A Novel Approach for the Oxidative Degradation of Organic Pollutants in Aqueous Solutions Mediated by Iron Tetrasulfophthalocyanine under Visible Light Radiation

Xia Tao, Wanhong Ma, Tianyong Zhang, and Jincai Zhao*[a]

Abstract: An efficient approach has been developed to decompose toxic organic pollutants. The photodegradation of Rhodamine B (RhB), salicylic acid, and Orange II was examined in the presence of iron tetrasulfophthalocyanine ([Fe(PcS)]) and H_2O_2 under visible irradiation. It was found that under visible light irradiation, organic poll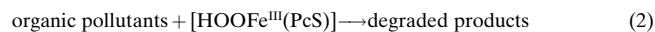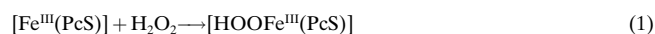utants in the [Fe(PcS)]/H_2O_2 system can be rapidly degraded, but the concentration of [Fe(PcS)] remains nearly unchanged, and this indicates that [Fe(PcS)] has a good catalytic character. EPR results and other experimental results suggest that the light-activated reaction process involves the formation and reaction of HO$^\bullet$ radicals. On the basis of the experimental results, a possible reaction mechanism for the degradation of organic pollutants under visible light illumination in the aqueous [Fe(PcS)]/H_2O_2 solutions is proposed.

Keywords: iron · photodegradation · photooxidation · phthalocyanines · pollutants

Introduction

Recently a renewed interest has been shown in the oxidative degradation of organic pollutants catalyzed by iron(III) tetrasulfophthalocyanine ([Fe(PcS)]), a biomimetic complex, in a reaction in the dark.[1] The reaction process involves a nucleophilic iron(III) peroxo complex, [HOOFe^{III}(PcS)], as an active species responsible for the degradation and mineralization of organic pollutants (such as trichlorophenol) (see Equations (1) and (2)).

$$[Fe^{III}(PcS)] + H_2O_2 \longrightarrow [HOOFe^{III}(PcS)] \tag{1}$$

$$\text{organic pollutants} + [HOOFe^{III}(PcS)] \longrightarrow \text{degraded products} \tag{2}$$

Since [Fe(PcS)] is a readily available biomimetic compound, which can be supported on ion-exchange resins rather than entering the environment to cause additional pollution, [Fe(PcS)] is an attractive alternative in the treatment of organic pollutants compared with the ferrous or ferric salts employed in the (photo-)Fenton system.[2] However, although the [Fe(PcS)]/H_2O_2 system can efficiently degrade organic pollutants, the mixed solvent of acetonitrile/H_2O must be employed in this catalytic system. If water is used as the sole solvent, the conversion rate of pollutants in this system will be greatly reduced, which places some limitations on the treatment of organic pollutants in an aqueous system.[3] Therefore, more studies are needed to search for novel methods for the treatment of persistent organic pollutants in aqueous solutions by utilizing the biomimetic system.

We recently found that under visible light irradiation ($\lambda >$ 470 nm) iron(III) tetrasulfophthalocyanine enabled organic pollutants to be degraded effectively in an aqueous system by H_2O_2 oxidation. Preliminary results reported in a recent communication[4] show that in the presence of [Fe(PcS)] and H_2O_2 visible light irradiation markedly accelerated the degradation of organic pollutants compared with the reaction in the dark, and that the photoassisted degradation process by visible radiation involves the formation and reaction of HO$^\bullet$ radicals with a high oxidative activity, which is significantly different from that in the reaction in the dark involving an iron(III) peroxo complex as mentioned above [Eqs. (1) and (2)].

In recent years, the textile and photographic industries have produced dye pollutants that are emerging as a major source of environmental contamination.[5] In China, above 1.6×10^9 m^3 year^{-1} dye-polluted wastewater drains into environmental water systems without treatment. Our group and others have reported that nonbiodegradable dye pollutants can be photodecomposed under visible irradiation in aqueous TiO_2 suspensions[6] and/or in the visible light-assisted (photo-)Fenton reaction.[7] Notwithstanding, developing new types of catalytic systems to degrade dye pollutants under visible light irradiation remains an important issue.

