Oxidative Degradation of Organic Pollutants by Hydrogen Peroxide in the Presence of $FePz(dtnCl_2)_4$ under Visible Irradiation

Jie Sun,[1,2] Yuping Sun,[1] Kejian Deng,*[1] Haobo Hou,[2] and Duoyuan Wang[1]
[1]*The Key Laboratory for Catalysis and Material Science in Hubei,*
South-Central University for Nationalities, Wuhan 430073, P. R. China
[2]*College of Resource and Environment, Wuhan University, Wuhan 430072, P. R. China*

(Received January 29, 2007; CL-070105; E-mail: dengkj@scuec.edu.cn)

A novel photocatalyst of iron(II)–tetra(5,6-dichloro-1,4-dithin)porphyrazine (abbreviated as $FePz(dtnCl_2)_4$) has been found to exhibit high catalytic activity to activate hydrogen peroxide for oxidative degradation of organic pollutants under visible light irradiation ($\lambda > 420$ nm) and wide pH range, in which Rhodamine B(RhB) and 4-nitro benzoic acid (NBA) were efficiently degraded and mineralized, while degraded residues and active oxygen species were also identified.

Hydrogen peroxide, is the "clean" oxidant for the degradation of persistent organic pollutants in water.[1] The famous utilized H_2O_2 system is Fenton reagent (Fe^{II}/H_2O_2), but it must be held in acid solution (pH <3) and only ultraviolet light can enhance the reactive rate to degrade organic pollutants.[2] To mimic the structure of iron-containing oxygenase enzymes such as the cytochrome P450, several synthetic analogous have catalytic prosperity to activate H_2O_2 in an extensive pH range. For example, Collins et al. synthesized an iron complex of tetraamidomacrocyclic (Fe-TAML), which can activate H_2O_2 in the dark for rapid total destruction of 2,4,6-trichlorophenol (TCP).[3,4] Meunier reported that chlorophenols in a CH_3CN/water mixture could be efficiently oxidized by H_2O_2 in the presence of iron–phthalocyaninesulfonate (FePcS) in the dark, and iron–peroxo species [Fe(OOH)(PcS)] was involved as an active oxygen intermediate.[5,6] Zhao's group successfully introduced visible light to FePcS/H_2O_2 system without adding CH_3CN, and HO• radicals were detected as the active oxygen species,[7] in which the photodegradation for RhB or Orange II can proceed efficiently in a wide pH range except for neutral solution.[8]

Iron porphyrazines (FePz) and relative derivatives are also a kind of N4-ligand complexes, which are of special prosperity in biomimic catalysis and photoreaction.[9,10] Herein, we reported a novel photocatalyst of iron(II)–tetra(5,6-dichloro-1,4-dithin)-porphyrazine [$FePz(dtnCl_2)_4$], with saturated solubility 7.9 µM in water, which can efficiently activate hydrogen peroxide in homogeneous conditions to degrade toxic pollutants [Rhodamine B(RhB), and 4-nitro benzoic acid(NBA)] under visible light irradiation ($\lambda > 420$ nm) and extensive pH range.

The reaction solution containing the catalyst of $FePz(dtnCl_2)_4$ and the substrate of RhB or NBA was first magnetically stirred in an 80-mL pyrex glass vessel over 2 min, then H_2O_2 was added, and whole reaction system was irradiated with a 500-W halogen lamp through a glass filter cutoff wavelength less than 420 nm, while the intensity of light was ca. 29000 lux. The reaction was monitored by a Shimadzu UV-2450 spectrophotometer for RhB and a VARIAN ProStar 210 HPLC (C18 reverse column) for NBA. At the end, the reation residues were treated with a headspace solid-phase microextraction (SPME) at 80 °C and immediately analyzed by GC-MS (Agilent, 6890GC-5973MS, HP-5 MS column) to determine the degraded components. Total organic carbon (TOC) change was detected by a Jena Muti2100 TOC analyzer.

The photodegradation of RhB (10 µM) at pH 2 solution in the presence of aqueous $FePz(dtnCl_2)_4$ and H_2O_2 with visible light illumination was shown in Figure 1, in which the maximum absorption peak of RhB in 554 nm rapidly decreased without any wavelength shift and the absorption band at wavelengths less than 400 nm gradually increased. This result indicated that the aromatic chromophore of RhB has been firstly cleaved to form smaller fragments, reaching 99% conversion of RhB within 80 min. The smaller fragments were further analyzed by GCMS, and up to 5 compounds were detected as possible degradation intermediates (Table 1). All of them were unequivocally identified using the NIST02.L library database with fit values higher than 92%, including: formic acid ($t_R =$ 2.75 min), acetic acid ($t_R = 3.27$ min), benzaldehyde ($t_R =$ 9.62 min), benzoic acid ($t_R = 13.81$ min), and phthalic acid ($t_R = 17.25$ min). All the identified compounds were organic acids, which was accorded with the trait of organic compounds in oxidative degradation. Meanwhile, TOC content of solution reduced from 6.75 to 2.53 mg/L, achieving 62.5% CO_2 formation within 80 min. Such high TOC removal indicated that both degradation and mineralization of RhB continuity occurred in $FePz(dtnCl_2)_4/H_2O_2$/visible light system, while high degradation rate and TOC removal of RhB were exciting in comparison with that of some biomimetic photocatalysis systems under similar condition.[7,11]

Control experiments of RhB degradation in the presence of H_2O_2 are illustrated in Figure 2. This compound was only slightly decomposed in the presence of H_2O_2 under visible light

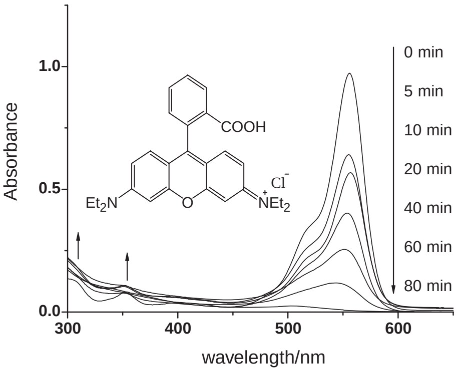

Figure 1. UV–vis spectra changes of RhB (10 µM, pH 2, 50 mL) in the presence of $FePz(dtnCl_2)_4$ (7.9 µM)/H_2O_2 (0.36 mM) under visible light irradiation ($\lambda > 420$ nm).

