0–9.0 at the Fe(III)-to-citrate ratio of 10:50 (10^{-6} M). However, when the concentration of citrate increased to 1.5×10^{-4} M, the formation rate of HO• increased in the order of pH 9.0 < 3.0 < 7.0 < 4.0 < 5.0. The pH-dependent HO• production was governed by the stability of Fe(II)/Fe(II)–citrate and the amount of $O_2^{\bullet-}$ in the solution. Propranolol can be efficiently photodegraded in Fe(III)–citrate system at pH 7.0 with pseudo-first-order constant 3.1×10^{-4} s^{-1}. HO• was verified to be the main reactive oxygen species (ROS) responsible for the photodegradation of propranolol. The presence of metal ions inhibited the Fe(III)–cit-induced photodegradation in the order of $Mn^{2+} > Cu^{2+} > Ca^{2+} > Mg^{2+}$. Both humic acid (HA) and fulvic acid (FA) markedly suppressed the degradation of propranolol. Moreover, the iron in Fe(III)–citrate system was reused by a simple addition of citrate to the reaction solution. By GC–MS analysis, the photoproducts of the propranolol were identified and the degradation pathway was proposed. This work suggests that Fe(III)–citrate complexes are good alternative for the advanced treatment of organic pollutants at neutral pH in aqueous solution.

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1. Introduction

Numerous studies have reported the occurrence of pharmaceuticals and personal care products (PPCPs) in surface water, groundwater, sewage water, and drinking water over the last decade. As one of the subclass of PPCPs, β-blockers have been used for the treatment of hypertension, angina pectoris, cardiovascular system and lately chronic heart failure [1]. β-Blockers cannot be completely eliminated in sewage treatment plants and they have been widely detected in surface waters [2–6]. The existence of β-blockers is detrimental to aquatic organisms [2]. It has been demonstrated that most β-blockers had a specific toxicity towards the green algae *Desmodesmus subspicatus* [7,8]. Among these β-blockers, propranolol has the highest acute and chronic toxicity [8].

The previous works showed that propranolol can undergo direct and indirect photodegradation in simulated natural waters, but it cannot be completely mineralized [9]. Advanced oxidation processes (AOPs) have been proven to be an effective alternative for the elimination of the drug. The common AOPs, including ozonation, UV/O_3, O_3/H_2O_2, UV/H_2O_2, and UV/TiO_2, have been used to treat propranolol [10–16]. Fe(III)-photocatalysis under sunlight is low-cost and has been employed for the treatment of organic pollutants since 1990s [17–19]. It is well-known that HO• is photochemically generated in Fe(III)–carboxylate solutions via ligand-to-metal charge transfer (LMCT) processes and subsequent Fenton reaction [20]. Citric acid (cit) is a naturally occurring hydroxycarboxylic acid and it can form complexes with iron, the ubiquitous element in the soil and waters. Fe(III)–cit complexes have been demonstrated to be excellent Fe(III)–photocatalysts with low toxicity and high photoreactivity [18,21,22].

For many Fe(III)–carboxylate complexes, aqueous hydroxide ions can outcompete carboxylate for complexation with Fe(III) and lead to loss of photoreactivity of the homogeneous catalysts. In view of the high stability constants of Fe(III)–cit complexes, it is theoretically likely to use the catalyst at neutral pH by changing the Fe(III)-to-cit molar ratio. Although the formation of HO• has been determined in the Fe(III)–cit system [23], the effect of Fe(III)-to-cit ratio at different pH was not studied. In addition, the metal ions such as Ca^{2+}, Mg^{2+}, Mn^{2+}, and Cu^{2+} can compete with Fe^{3+} for cit [24]. Humic substances can complex with Fe^{3+} and exhibit light screen effect [25]. The anions including SO_4^{2-}, HCO_3^-, and NO_3^- are also ubiquitous coexistent anions in waters [26]. Those ions and humic substances may influence the photoreactivity of Fe(III)–cit complexes. To our best knowledge, very few data are

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available concerning the effects of these environmental media on the Fe(III)-photocatalysis.

The present work, therefore, was to determine the formation of HO• at different Fe(III)-to-cit molar ratios within the pH range of 3.0–9.0. The optimal Fe(III)-to-cit ratio was chosen for the elimination of propranolol by Fe(III)–cit complexes. The effects of environmental media, including Ca^{2+}, Mg^{2+}, Mn^{2+}, Cu^{2+}, $SO_4{}^{2-}$, $HCO_3{}^-$, $NO_3{}^-$, and humic substances, on the photoreactivity of Fe(III)–cit complexes were first examined. Iron was reused by the addition of cit to reaction solution at pH 7.0 to examine the feasible application of Fe(III)–cit complexes. Furthermore, the photoproducts of the propranolol were determined by GC–MS, and the photodegradation pathway was proposed.

2. Materials and methods

2.1. Materials

Propranolol hydrochloride (CAS: 318-98-9, 99%) and humic acid (HA) was purchased from Sigma and used as received. Fulvic acid (FA) was obtained from Serva Corporation (Germany). Ferric chloride (99%) and trisodium cit dehydrate (99%) were obtained from Fengchuan Chemicals Corporation (Tianjin, China). $CaCl_2$, $MgCl_2{\cdot}6H_2O$, $MnCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}6H_2O$, isopropanol, and benzene were supplied by Wuhan Chemicals Corporation. Stock solution of propranolol was prepared from the solid in deionized water for photolysis experiments. All chemicals used were of at least analytical-reagent grade.

2.2. Photolysis experiments

The photolysis experiments were performed under 150-W Xenon Short Arc Lamp in a 60 mL capped cylindrical Pyrex vessel (40 mm i.d., containing 50 mL solution). The radiation of wavelengths less than 300 nm was filtered with the Pyrex glass to simulate the sunlight. Lamp output was monitored over time by ferrioxalate actinometry [27]. The incent intensity of the lamp is 1.5×10^{-5} einstein/s. All solutions for the photolysis experiments were freshly prepared prior to irradiation. In general, the initial concentration of propranolol was 2.0×10^{-5} M. HO• quenching experiment was conducted by the addition of 1.0×10^{-3} M isopropanol to the reaction solutions. Aliquots of samples were withdrawn at various intervals and substrate decay was measured by high performance liquid chromatography.

