

A Novel β -CD–Hemin Complex Photocatalyst for Efficient Degradation of Organic Pollutants at Neutral pHs under Visible Irradiation

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A novel photooxidative system for degrading toxic organic pollutants, including organic dyes and small molecular compounds such as Rhodamine B (RhB) and 2,4-dichlorophenol (DCP), is reported. A metal–organic complex (β -cyclodextrin–hemin, CDH), synthesized by combining β -CD with the bioactive small molecule hemin, can efficiently activate hydrogen peroxide to oxidize and mineralize the target compounds in aqueous media at neutral pHs under ambient conditions of temperature and pressure and with visible light irradiation ($\lambda > 450$ nm). The RhB and DCP were mineralized at yields of 72% and 85% at ratios of catalyst to substrate of 1:200 and 1:1000, respectively. Meanwhile, the catalyst exhibited excellent stability. The photoreaction processes were examined by UV/vis spectroscopy, high-performance liquid chromatography, ion chromatography, IR, spin-trapping electron paramagnetic resonance, and total organic carbon measurements. A possible photooxidative mechanism for the degradation of organic pollutants in aqueous CDH/H₂O₂ solutions under visible light illumination is proposed on the basis of the experimental results.

Introduction

Some water-soluble metal complexes can mimic peroxidase and P450 enzymes to catalytically activate oxidants such as H₂O₂, O₂, and KHSO₅ for the degradation of toxic organic pollutants.^{1–4} Meunier et al.^{5,6} reported a novel system in which iron tetrasulfophthalocyanine (FePcS) in solution or supported on a resin was used as a catalyst to degrade chlorophenol in a CH₃CN/H₂O solvent mixture. A 14% mineralization of 2,3,6-trichlorophenol (TCP) was obtained using H₂O₂/KHSO₅ as an oxidant in a mixed CH₃CN/H₂O solvent system. The reaction rate was greatly reduced, however, when water was used as the sole solvent. The requirement of an organic cosolvent component would hinder the application of this treatment method for organic pollutants. Collins and co-workers⁷ described an effective oxidation method in which tetraamido macrocyclic ligand (TAML) iron was used as a catalyst to destroy the priority pollutants pentachlorophenol (PCP) and TCP by H₂O₂ in water. However, the catalyst was relatively unstable and was degraded along with the pollutants. Recently, we have shown that visible light irradiation could accelerate the degradation of salicylic acid, Orange II, and Rhodamine B (RhB) in the presence of FePcS and H₂O₂ without the addition of CH₃CN.⁴ However, FePcS exhibited lower activity (TON = 3 for the RhB system) and poor stability. The activity was particularly poor in solutions at neutral pHs. It is known that FePcS and Fe (Mn) TAML mimic

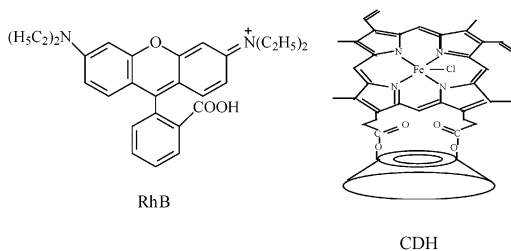
the catalytic sites of peroxidase.⁸ Obviously, more effective enzyme mimics must be developed for possible commercialization of this pollution treatment method.

Cyclodextrins are extremely attractive components of artificial enzymes, and attachment of a simple catalytic group to a cyclodextrin can afford interesting enzyme mimics.⁹ β -Cyclodextrin (β -CD) is an excellent enzyme model because it has a fairly hydrophobic inner cavity of appropriate size and a hydrophilic outer surface.^{10,11} Hemin is a biologically active molecule containing an iron–porphyrin complex, which can be coupled to β -CD through covalent interactions to form β -CD–hemin (CDH). CDH can be used as an analogue for the peroxidase model. So, CDH can make a potentially more powerful catalyst than ordinary metal complexes for the activation of oxidants to oxidize organic pollutants.