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In this paper, the photooxidation of two kinds of non-biodegradable dyes with different structures, Rhodamine B (RhB) and Orange II, as the target pollutants was carried out under visible light irradiation in the aqueous [Fe(PcS)]/H_2O_2 solution. For comparison, the photodegradation of a small molecular compound, salicylic acid, was also examined in this system.

During the photoreaction, the formation of hydroxyl radicals was detected by EPR spectroscopy as well as by the photodegradation rate variations of RhB or Orange II upon addition of ethanol to the reaction system. The degradation rate of RhB and the depletion of H_2O_2 as a function of irradiation time were determined in the presence and absence of fluoride ions to elucidate the effect of ligands on the photodegradation. The photodegradation of RhB and Orange II were also carried out under irradiation by monochromatic light to reveal some details of the photoreaction pathway. A possible photochemical reaction mechanism of the pollutant degradation, particularly for the primary reaction mechanism, is proposed on the basis of experimental results.

This study may provide a novel approach for the oxidative degradation of organic pollutants in aqueous solutions with the biomimetic compound [Fe(PcS)] under visible light irradiation.

Results and Discussion

Degradation of RhB: The temporal absorption spectra changes taking place in the presence of [Fe(PcS)] and H_2O_2 under visible light illumination are displayed in Figure 1. The
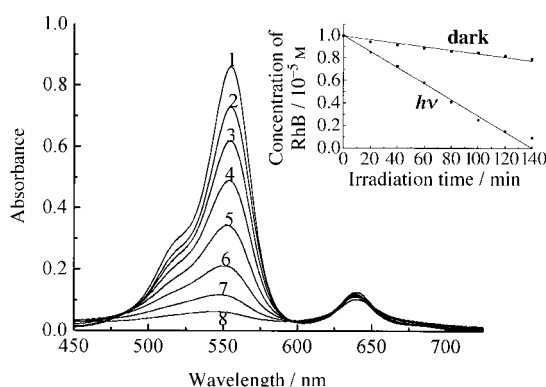

Figure 1. UV/Vis spectral changes of RhB as a function of irradiation time in aqueous [Fe(PcS)]/H_2O_2 solutions under visible light irradiation. The initial concentrations of the reaction system: RhB (1×10^{-5} M), [Fe(PcS)] (1.7×10^{-5} M), and H_2O_2 (1×10^{-3} M). pH 3. Spectra 1, 2, 3, 4, 5, 6, 7, and 8 denote irradiation for 0, 20, 40, 60, 80, 100, 120, and 140 min, respectively. Inset shows concentration changes of RhB both in the dark and under visible irradiation.

maximum absorption wavelengths corresponding to RhB and [Fe(PcS)] are at approximately 555 and 639 nm, respectively. RhB as well as [Fe(PcS)] can be simultaneously excited by visible light irradiation ($\lambda > 470$ nm). As can be seen from Figure 1, under irradiation, the characteristic absorption band

of RhB at approximately 555 nm decreased in size rapidly and disappeared after irradiation of 140 min, whereas the 639 nm band was almost unchanged with increasing irradiation time; concomitantly, the color of the reaction solution changed from the initial pink-red to light blue (the color of [Fe(PcS)]). This indicates that the chromophoric structure of the RhB is destroyed. The pH value of the solution decreased slightly (from the initial pH 3.0 to 2.9) after the photoreaction. During the photodegradation, no significant changes of the [Fe(PcS)] UV/Vis spectra were observed, and no free Fe^{2+} or Fe^{3+} ions were detected; this indicated that [Fe(PcS)] can be regarded as an efficient photocatalyst to degrade the persistent dye pollutants. Furthermore, it was found that after the degradation of the dye RhB, the bleaching of [Fe(PcS)] was rather slow ($\Delta C/\Delta t = 1.8 \times 10^{-8}$ mol L^{-1} min^{-1}); this indicated that during the photodegradation [Fe(PcS)] was relatively stable. As reported in the recent communication,[4] an apparent reduction of TOC (total organic carbon) was obtained in the aqueous RhB/[Fe(PcS)]/H_2O_2 system under visible light irradiation (ca. 30% TOC removal of RhB after irradiation of 8 h).