2.3. Determination of HO•

Benzene (7×10^{-3} M) was used as the probe to detect HO• generated in the irradiated Fe(III)–cit solutions [28]. The HO• was quantified by phenol, the hydroxylation product of benzene. The concentration of phenol was determined by HPLC. The generation of HO• was determined in Fe(III)–cit solutions with three ratios of Fe(III)-to-cit (10:50, 10:150, 10:500) within the pH range of 3.0–9.0 under simulated sunlight.

2.4. HPLC analysis

The concentration of propranolol was analyzed by Shimadzu Essentia LC-15C HPLC system with Agilent HC-C18 column (5 μm, 250 mm × 4.6 mm). The mobile phase was a mixture of acetonitrile and pH 2.5 KH_2PO_4 buffer (0.01 M) with a ratio of 35:65. The flow rate was 1.0 mL/min and the detector wavelength was set at 213 nm. Phenol concentration was analyzed with a mobile phase of 40:60 acetonitrile:H_2O and the detector wavelength was set at 270 nm. Cit concentration was detected with a mobile phase of 10:90 MeOH:H_2O (0.01 M KH_2PO_4 buffer and pH 2.5) and the detector wavelength was set at 268 nm. The calibration curves for the detection of propranolol and phenol are shown in Fig. A1.

2.5. Photoproducts identification

Photoproducts of propranolol were obtained after about 80% of the parent compound had been degraded by Fe(III)–cit complexes at pH 7.0. The reaction solution was evaporated to dryness by rotary evaporator. The residue was trimethylsilylated with 0.1 mL hexamethyldisilazane and 0.05 mL chlorotrimethylsilane at room temperature. All photoproducts were extracted and identified as silylation forms except 4-hydroxypropranolol. GC–MS analysis was carried out on an Agilent 7890A/5975C system with a HP-5 MS capillary column. The GC was operated in a temperature programming mode with an initial temperature of 80 °C held for 20 min, ramp at 5 °C min^{-1} to 280 °C, and held at this temperature for 3 min. The injection port and MSD were held at 250 and 280 °C, respectively.

3. Results and discussion

3.1. Photoformation of HO• in Fe(III)–cit solution

The HO• was quantified in Fe(III)–cit system at three different Fe(III)-to-cit molar ratios of 10:50, 10:150, and 10:500 (10^{-6} M). As shown in Fig. 1a, the generation of HO• decreased with increasing pH within the range of 3.0–9.0 at the Fe(III)-to-cit molar ratio of 10:50 (10^{-6} M). A similar trend was observed by Zhang et al. at the Fe(III)-to-cit molar ratio of 30:30 (10^{-6} M) [23]. However, when the concentration of cit increased to 1.5×10^{-4} M, the formation rate of HO• increased in the order of pH 9.0 < 3.0 < 7.0 < 4.0 < 5.0 (Fig. 1b). Further increase of cit concentration did not affect the order of pH for HO• production (Fig. 1c). This indicated that it was likely to extend pH to neutral for the elimination of organic pollutants in Fe(III)–cit system.

Balmer and Sulzberger have reported a similar result for the photoreactivity of Fe(III)–oxalate complexes [29]. According to the studies of pH-dependent degradation of atrazine, the degradation rate increased in the order of pH 7.5 < 5.6 < 3.2 < 4.3 at the Fe(III)-to-oxalate ratio of 6:18 (10^{-6} M). In contrast, the pH followed the order of pH 7.9 < 3.2 < 4.6 ≈ 5.4 at the Fe(III)-to-oxalate ratio of 6:180 (10^{-6} M) [29]. Jeong and Yoon also gave a similar report for the degradation of 2,4-dichlorophenoxyacetic acid in photo/ferrioxalate system [30]. For both Fe(III)–cit and Fe(III)–oxalate complexes, higher Fe(III)-to-carboxylate ratio is more favorable for HO• formation at lower pH. However, lower Fe(III)-to-carboxylate ratio renders the trend of HO• formation different due to the presence of excessive carboxylate in the solutions.

3.2. HO• formation mechanism

The generation of HO• depends on the Fe(III) species in aqueous solutions, which are the function of pH and Fe(III)-to-ligand ratios. In Fe(III)–cit system, there is some discrepancy in literature concerning the Fe(III)–cit species dominant in solution at different pHs [31]. According to Field and Stumm, the main Fe(III)–cit species include Fecit, $FeHcit^+$, $FeOHcit^-$, and $Fe_2(OH)_2(cit)_2{}^{2-}$ [24,32]. Fig. 2 illustrates the fraction of Fe(III) species in the Fe(III)–cit aqueous solution based on the data from Medusa soft (version: 18 February 2004). Although hydrous ferric oxyhydroxide precipitation is thermodynamically expected at pH > 7.0, the precipitation kinetics was slow, resulting in the presence of homogeneous Fe(III)–cit catalyst within the pH range studied according to the UV–vis spectra (Fig. A2). At low pH, Fecit is the predominant species. With increasing pH (pH > 4), $FeOHcit^-$ and $Fe_2(OH)_2(cit)_2{}^{2-}$ become the main