In this study, for the first time CDH was used as a photocatalyst. Two toxic and nonbiodegradable organic compounds, RhB and 2,4-dichlorophenol (DCP), were chosen as target pollutants (see Chart 1 for structures). These compounds were degraded with H₂O₂ as the oxidant under ambient conditions at neutral pHs and with visible light irradiation. The results show that RhB and DCP are almost completely degraded at ratios of catalyst to substrate of 1:200 and 1:1000 with mineralization yields of 72% and 85%, respectively. CDH also provides much higher catalytic activity as compared to the corresponding water-soluble metal–organic complex catalysts. A notable advantage of the CDH catalyst is its stability against decomposition by self-catalytic oxidation under the experimental

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CHART 1: Molecular Structures of RhB and CDH



conditions. The photocatalytic activity is retained after 20 repeated experiments. Interestingly, the oxidant H_2O_2 is not consumed if organic pollutants are not present in this treatment system. The high catalytic activity of CDH over a wide pH range and the efficient use of H_2O_2 make this system ideal for the treatment of toxic nonbiodegradable organic pollutants in water. The photoreaction mechanism and the relationship between the structure of the catalyst and activity are also discussed in this paper.

Experimental Section

Materials. RhB was of analytical reagent grade quality and was used without further purification. CDH was synthesized by a procedure as follows:¹² Hemin and β -CD with dicyclohexylcarbodiimide as a condensation reagent in the presence of pyridine and zeolite (4 Å) were reacted in dry dimethylformamide at 0 °C for 8 days. After standing at room temperature for 24 h and after evaporation under reduced pressure, the product was recrystallized from ethanol/acetone/water. DMPO (5,5-dimethyl-1-pyrroline *N*-oxide) used as the spin-trapping reagent was obtained from Sigma Chemical Co. Horseradish peroxidase (POD) was purchased from Huamei Biologic Engineering Co. and *N,N*-dimethyl-*p*-phenylenediamine (DPD) reagent from Merck. NaOH and HClO_4 solutions were used to adjust the pH of the solution. All aqueous solutions were made up in deionized and doubly distilled water. The molecular structures of CDH and RhB are shown in Chart 1.

Photoreactor and Light Source. A 500 W halogen lamp (Institute of Electric Light Sources, Beijing) used as a visible light source was positioned inside a cylindrical Pyrex vessel surrounded by a jacket with circulating water (Pyrex) to cool the lamp. A cutoff filter (diameter 3 cm) was used to completely remove wavelengths less than 450 nm and to ensure irradiation only by visible light ($\lambda > 450$). The distance between the reaction vessel and the light source was 10 cm.

Procedures and Analyses. Unless otherwise noted, all the experiments were carried out in a Pyrex vessel (60 mL) in aerated solutions without adjusting the pH. At given irradiation time intervals, 3 mL samples were collected and analyzed immediately by observation of variations in the UV/vis spectra using a Hitachi 3010 spectrophotometer. The amounts of chloride ions were analyzed by a DX-120 ion chromatograph (DIONEX) using an eluent composed of Na_2CO_3 (1.8 mM) and NaHCO_3 (1.7 mM). The photodegradation of DCP (no absorption in the visible region) was analyzed by high-performance liquid chromatography (HPLC) on an inersil ODS-3 5 μm column (250 \times 4.6 mm) at room temperature. The HPLC system consisted of a Dionex P580 pump and a built-in UVD 340S diode array detector. DCP were detected at 283 nm by using an eluent composed of methanol/water (50:50 v/v) at a flow rate of 1.0 mL/min. An Apollo 9000 TOC instrument was used for measurements of total organic carbon (TOC) values of the degraded solutions.

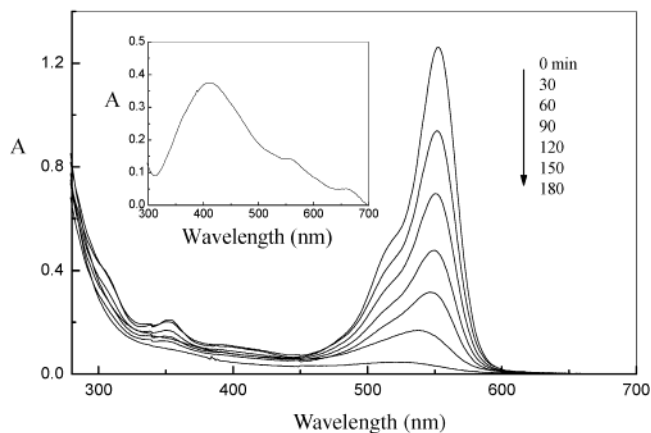


Figure 1. Temporal absorption spectral changes for the degradation of RhB under visible light irradiation, pH 4.9, $[\text{RhB}] = 1.25 \times 10^{-5}$ M, $[\text{CDH}] = 6.25 \times 10^{-8}$ M, $[\text{H}_2\text{O}_2] = 1.2 \times 10^{-3}$ M. The inset shows the absorption spectrum of a 1.0×10^{-4} M CDH aqueous solution at pH 4.9.