The inset in Figure 1 shows the temporal concentration changes of RhB under visible light illumination and in the dark. Under both sets of conditions, zero-order kinetics, at least for the first 100 min of reaction, were obtained ($k_{hv} = 7.5 \times 10^{-3}$ mol L^{-1} min^{-1}, $k_{dark} = 1.1 \times 10^{-3}$ mol L^{-1} min^{-1}). Evidently, visible light irradiation accelerates markedly the degradation of RhB in the presence of [Fe(PcS)] and H_2O_2 compared with the reaction in the dark. Control experiments showed that under visible irradiation RhB did not degrade in the presence of [Fe(PcS)], and degraded to a small extent in the presence of H_2O_2, under otherwise identical experimental conditions.

Figure 2 shows the concentration changes of H_2O_2 during the whole degradation process under visible irradiation. Within the initial 100 min of photoreaction, the rapid degradation of RhB occurred concomitantly with the decomposition of H_2O_2. After the initial RhB had degraded to a large extent, a definite amount of RhB (ca. the same concentration as the initial solution) was added again into
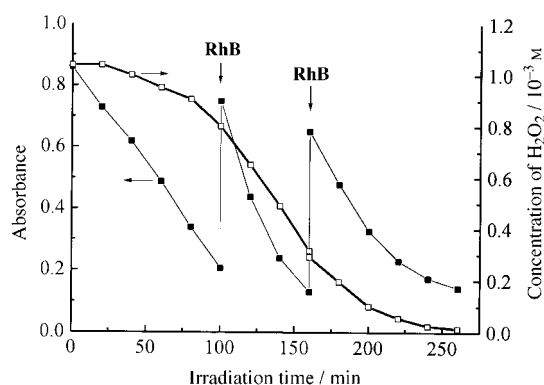

Figure 2. Variations in absorption spectra of RhB (initial concentration 1×10^{-5} M) and concentration changes of H_2O_2 (initial concentration 1.0×10^{-3} M) with irradiation time in the presence of [Fe(PcS)] (1.4×10^{-5} M). At 100 min and 160 min each, RhB (2.5×10^{-3} M, 100 μL) was added to the reaction system (total volume: 50 mL). pH 3.

the system undergoing degradation. It was found that the second amount of RhB added also degraded at a fast rate concomitantly with further decomposition of the residual H_2O_2. Similarly, upon the third addition of RhB to the reaction system, RhB was still degraded, although the degradation rate of RhB decreased owing to the decrease in the concentration of H_2O_2 in the system. The observed H_2O_2 depletion rate seems to be related to the degradation rate of RhB, although a direct quantitative relationship between them was not obtained owing to the complicated reaction mechanisms (see below for discussion of the mechanisms). Of importance is that during the whole process above no apparent degradation of [Fe(PcS)] was observed. Control experiments on the H_2O_2 determination were also carried out under otherwise identical conditions but in the dark. It was found that in the dark the decomposition of H_2O_2 was negligible, which is consistent with the result of the very slow degradation of RhB in the dark (see inset in Figure 1), but this is completely different from that in the photoreaction.

Formation of radicals: To gain insight into the nature of short-lived radicals formed during the photodegradation under visible irradiation, the EPR technique was employed to provide useful information on the reaction mechanism. A visible light source (500 W halogen lamp, $\lambda > 470$ nm) was employed as the irradiation light for detecting EPR signals of the RhB/[Fe(PcS)]/H_2O_2 system. The characteristic four peaks of DMPO−˙OH (DMPO = 5,5-dimethyl-1-pyrroline-N-oxide) adducts with an intensity of 1:2:2:1 are consistent with similar spectra reported by others for HO˙ adducts,[8] and this indicates that HO˙ radicals are generated and participate in the photodegradation of RhB. Figure 3 shows that the