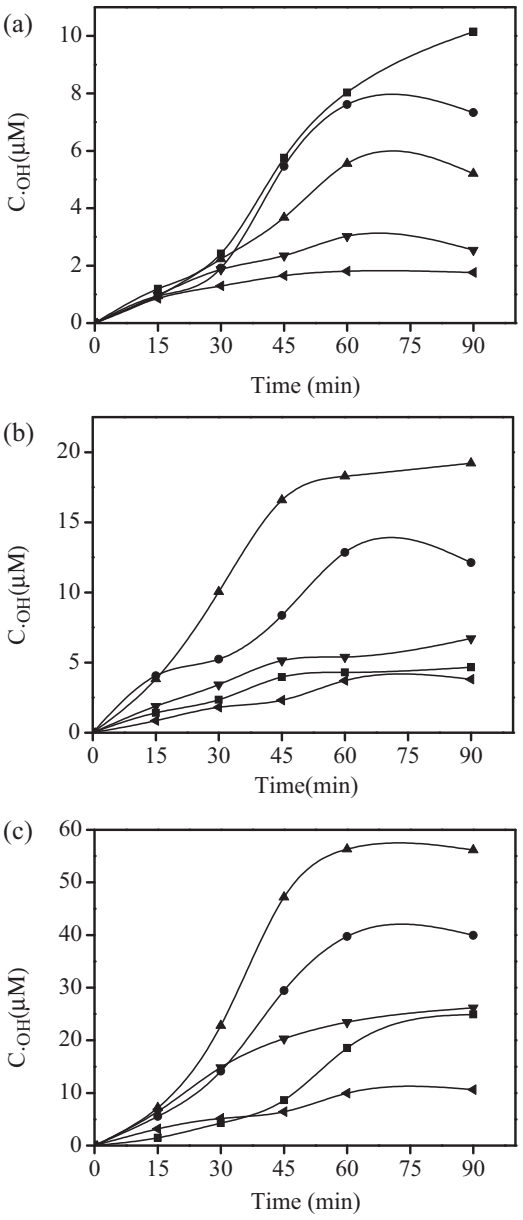

Fig. 1. Determination of HO• at different $[Fe(III)]_0/[cit]_0$ ratios: (a) $[Fe(III)]_0/[cit]_0 = 10/50$, (b) $[Fe(III)]_0/[cit]_0 = 10/150$, and (c) $[Fe(III)]_0/[cit]_0 = 10/500$ within the pH range of 3.0–9.0: (■) pH 3.0, (●) pH 4.0, (▲) pH 5.0, (▼) pH 7.0, and (◄) pH 9.0.

species gradually. Fecit and $FeOHcit^-$ are reported to photochemically induce HO• via the following reactions [18,33–36].

$$Fecit + h\nu \xrightarrow{LMCT} Fe(II) + cit^{\bullet 2-} \quad (1)$$

$$FeOHcit^- + h\nu \xrightarrow{LMCT} Fe(II) + 3\text{-}HGA^{\bullet 2-} \quad k = 1.3 \times 10^{-2}\ M^{-1}\ s^{-1} \quad (2)$$

$$cit^{\bullet 2-} + O_2 \rightarrow 3\text{-}OGA^{2-} + CO_2 + O_2^{\bullet -} \quad (3)$$

$$3\text{-}HGA^{\bullet 2-} + O_2 \rightarrow 3\text{-}HGA^{2-} + O_2^{\bullet -} \quad k = 1.0 \times 10^{6}\ M^{-1}\ s^{-1} \quad (4)$$

$$HO_2^{\bullet} \leftrightarrow H^+ + O_2^{\bullet -} \quad K_a = 10^{-4.8}\ M \quad (5)$$

$$Fe(II) + O_2^{\bullet -} \xrightarrow{2H^+} Fe(III) + H_2O_2 \quad k = 1.0 \times 10^{7}\ M^{-1}\ s^{-1} \quad (6)$$

$$Fe(II) + HO_2^{\bullet} \xrightarrow{H^+} Fe(III) + H_2O_2 \quad k = 1.2 \times 10^{6}\ M^{-1}\ s^{-1} \quad (7)$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO^{\bullet} + OH^- \quad k = 63\ M^{-1}\ s^{-1} \quad (8)$$

$$Fe(II)cit^- + H_2O_2 \rightarrow Fe(III)cit + HO^{\bullet} + OH^- \quad (9)$$

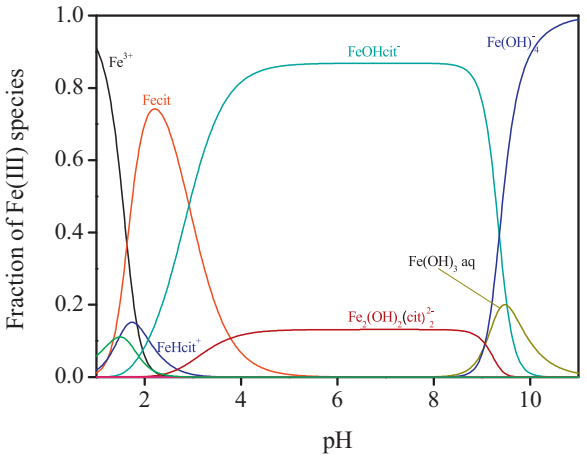

Fig. 2. The fraction of Fe(III) species based on the stability constants of Fe(III)–cit and Fe(III)–hydroxo species as a function of pH ($[Fe(III)]_0/[cit]_0 = 10/150$; data of stability constants is from Medusa soft, formation of iron precipitation was omitted).

According to Eq. (1) and Fig. 2, Fecit complex undergoes a rapid LMCT process with generation of Fe^{2+} and $cit^{\bullet 2-}$ within the pH range of 2–4. In the presence of oxygen, $O_2^{\bullet -}$ is formed and lead to H_2O_2 which, in turn, reacts with Fe(II) via a Fenton process to produce HO• (Eqs. (3), (6) and (8)). Like Fenton reaction, lower pH (in a range of 3.0–9.0) favored the formation of HO• in Fe(III)–cit system at Fe(III)-to-cit ratio of 10:50 (10^{-6} M). As the increase of cit concentration (1.5×10^{-4} M), the amount of cit was far enough for the complexation with Fe(III). So it has the ability to outcompete hydroxide ions for Fe(III) at higher pH and the Fe(III) species are present as $FeOHcit^-$ and $Fe_2(OH)_2(cit)_2^{2-}$ (Fig. 2). Like Fecit, $FeOHcit^-$ has a considerable photoreactivity. $O_2^{\bullet -}$ was generated after a LMCT process in the presence of $FeOHcit^-$ (Eqs. (2) and (4)). In comparison with $HO_2^{\bullet}$, $O_2^{\bullet -}$ are more favorable for the generation of H_2O_2 [30], the key factor for production of HO• (Eqs. (6) and (7)). The pK_a for $HO_2^{\bullet}/O_2^{\bullet -}$ equilibrium is 4.8 [34], suggesting that $O_2^{\bullet -}$ account for approximately 99% in the solution at pH > 6.8. Accordingly, higher pH (until pH 6.8) facilitates the formation of $O_2^{\bullet -}$ and consequently H_2O_2.