Table 1. Retention times and identified molecular structure of products formed in the photoreaction of RhB

Peak	Products	Retention time/min	Peak area /%
A	Formic acid	2.75	6.16
B	Acetic acid	3.27	4.21
C	Benzaldehyde	9.62	4.72
D	Benzoic acid	13.81	18.45
E	Phthalic acid	17.25	66.45

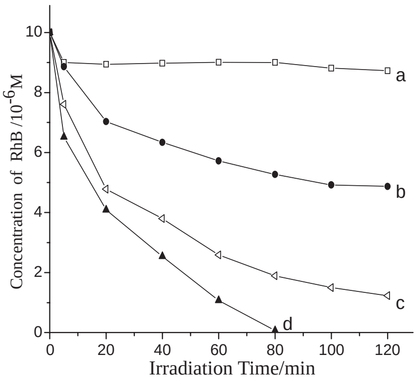

Figure 2. Kinetic curves of RhB degradation in the presence of H_2O_2 at different conditions: a) under visible light; b) with FePz(dtnCl$_2$)$_4$ in the dark; c) with FePz(dtnCl$_2$)$_4$ and 2-propanol (0.5 mM) under visible light; d) with FePz(dtnCl$_2$)$_4$ under visible light. H_2O_2 (0.36 mM), RhB (10 µM), FePz(dtnCl$_2$)$_4$ (7.9 µM), pH 2.

(curve a). In contrast, approximately 40% of RhB was degraded when FePz(dtnCl$_2$)$_4$ and H_2O_2 were present in the dark for 80 min (curve b), while irradiation with visible light evidently accelerated photodegradation rate of RhB (curve d). The catalytic phenomenon as above was similar to FePcS/H_2O_2 system. However, when we plunged 2-propanol as scavenger of HO• radicals into the photoreaction system, it did not cause the main changes (curve c). The quenching result indicated that RhB oxidation was not predominately mediated by HO• radicals generated from a possible mental-assisted homolysis of the weak peroxidic bond of H_2O_2, which is very different from the photomechanism of FePcS/H_2O_2 or Fenton system.[2] Based on the mechanism of biomimetic catalysis,[11,12] we proposed iron-centered oxidizing species (PzFe^{III}OOH or PzFe^{IV}=O) as the main active intermediates involved in the FePz(dtnCl$_2$)$_4$/H_2O_2/visible light system.

NBA is a very refractory organic pollutant and does not absorb light at wavelengths longer than 320 nm. Figure 3 shows the photocatalytic degradation of NBA (0.1 mM) proceeded efficiently, in which the peak intensity of NBA reduced gradually and about 89% of NBA was decomposed after 590 min of irradiation in the aqueous FePz(dtnCl$_2$)$_4$/H_2O_2 solutions at pH 3. Meanwhile, from this HPLC spectra, we found the peak intensity of FePz(dtnCl$_2$)$_4$ did not decrease during the whole of photoreaction, which indicated it is an stable photocatalyst. The degraded residues of NBA were also identified as organic acids by GCMS, including: formic acid ($t_R = 3.68$ min), acetic acid ($t_R = 4.15$ min), benzoic acid ($t_R = 13.63$ min). These results demonstrate that the photoexcitation of substrates does not play a major role and that hydrogen peroxide activated by excitated FePz(dtnCl$_2$)$_4$ initiates the degradation process.

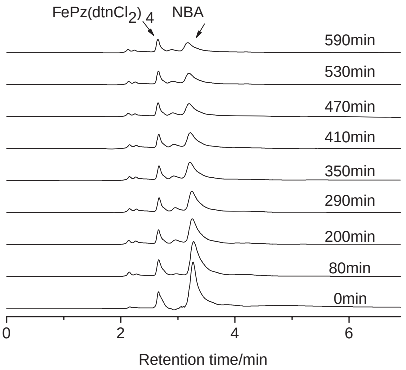

Figure 3. HPLC spectra of NBA (0.1 mM, pH 2) in the presence of FePz(dtnCl$_2$)$_4$ (7.9 µM)/H_2O_2 (0.36 mM) under visible light irradiation ($\lambda > 420$ nm).

The pH effect on RhB (10 µM) photodegradation in FePz(dtnCl$_2$)$_4$/H_2O_2/visible light system was investigated, e.g., 81% conversion at pH 7 and 55% conversion at pH 11 within 80 min, while the photocatalytic degradation of NBA (0.1 mM) at pH 7 can also achieve 60% conversion within 590 min. Additionally, it is noted that the local intensity of sun light was ca. 90000 lux, which was obviously higher than that of our experimental light (ca. 29000 lux). So this work provided a simple and efficient photocatalyst of FePz(dtnCl$_2$)$_4$ for oxidative degradation of organic pollutants by activated hydrogen peroxide in natural conditions.

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