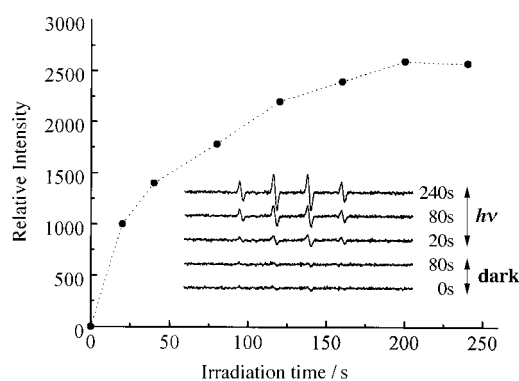Figure 3. Relevant intensity of DMPO−˙OH adducts in the RhB $(1 \times 10^{-4}\text{M})$/[Fe(PcS)] $(1 \times 10^{-4}\text{M})$/$H_2O_2$ $(2.5 \times 10^{-2}\text{M})$ system measured as a function of visible illumination time. DMPO, 0.15 M; pH 3. The inset shows EPR signals of the DMPO−˙OH adducts both in the dark and under visible illumination.

intensity of the four peaks of DMPO−˙OH was significantly enhanced with increasing irradiation time from 0 to 240 s. The inset in Figure 3 shows the signal changes of DMPO−˙OH in the dark and in the photoreaction, respectively. The EPR results indicated that in the dark (even if the reaction in the dark proceeds for 10 min) no signals with a significant intensity were observed, which is in good agreement with

the results reported by Meunier et al.[9] that the reaction in the dark does not involve the formation and reaction of HO˙ radicals, whereas in the photoreaction, visible light irradiation can greatly enhance the generation of HO˙ radicals and hence accelerate the degradation of RhB.

In order to further verify whether HO˙ radicals are involved in the course of photocatalytic degradation of RhB or Orange II, we carried out the experiment in the presence of ethanol, an effective HO˙ radical scavenger, to inhibit the degradation reaction mediated by hydroxyl radicals. The result showed that addition of 50 or 100 equivalents of ethanol with respect to the RhB $(1 \times 10^{-5}\text{M})$ markedly retarded the oxidative degradation of RhB $(k'_{h\nu} = 6.0 \times 10^{-7} \text{ mol L}^{-1}\text{min}^{-1})$ in the solutions containing [Fe(PcS)] $(1.4 \times 10^{-5}\text{M})$ and H_2O_2 $(1 \times 10^{-3}\text{M})$. A similar result was also obtained upon addition of ethanol to the Orange II/[Fe(PcS)]/H_2O_2 system. All these results strongly suggest that HO˙ radicals are indeed involved in the visible light assisted photodegradation reaction of RhB or Orange II, which is also consistent with the EPR spectra under visible light irradiation (see Figure 3).

Degradation of small organic molecule: In order to further examine the role of [Fe(PcS)] in the photoreaction, the degradation of salicylic acid (SA, a small organic molecule, no absorption in the visible region) was investigated by a HPLC analyzer. As the degradation proceeded, the peak intensity of SA decreased, and approximately 70 % of SA was degraded after 520 min of irradiation in the aqueous solutions containing [Fe(PcS)] and H_2O_2. From the HPLC spectra, we cannot determine the change of the amount of H_2O_2 because H_2O_2 and the solvent have the same retention time. Therefore, the concentration variations of H_2O_2 during the photodegradation of SA were also determined by the DPD (N,N-dimethyl-p-phenylenediamine) method.[10] The plot of concentration variations of SA, [Fe(PcS)], and H_2O_2 versus irradiation time is shown in Figure 4. It was found that the concentration of
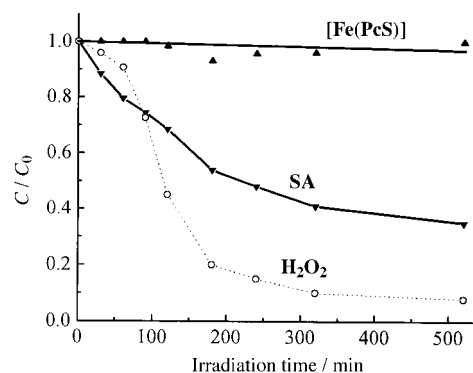

Figure 4. The plot of concentrations of SA, [Fe(PcS)], and H_2O_2 versus irradiation time during the photodegradation of salicylic acid (SA, $1 \times 10^{-4}\text{M}$) in the presence of [Fe(PcS)] $(1.7 \times 10^{-5}\text{M})$ and H_2O_2 $(1 \times 10^{-3}\text{M})$ at pH 3.