Furthermore, the redox potential of Fe(III)cit/Fe(II)cit ($E^0_{Fe(III)cit/Fe(II)cit}$) is calculated to be 0.34 V according to the standard redox potential of Fe(III)/Fe(II) ($E^0_{Fe(III)/Fe(II)} = 0.77$ V) [37]. The $E^0_{Fe(III)cit/Fe(II)cit}$ is far below $E^0_{Fe(III)/Fe(II)}$, indicating that Fe(II)–cit is more readily oxidized compared to Fe(II) in alkaline solution. Therefore, the Fenton-like reaction (Eq. (9)) is more rapid than Fenton reaction (Eq. (8)). Meanwhile, as the increase of pH, Fe(II) can also be oxidized into Fe(III) more easily via reaction with O_2 according to the well-known reaction equation [38]:

$$-\frac{dFe(II)}{dt} = k[Fe(II)]p_{O_2}[OH^-]^2 \quad (10)$$

Likewise, Fe(II)–cit is more easily oxidized by O_2 at higher pH in aerated aqueous solution. Accordingly, an increase of pH facilitates the formation of $O_2^{\bullet -}$ (pH < 6.8), whereas it is unfavorable for the stable presence of Fe(II) reduction state including Fe(II) and Fe(II)–cit. The contrary effect on Fenton (or Fenton-like) reaction (Eqs. (8) or (9)) led to the optimal pH 5.0 for the production of HO• in the experiment at Fe(III)-to-cit ratio of 10:150 (10^{-6} M). Therefore, the $O_2^{\bullet -}$ production and the stability of Fe(II)/Fe(II)–cit were two predominant factors for the pH-dependent formation of HO• in the Fe(III)–cit solutions.

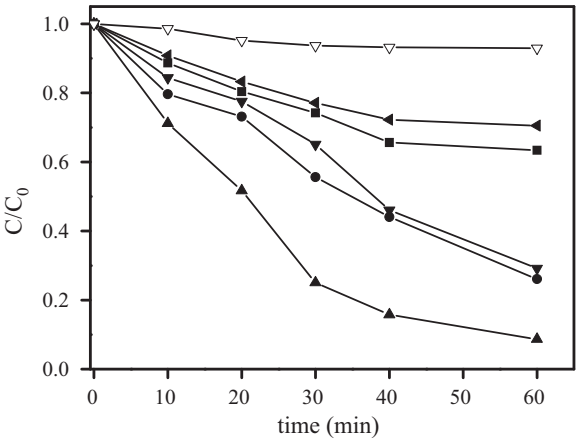

Fig. 3. Photodegradation of propranolol in Fe(III)–cit solutions at different conditions: (■) pH 3.0, (●) pH 4.0, (▲) pH 5.0, (▼) pH 7.0, (◄) pH 9.0, and (▽) pH 7.0 with the addition of isopropanol. Initial conditions: $[Fe(III)]_0/[cit]_0 = 10/150$, $[propranolol]_0 = 2.0 \times 10^{-5}$ M, $[isopropanol]_0 = 1.0 \times 10^{-3}$ M.

3.3. Photodegradation of propranolol

According to the determination of HO• production, the Fe(III)-to-cit ratio of 10:150 (10^{-6} M) was satisfactory for treatment of pollutants at neutral pH. The bimolecular rate constant for the reaction between propranolol and HO• ($k_{HO•}$) was $(8.7 \pm 0.3) \times 10^9$ M^{-1} s^{-1} [9], indicating that propranolol reacts at near diffusion-controlled limits with HO•. Fig. 3 illustrates the effect of pH on the photodegradation of propranolol within the pH range of 3.0–9.0 in Fe(III)–cit solution. The removal rate of propranolol increased in the order of pH 9.0 < 3.0 < 7.0 < 4.0 < 5.0, which agreed well with the trend for the HO• production at the Fe(III)-to-cit ratio of 10:150 (10^{-6} M). The similar pH trend for the generation of HO• and degradation of propranolol suggested that the photodegradation of propranolol was related to HO• formed in Fe(III)–cit solution.

The photodegradation mechanism was investigated by the HO• quenching experiments. As shown in Fig. 3, the photodegradation of propranolol was markedly inhibited in the presence of isopropanol. It was further verified that HO• was the main reactive oxygen species (ROS) responsible for the photodegradation of propranolol in Fe(III)–cit solution. The photodegradation followed pseudo-first-order kinetics. At pH 7.0 the apparent rate constant (k_{obs}) was 3.1×10^{-4} s^{-1}, corresponding to a half-life 2.2×10^3 s (Fig. 3). According to bimolecular rate constant for the reaction between propranolol and HO•, the steady-state concentration of HO• ($k_{obs}/k_{HO•}$) was calculated to be 3.6×10^{-14} M in the Fe(III)–cit solution at pH 7.0.

3.4. Effect of cations and anions on the photodegradation

The metal ions including Ca^{2+}, Mg^{2+}, Mn^{2+}, and Cu^{2+} were added to the Fe(III)–cit solutions to better understand the environmentally photochemical removal of propranolol. The presence of metal ions inhibited the photodegradation of propranolol at pH 7.0 (Fig. 4). The inhibition effect followed the order of $Mn^{2+} > Cu^{2+} > Ca^{2+} > Mg^{2+}$. According to the UV–vis spectra, the absorbance of the mixture of each metal ion and propranolol was equal to the sum of single absorption, suggesting that the no complexation occurred between the metal ions and propranolol (Fig. A3). Thus, the inhibition effect may be attributed to the competitive complexation of these metal ions for cit with Fe(III), which gave rise to decrease of photoreactivity of Fe(III)–cit complexes. The first logarithms values of the stability constant for formation of Mn^{2+}, Cu^{2+}, Ca^{2+}, and Mg^{2+}–cit complexes are 5.5, 7.2, 4.7, and 4.7, respectively [24]. According to the stability constants, it appears

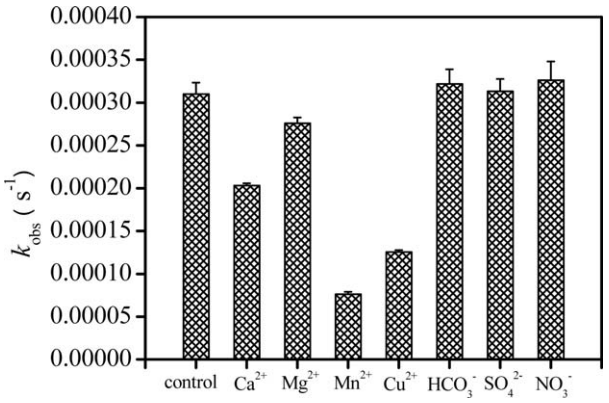

Fig. 4. Effect of cations and anions on the photodegradation of propranolol. Initial conditions: $[Fe(III)]_0/[cit]_0 = 10/150$, $[propranolol]_0 = 2.0 \times 10^{-5}$ M, $[ion]_0 = 2.0 \times 10^{-5}$ M, pH 7.0.

that Cu^{2+} will show more inhibition than Mn^{2+}, but opposite phenomenon was observed in this experiment. This is likely due to the photoreactivity of Cu^{2+}–cit complexes [20]. Cu^{2+} can accept electron from $HO_2•/O_2•^-$ and be reduced to Cu^+, which reacts with H_2O_2 and produce HO• according to Eqs. (11)–(13) [20,39]

$$Cu(II) + O_2•^- \rightarrow Cu(I) + O_2 \quad (11)$$

$$Cu(II) + HO_2•^- \rightarrow Cu(I) + O_2•^- + H^+ \quad (12)$$

$$Cu(I) + H_2O_2 \rightarrow Cu(II) + HO• + HO^- \quad (13)$$

$$Mn(II) + H_2O_2 \rightarrow Mn(III) + HO• + HO^- \quad (14)$$

Nevertheless, Cu(II) was involved in the redox cycle of $HO_2•/O_2•^-$ and thus affected the Fenton reaction of Fe(III)–cit, which has higher photoreactivity than Cu(II)–cit. Likewise, the addition of Mn(II) in Fe(III)–cit system may induce the Fenton-type reaction (Eq. (14)) [39]. Meanwhile, the reduction-state Mn^{2+} in the solution could be oxidized to Mn^{3+} by HO• and the Mn^{3+}, in turn, is reduced by $HO_2•/O_2•^-$. Therefore, the multivalent metal-ions affect the Fe(III)–cit-induced photodegradation by involving the redox cycling in the system.

As shown in Fig. 4, the addition of HCO_3^-, SO_4^{2-}, and NO_3^- to the reaction solutions exhibited negligible effect on the photodegradation of propranolol in the Fe(III)–cit solutions. A similar phenomenon is observed for the photodegradation of organic dyes in the presence of [Fe(III)–salen]Cl and H_2O_2 [26]. It is well-known that HO• can directly oxidize HCO_3^- and SO_4^{2-} via electron-transfer reactions [40]:

$$HCO_3^- + HO• \rightarrow CO_3•^- + H_2O_2 \quad (15)$$

$$SO_4^{2-} + HO• \rightarrow SO_4•^- + HO^- \quad (16)$$

The bimolecular rate constants for the reactions of HCO_3^- and SO_4^{2-} with HO• are 8.5×10^6 and 3.5×10^5 $L\,mol^{-1}\,s^{-1}$ [40], which are 3–4 order-of-magnitude lower than that of propranolol [9]. Therefore, the indirect photodegradation of propranolol was not affected in the presence of those anions with low concentrations.

3.5. Effect of humic substances on the photodegradation

Humic substances are ubiquitous in natural waters. The effect of humic substances, including HA and FA, on the photodegradation of propranolol was examined in the Fe(III)–cit system. As shown in Fig. 5, the addition of HA and FA markedly suppressed the photodegradation. The inhibition increased with increasing concentration of HA (Fig. 5a) or FA (Fig. 5b). The degradation of propranolol was slower with the addition of FA compared to that

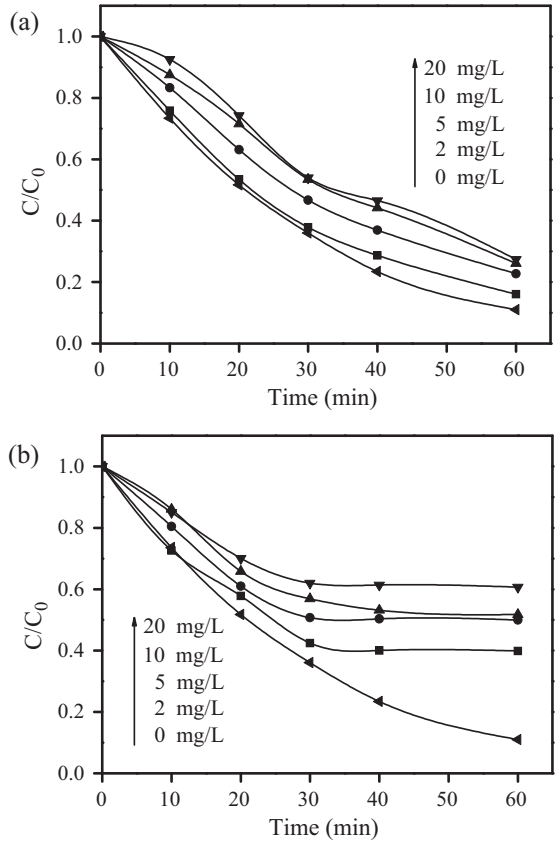

Fig. 5. Effect of humic acid (a) and fulvic acid (b) on the photodegradation of propranolol. Initial conditions: $[Fe(III)]_0/[cit]_0 = 10/150$, $[propranolol]_0 = 2.0 \times 10^{-5}$ M, pH 7.0.