H_2O_2 decreased concomitantly with the degradation of SA. Of particular relevance are the signals of [Fe(PcS)], the intensity of which remains nearly unchanged during the course of the photooxidation, and this indicates that [Fe(PcS)] as an

efficient photocatalyst can also degrade the small organic molecules in the presence of H_2O_2 under visible illumination. Control experiments show that, under otherwise identical conditions, no degradation of SA was observed in the presence of [Fe(PcS)] alone or H_2O_2 alone. Also, SA could not be degraded in the dark in the presence of both [Fe(PcS)] and H_2O_2.

The EPR experimental results also showed that the hydroxyl radicals were indeed generated by irradiating the reaction system of SA/[Fe(PcS)]/H_2O_2 with the visible light source (500 W halogen lamp, $\lambda > 470$ nm) as described above. Furthermore, the signal intensity of the DMPO$-$·OH adducts was enhanced gradually with increasing illumination time, which is paralleled with the ESR results for the RhB/[Fe(PcS)]/H_2O_2 system (see Figure 3). Control experiments show that in the dark no significant signals of DMPO$-$·OH adducts were observed at the same initial concentrations of SA/[Fe(PcS)]/H_2O_2 as employed in the photoreaction. These results suggest that in the SA/[Fe(PcS)]/H_2O_2 system, visible light irradiation can also generate HO· radicals and hence accelerate greatly the degradation of SA.

Effect of axial ligands: It is well known that fluoride ions (F^-) are good axial ligands for [Fe^{III}(PcS)]. Figure 5 depicts the concentration changes of RhB when KF at different concentrations was added to the RhB/[Fe(PcS)]/H_2O_2 system. It can
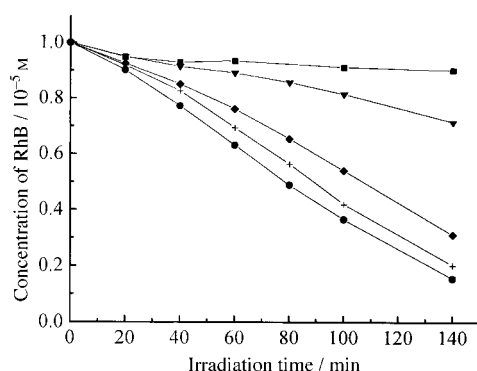
Figure 5. Effect of adding fluoride ions (F^-) at different concentrations to the reaction system (RhB 1×10^{-5} M, [Fe(PcS)] 1.4×10^{-5} M, and H_2O_2 1×10^{-3} M) on the degradation rate of RhB. The initial concentrations of KF: 4.5×10^{-3} M (■), 4.5×10^{-4} M (▼), 4.5×10^{-5} M (♦), 4.5×10^{-6} M (+), and no KF (●). pH 3.

be seen that the degradation of RhB was gradually inhibited with increasing concentration of fluoride. Addition of 450 equivalents of KF versus RhB (1×10^{-5} M) significantly inhibited the degradation rate of RhB; meanwhile, it was also found that during the irradiation of the RhB/[Fe(PcS)]/H_2O_2/KF system, no concentration variations of H_2O_2 were observed. These results indicate that [Fe(PcS)] will lose the photocatalytic activity if the axial positions of the central iron ion are occupied by fluoride ions instead of H_2O_2.