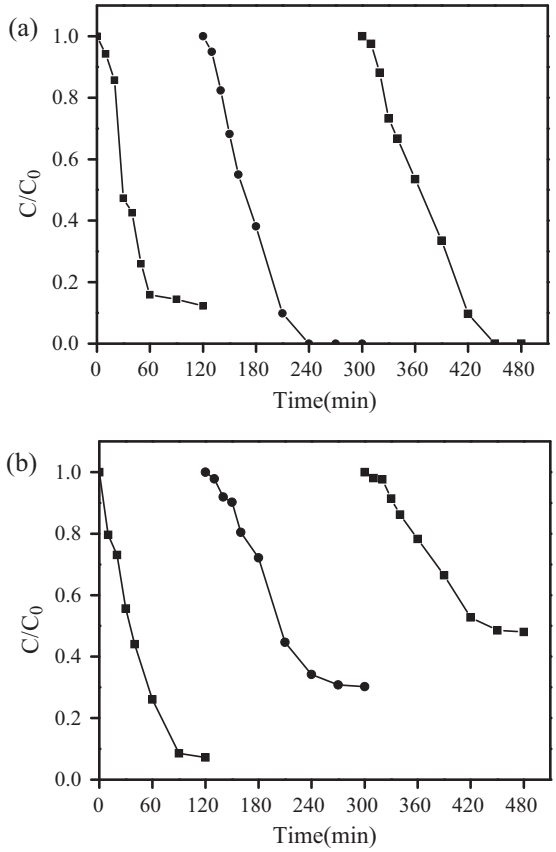

Fig. 6. (a) Decay of cit concentration after the addition of equimolar cit (1.5×10^{-4} M) in the Fe(III) solution (1.0×10^{-5} M) and corresponding photodegradation of propranolol during the three runs at pH 7.0 (b).

of HA under otherwise identical conditions. For example, the addition of 10 mg/L HA and FA inhibited the degradation of propranolol by 1.8- and 3.7-fold, respectively. In addition, the indirect photodegradation was nearly stopped after 30 min in the presence of FA.

Humic substances could complex with iron because they contain a high density of carboxylate functional groups [25]. The competitive complexation of humic substances with cit for Fe(III) led to decrease of the concentration of Fe(III)–cit complexes, thereby affecting $HO^{\bullet}$ production. Although Fe(III)–humic substances complexes have the ability to generate $HO^{\bullet}$, the photoreactivity is lower compared to Fe(III)–cit complexes. Moreover, humic substances can react with $HO^{\bullet}$ and thus disfavor the degradation of propranolol. More importantly, humic substances can absorb the UV–vis light and have light screening effect on the photodegradation. The extinction coefficient of FA was higher than HA [9], resulting in greater inhibition of the degradation.

3.6. Reuse of Fe(III)/Fe(II) in the solution

According to the above discussion, the Fe(III)-to-cit molar ratio affected the pH application range for the degradation of propranolol. At definite concentration of Fe(III), the main effect factor was the concentration of cit, which is depleted during the photochemical reactions. In contrast, iron is present in the solution throughout, which is only cycled between the +2 and +3 oxidation states. Overuse of iron can give rise to increase of process cost and colourity of water. Therefore, it was necessary to reuse the Fe(III)/Fe(II) in the solution. As shown in Fig. A4, the photodegradation of propranolol in Fe(III)–cit and Fe(II)–cit solutions made no difference at pH 7.0, suggesting that the oxidation state of iron did not affected the degradation. This was because Fe(II)–cit was easily oxidized to Fe(III)–cit at pH 7.0. Accordingly, it was very convenient to reuse the iron at any reaction period by a simple addition of cit to Fe(III)–cit solution.

In this study, three runs were conducted to investigate the depletion of cit and the corresponding photodegradation of propranolol. Initially, the photodegradation of propranolol was carried out in Fe(III)–cit solution at Fe(III)-to-cit ratio of 10:150 (10^{-6} M). After 120 and 300 min, 1.5×10^{-4} M cit was added to the solution, respectively. As shown in Fig. 6a, the depletion of cit was very rapid within 60 min in the first run. It became slower in the subsequent runs. The apparent depletion rate constants of cit were 5.3×10^{-4}, 2.8×10^{-4}, and 1.8×10^{-4} s^{-1}, respectively. Correspondingly, the photodegradation rate constants of propranolol were 3.6×10^{-4}, 9.5×10^{-5}, 7.2×10^{-5} s^{-1}, respectively (Fig. 6b). The photodegradation of propranolol decreased more obviously compared to cit after each run. This can be attributed to the accumulation of intermediates produced in the former run, which reacted competitively with $HO^{\bullet}$ in Fe(III)–cit solution and led to further mineralization.

3.7. Photodegradation products and pathway

The reaction intermediates and products of propranolol were identified by GC–MS. The main intermediates formed in Fe(III)–cit system are shown in Table A1. All of these compounds were unequivocally identified using the NIST98 library database and the comparison of mass spectra between standard compounds and the photoproducts is illustrated in Fig. A5. As shown in Table A1, most of the intermediates are hydroxylation products, mainly including naphthalen-1-o1, 4-hydroxypropranolol, 1,5-dihydroxy-naphalene, 1,6-dihydroxy-naphalene and some benzene series