Effect of pH: Figure 6 presents the effect of pH on the oxidative degradation rate of Rhodamine B and Orange II in the [Fe(PcS)]/H_2O_2 system under visible light irradiation. Evidently, in this catalytic system, the degradation reaction,
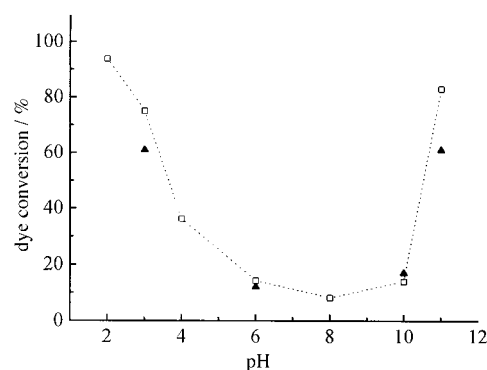
Figure 6. Effect of pH on the photodegradation of RhB (□) and Orange II (▲) in the reaction system containing RhB (1×10^{-5} M)/Orange II (2.5×10^{-5} M), [Fe(PcS)] (1.4×10^{-5} M), and H_2O_2 (1×10^{-3} M) within 100 min of visible light irradiation.

distinct from the (photo-)Fenton reaction, in which iron ions will cause the precipitation of $Fe_2O_3 \cdot nH_2O$ at pH greater than 3,[11] can proceed in a wide range of pH from 2 to 11. For an initial solution containing RhB (1×10^{-5} M), [Fe(PcS)] (1.4×10^{-5} M), and H_2O_2 (1×10^{-3} M), 95% conversion of RhB at pH 2, 75% at pH 3, 38% at pH 4, and 15% at pH 6 were observed within 100 min of irradiation. When the degradation reaction was conducted in alkaline media, the conversion rate of RhB at the same irradiation time was 10% at pH 8, 15% at pH 10, and 83% at pH 11. For the Orange II/[Fe(PcS)]/H_2O_2 system, almost the same photodegradation tendency of Orange II as RhB was also obtained in a wide range of pH. Evidently, the photodegradation of both RhB and Orange II in the [Fe(PcS)]/H_2O_2 system can still proceed at higher rates even under alkaline conditions, which is superior to the Fenton reaction.

Photodegradation of RhB and Orange II with monochromatic light excitation: Taking into consideration that RhB, Orange II, and [Fe(PcS)] all can absorb visible light, we employed a kind of monochromatic light (with a Japan Optical Co. Interference filter $\lambda = 640 \pm 10$ nm) near to the maximum absorption wavelength of [Fe(PcS)] only to excite [Fe(PcS)]. In the monochromatic light range, RhB and Orange II have a low light absorption. Under monochromatic light irradiation in the RhB/[Fe(PcS)]/H_2O_2 system, the photodegradation rate of RhB as well as the photoefficiency (herein symbolized as ξ) of RhB were examined, respectively. The photon flow of the 500 W halogen lamp at 640 ± 10 nm determined by Reineckate actinometry[12] (0.025 M, 50 mL) was 1.0×10^{-8} einsteins^{-1}. The photodegradation rate of RhB with the monochromatic light excitation under the same conditions as those employed for the photon flow measurements is shown in Figure 7. Combined with the photon flow data measured, the photoefficiency obtained by observation of the changes in the absorption spectra with 640 ± 10 nm monochromatic light irradiation was $\zeta = 0.004$ for the RhB degradation within 40 min of photoreaction in the [Fe(PcS)]/H_2O_2 system. It was also found that upon excitation of [Fe(PcS)] by monochromatic light irradiation, Orange II could also be degraded at a faster rate compared with the reaction in the dark (see Figure 7).
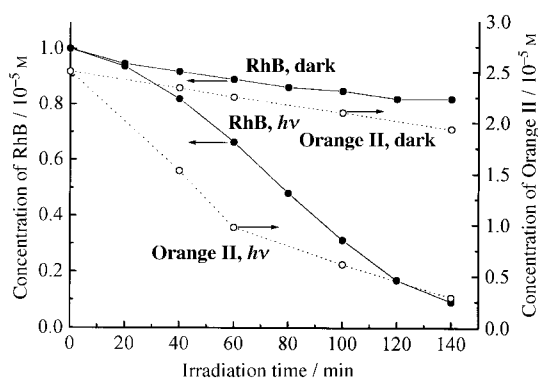
Figure 7. Degradation of RhB $(1 \times 10^{-5} M)$/Orange II $(2.5 \times 10^{-5} M)$ as a function of irradiation time under monochromatic light irradiation $(\lambda_{max} = 640 \pm 10\ nm)$ in the aqueous $[Fe(PcS)]$ $(1.4 \times 10^{-5} M)/H_2O_2$ $(1 \times 10^{-3} M)$ solutions.