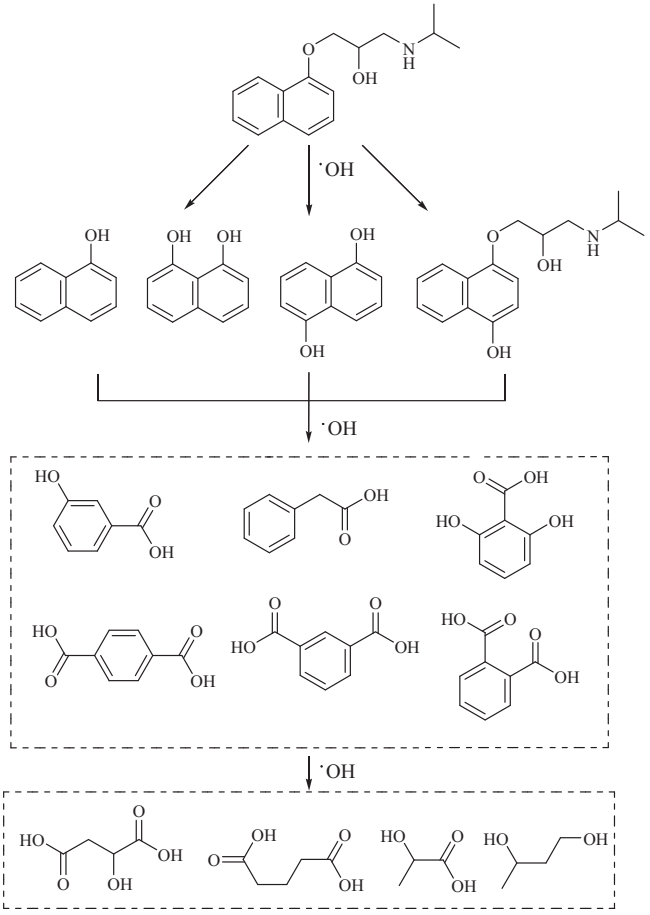

Fig. 7. The proposed pathways for the indirect photodegradation of propranolol in Fe(III)–cit system.

compounds. These hydroxylation products can be further attacked by HO•, leading to oxidative cleavage of benzene ring. The results further verified that HO• was the main ROS for the photodegradation of propranolol in Fe(III)–cit system. According to the above results, the proposed pathway for the indirect photodegradation of propranolol is illustrated in Fig. 7. The first attack of HO• occurred in the side chain and benzene ring of propranolol, leading to naphthalen-1-o1 and 4-hydroxypropranolol, which have been detected as HO• product by Song et al. [41]. The further oxidation of naphthalen-1-o1 yielded 1,5-dihydroxynaphalene, and 1,6-dihydroxynaphalene. The subsequent cleavage of one of the benzene ring gave rise to the production of some benzene series compounds such as benzeneacetic acid, 3-hydroxybenzoic acid, 1,3-benzenedicarboxylic acid, 1,4-benzenedicarboxylic acid, and 2,6-dihydroxybenzoic acid. In addition, HO• further reacted with the intermediates and generated a series of low-molecular-weight carboxylic acids.

4. Conclusions

Fe(III)–cit-induced HO• formation rate increased with decreasing pH at the Fe(III)-to-cit ratio of 10:50 (10^{-6} M). Lower ratio such as 10:150 and 10:500 led to different orders for HO• formation: pH 5.0 > 4.0 > 7.0 > 3.0 > 9.0. The pH-dependent HO• production are governed by the stability of Fe(II)/Fe(II)–cit and amount of $O_2^{\bullet -}$. The presence of metal ions inhibited the photodegradation of propranolol in the order of $Mn^{2+} > Cu^{2+} > Ca^{2+} > Mg^{2+}$, while HCO_3^-, SO_4^{2-}, and NO_3^- did not affect the degradation in Fe(III)–cit system. Both HA and FA markedly suppressed the photodegradation of propranolol. Reuse of iron in Fe(III)–cit solution was convenient by a simple addition of cit to the reaction solution. The attack of HO• on propranolol led to 4-hydroxypropranolol, naphthalen-1-o1, 1,5-dihydroxy-naphalene, 1,6-dihydroxy-naphalene, some benzene series compounds, and low-molecular-weight carboxylic acids.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.07.081.

References

[1] J. Franciosa, β-Adrenergic blocking agents: past, present, and future perspectives, Coron. Artery Dis. 10 (1999) 369–376.
[2] D.B. Huggett, B.W. Brooks, B. Peterson, C.M. Foran, D. Schlenk, Toxicity of select beta adrenergic receptor-blocking pharmaceuticals (β-blockers) on aquatic organisms, Arch. Environ. Contam. Toxicol. 43 (2002) 229–235.
[3] M.J. Gómez, M.J. Martínez Bueno, A. Agüera, M.D. Hernando, A.R. Fernández-Alba, M. Mezcua, Evaluation of ozone-based treatment processes for wastewater containing microcontaminants using LC-QTRAP–MS and LC–TOF/MS, Water Sci. Technol. 57 (2008) 41–48.
[4] D. Ashton, M. Hilton, K.V. Thomas, Investigating the environmental transport of human pharmaceuticals to streams in the United Kingdom, Sci. Total Environ. 333 (2004) 167–184.
[5] D.B. Hugger, I.A. Khan, C.M. Foran, D. Schlenk, Determination of beta-adrenergic receptor blocking pharmaceuticals in United States wastewater effluent, Environ. Pollut. 121 (2003) 199–205.
[6] S. Kim, D.S. Aga, Potential ecological and human health impacts of antibiotics and antibiotic-resistant bacteria from wastewater treatment plants, J. Toxicol. Environ. Health B 10 (2007) 559–573.
[7] K. Fent, A. Weston, D. Caminada, Ecotoxicology of human pharmaceuticals, Aquat. Toxicol. 76 (2006) 122–159.
[8] B.I. Escher, N. Bramaz, M. Richter, J. Lienert, Comparative ecotoxicological hazard assessment of beta-blockers and their human metabolites using a mode-of-action-based test battery and a Qsar approach, Environ. Sci. Technol. 40 (2006) 7402–7408.
[9] Y. Chen, C. Hu, X.X. Hu, J.H. Qu, Indirect photodegradation of amine drugs in aqueous solution, Environ. Sci. Technol. 43 (2009) 2760–2765.
[10] J. Benner, T. Ternes, Ozonation of propranolol: formation of oxidation products, Environ. Sci. Technol. 43 (2009) 5086–5093.
[11] R. Andreozzi, L. Campanella, B. Fraysse, Effects of advanced oxidation processes (AOPs) on the toxicity of a mixture of pharmaceuticals, Water Sci. Technol. 50 (2004) 23–28.
[12] I. Kim, H. Tanaka, Photodegradation characteristics of PPCPs in water with UV treatment, Environ. Int. 35 (2009) 793–802.
[13] A. Piram, A. Salvador, C. Verne, Photolysis of β-blockers in environmental waters, Chemosphere 73 (2008) 1265–1271.
[14] I.H. Kim, N. Yamashita, Y. Kato, Discussion on the application of UV/H_2O_2, O_3 and O_3/UV processes as technologies for sewage reuse considering the removal of pharmaceuticals and personal care products, Water Sci. Technol. 59 (2009) 945–955.
[15] V. Romero, N. De la Cruz, R.F. Dantas, P. Marco, J. Giménez, S. Esplugas, Photocatalytic treatment of metoprolol and propranolol, Catal. Today 161 (2011) 115–120.
[16] H. Yang, T.C. An, G.Y. Li, W.H. Song, W.J. Cooper, H.Y. Luo, X.D. Guo, Photocatalytic degradation kinetics and mechanism of environmental pharmaceuticals in aqueous suspension of TiO_2: a case of beta-blockers, J. Hazard. Mater. 179 (2010) 834–839.
[17] N. Brand, G. Mailhot, M. Bolte, Degradation photoinduced by Fe(III): method of alkylphenol ethoxylates removal in water, Environ. Sci. Technol. 32 (1998) 2715–2720.
[18] N.S. Deng, F. Wu, F. Luo, M. Xiao, Ferric cit-induced photodegradation of dyes in aqueous solutions, Chemosphere 36 (1998) 3101–3112.
[19] Y.G. Zuo, J. Hoigné, Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron(III)–oxalato complexes, Environ. Sci. Technol. 26 (1992) 1014–1022.
[20] P. Cieśla, P. Kocot, P. Mytych, Z. Stasicka, Homogeneous photocatalysis by transition metal complexes in the environment, J. Mol. Catal. A: Chem. 224 (2004) 17–33.