Reaction mechanism discussion: Based on all the above results, a reasonable mechanism for the degradation of organic pollutants, especially for the primary reaction, in the aqueous $[Fe(PcS)]/H_2O_2$ system under visible light irradiation is outlined in Scheme 1.
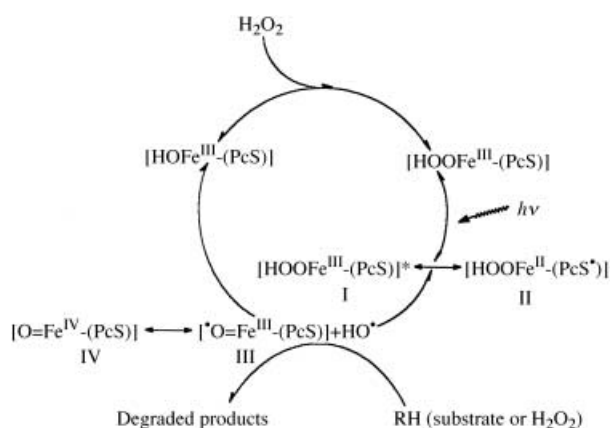
Scheme 1. Proposed photodegradation mechanism of organic pollutants in the aqueous $[Fe(PcS)]/H_2O_2$ system under visible light irradiation.

In an aqueous solution, $[Fe(PcS)]$ is more likely to exist in the form of aquo complex $([HOFe^{III}(PcS)])$.[3] Early work has demonstrated that the primary chemistry of H_2O_2 involves nucleophilic addition to the electrophilic metal center of the transition metal complex at the axial ligand.[13–16] Thus, in the present system H_2O_2 is added to the iron center of $[Fe(PcS)]$ to give $[HOOFe^{III}(PcS)]$. Upon visible light irradiation, $[HOOFe^{III}(PcS)]$ can be excited to form a transition state, which can also undergo metal–ligand charge transfer (MLCT) (see **I** and **II** in Scheme 1).[17] Then the bond $[HO–OFe^{III}(PcS)]$ of the transition state can be rapidly cleaved to generate the active species, namely, HO• radicals and the high-valent iron-oxo species **III** or **IV** (see Scheme 1). Because the oxidative activity of HO• radicals is much higher than that of species **III** or **IV**,[18–20] the photodegradative reaction with HO• radicals is predominant in the organics/ $[Fe(PcS)]/H_2O_2$ system under visible irradiation. These HO• radicals generated by the photoreaction of $[Fe(PcS)]$ and H_2O_2 will react immediately with organic pollutants and

degrade them effectively. Without organic pollutants in the $[Fe(PcS)]/H_2O_2$ system, the HO• radicals could rapidly recombine with the species **III** or **IV** or react with H_2O_2 or themselves.

In addition, we carried out the experiments on the photo-degradation of organic pollutants under nitrogen bubbling conditions. Almost the same degradation rates of pollutants were obtained as those under aerated conditions, and this indicates that $[Fe(PcS)]$ is not a good catalyst for reactions with oxygen but for reactions of H_2O_2 as reported in the literature.[21] Therefore, in terms of the current experimental results, we are unable to confirm that oxygen is bound to participate in the photoreaction, although the incorporation or the partial incorporation of oxygen in the Fenton reaction has been reported.[22]

Conclusion

The refractory organic pollutants, Rhodamine B and Orange II, can be efficiently photodegraded in an aqueous $[Fe(PcS)]/H_2O_2$ system under visible illumination. The process involves the photogeneration and reaction of HO• radicals. The photocatalytic system of $[Fe(PcS)]/H_2O_2$ under visible light irradiation provides another approach for the oxidative removal of nonbiodegradable organic pollutants in an aqueous system.

Experimental Section

Materials: RhB was of analytical reagent grade and used without further purification. Orange II was obtained from Fluka Co. $[Fe(PcS)]$ was prepared according to a method in the literature.[23] Hydrogen peroxide (30 wt %) was obtained from Beijing Chemicals Co. The reagent 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) used as the spin-trapping agent was purchased from Sigma Chemical Co. Horseradish peroxidase (POD) was purchased from Huamei Biologic Engineering Co. and N,N-dimethyl-p-phenylenediamine (DPD) reagent from Merck (p.a.). The pH of the solutions was adjusted by diluted aqueous solution of NaOH or HClO$_4$. Deionized and double distilled water was used throughout the study. For reference, the structures of RhB, Orange II, and $[Fe(PcS)]$ are shown below.

Rhodamine B (RhB)

Tetrasulfophthalocyanine Iron (III) $[Fe^{III}(PcS)]$

Orange II
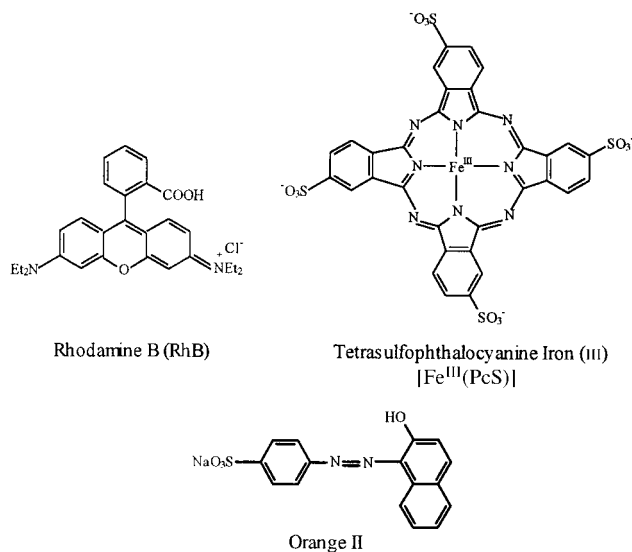
Photoreactor and light source: A 500 W halogen lamp (Institute of Electric Light Source, Beijing) was positioned inside a cylindrical Pyrex vessel surrounded by a jacket with circulating water (Pyrex) to cool the lamp. The jacket was wrapped in a piece of black paper with a small window. A cutoff filter was placed on the small window (diameter 3 cm) to remove completely wavelengths less than 470 nm and to ensure irradiation only by visible light. The center distance between the reaction vessel and the light source was 10 cm.

Procedures and analyses: Unless otherwise noted, all the irradiation experiments were carried out in a Pyrex vessel (60 mL) in aerated solution at an initial pH of 3.0 adjusted with $HClO_4$. At given irradiation time intervals, samples (3 mL) were taken out and then analyzed by observation of variations in UV/Vis spectra with a Lambda Bio 20 spectrophotometer (Perkin-Elmer). Electron paramagnetic resonance (EPR) signals of radicals spin-trapped by DMPO were examined with a Brucker EPR 300E spectrometer; the irradiation source was a halogen lamp with a cutoff filter ($\lambda > 470$ nm). The settings for the EPR spectrometer were: center field, 3486.70 G; sweep width, 100.0 G; microwave frequency, 9.82 GHz; power, 5.05 mW. The photodegradation of the small molecule (salicylic acid, SA, no absorption in visible region) was analyzed by High Performance Liquid Chromatography (HPLC) on an Inertsil ODS-3 5 μm column (250×4.6 mm) at room temperature. The HPLC system consisted of a 7725 autoinjector fitted with a 20 μL sample loop, a Dionex P580 pump, and a built-in UVD 340s diode array detector. Signals for SA were detected at 295 nm by using an eluent composed of methanol/water (70:30, v/v) at a flow rate of 1.0 mL min^{-1}. HPLC analysis was immediately done after sampling. Hydrogen peroxide concentration was measured by the DPD method[10] (a photometric method), in which the DPD reagent is oxidized by H_2O_2 based on the peroxidase catalyzed reaction ($\lambda_{max} = 531$ nm, $\varepsilon = 21000$ M^{-1} cm^{-1}). The intensity of the monochromatic light was determined by Reineckate actinometry.

Acknowledgements

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