[21] J. Guo, Y.Y. Du, Y.Q. Lan, J.D. Mao, Photodegradation mechanism and kinetics of methyl orange catalyzed by Fe(III) and citric acid, J. Hazard. Mater. 186 (2011) 2083–2088.
[22] X. Ou, X. Quan, S. Chen, Photocatalytic reaction by Fe(III)–citrate complex and its effect on the photodegradation of atrazine in aqueous solution, J. Photochem. Photobiol. A 197 (2008) 382–388.
[23] C. Zhang, L. Wang, F. Wu, N.S. Deng, Quantitation of hydroxyl radicals from photolysis of Fe(III)–cit complexes in aerobic water, Environ. Sci. Pollut. Res. 13 (2006) 156–160.
[24] W. Stumm, J.J. Morgan, Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, 3rd edition, Wiley, New York, 1996, pp. 332–333.
[25] E. Tipping, C. Rey-Castro, S.E. Bryan, J. Hamilton-Taylor, Al(III) and Fe(III) binding by humic substances in freshwaters, and implications for trace metal speciation, Geochim. Cosmochim. Acta 66 (2002) 3211–3224.
[26] S. Gazi, R. Ananthakrishnan, N.D. Pradeep Singh, Photodegradation of organic dyes in the presence of [Fe(III)–salen]Cl complex and H_2O_2 under visible light irradiation, J. Hazard. Mater. 183 (2010) 894–901.
[27] C.G. Hatchard, C.A. Parker, A new sensitive chemical actinometer. II. Potasium ferrioxalate as a standard chemical actinometer, Proc. R. Soc. A 235 (1956) 518–536.
[28] X.L. Liu, F. Wu, N. Deng, Photoproduction of hydroxyl radicals in aqueous solution with algae under high-pressure mercury lamp, Environ. Sci. Technol. 38 (2004) 296–299.
[29] M.E. Balmer, B. Sulzberger, Atrazine degradation in irradiated iron/oxalate systems: effects of pH and oxalate, Environ. Sci. Technol. 33 (1999) 2418–2424.
[30] J. Jeong, J. Yoon, pH effect on OH radical production in photo/ferrioxalate system, Water Res. 39 (2005) 2893–2900.
[31] N. Quici, M.E. Morgada, R.T. Gettar, M. Bolte, M.I. Litter, Photocatalytic degradation of citric acid under different conditions: TiO2 heterogeneous photocatalysis against homogeneous photolytic processes promoted by Fe(III) and H_2O_2, Appl. Catal. B: Environ. 71 (2007) 117–124.
[32] T.B. Field, J.L. McCourt, W.A.E. McBryde, Composition and stability of iron and copper citrate complexes in aqueous solution, Can. J. Chem. 52 (1974) 3119–3124.
[33] S.J. Hug, L. Canonica, M. Wegelin, D. Gechter, U. Gunten, Solar oxidation and removal of arsenic at circumneutral pH in iron containing waters, Environ. Sci. Technol. 35 (2001) 2114–2121.
[34] B.H.J. Bielski, D.E. Cabelli, R.L. Arudi, A.B. Ross, Reactivity of HO_2/O_2^- radicals in aqueous solution, J. Phys. Chem. Ref. Data 14 (1985) 1041–1100.
[35] J.D. Rush, B.H.J. Bielski, Pulse radiolytic studies of the reactions of HO_2/O_2^- with Fe(II)/Fe(III) ions. The reactivity of HO_2/O_2^- with ferric ions and its implication on the occurrence of the Haber–Weiss reaction, J. Phys. Chem. 89 (1985) 5062–5066.
[36] T.J. Hartwick, The rate constant of the reaction between ferrous ions and hydrogen peroxide in acid solution, Can. J. Chem. 35 (1957) 428–436.
[37] A.N. Pham, T.D. Waite, Oxygenation of Fe(II) in the presence of citrate in aqueous solutions at pH 6.0–8.0 and 25 °C: interpretation from an Fe(II)/citrate speciation perspective, J. Phys. Chem. A 112 (2008) 643–651.
[38] J.D. Willey, R.F. Whitehead, R.J. Kieber, D.R. Hardison, Oxidation of Fe(II) in rainwater, Environ. Sci. Technol. 39 (2005) 2579–2585.
[39] J. Sýkora, Photochemistry of copper complexes and their environmental aspects, Coord. Chem. Rev. 159 (1997) 95–108.
[40] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate-constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($^{\bullet}OH/O^{\bullet -}$) in aqueous solution, J. Phys. Chem. Ref. Data 17 (1988) 513–886.
[41] W. Song, W.J. Cooper, S.P. Mezyk, J. Greaves, B.M. Peake, Free radical destruction of beta-blockers in aqueous solution, Environ. Sci. Technol. 42 (2008) 1256–1261.