The concentration of H_2O_2 was measured by the POD method in which the DPD is oxidized by H_2O_2 on the basis of the POD-catalyzed reaction ($\epsilon = 2.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).¹³

Infrared analysis was carried out by means of a TENSOR 27 (Bruker) FTIR spectrophotometer. The samples for the photodegradation of RhB were prepared as follows: The solvent of the reacted solution was evaporated directly (temperature below 323 K) under reduced pressure until water was mostly removed. Finally, the dried samples were further kept in a vessel containing P_2O_5 for more than 24 h. The samples for IR were supported on anhydrous KBr.

A Bruker model EPR 300E spectrometer equipped with a Quanta-Ray Nd:YAG laser (355 and 532 nm) was used for measurement of the electron paramagnetic resonance (EPR) signals of radicals spin-trapped by DMPO. The settings were center field 3486.7 G, sweep width 100.0 G, microwave frequency 9.82 GHz, and power 5.05 mW. To minimize experimental errors, the same quartz capillary tube was used for all EPR measurements.

Results and Discussion

Degradation of RhB. Figure 1 displays the temporal absorption spectral changes in the degradation of RhB in the presence of CDH and H_2O_2 under visible light irradiation. The inset in Figure 1 shows the absorption spectrum of a 1.0×10^{-4} M CDH solution. It is a broad band from 320 to 700 nm with a maximum absorption at 420 nm ($\epsilon = 3.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). It can be seen from Figure 1 that the absorbance of RhB at 553 nm drops rapidly and disappears completely after irradiation for about 180 min. This indicates efficient degradation of the dye molecules.¹⁴

The degradation dynamics of RhB with and without visible light irradiation are shown in Figure 2. RhB was not decomposed in either CDH or H_2O_2 solution (curves a and b) under visible light irradiation. Degradation of RhB was barely observable in a mixture of CDH/ H_2O_2 (curve c) when the reaction was carried out in the dark. On the other hand, very significant degradation of RhB occurred in the CDH/ H_2O_2 mixed system under visible light irradiation (curve d).

The TOC change during the photochemical degradation of RhB was also measured, and the results are shown in Figure 2 (curve e). TOC values dropped by about 36% and 62% after 80 and 220 min of irradiation, respectively. The TOC of the CDH catalyst was only 0.5 mg/L, which is negligible for the

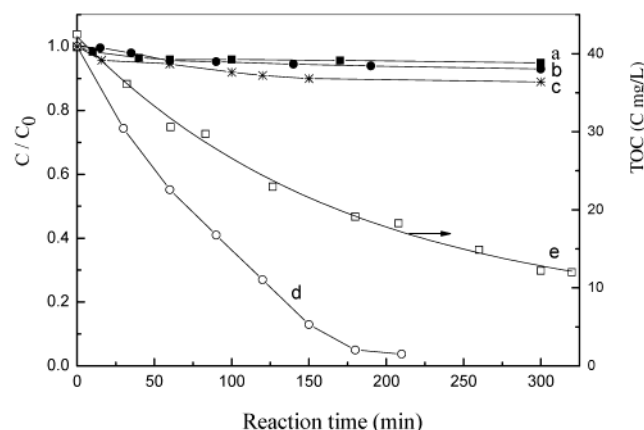


Figure 2. Degradation of RhB under different conditions: (a) RhB/CDH, visible light; (b) RhB/H₂O₂, visible light; (c) RhB/H₂O₂/CDH, in the dark; (d) RhB/H₂O₂/CDH, visible light. Reactions a–d were done at pH 4.9, [RhB] = 1.25×10^{-5} M, [CDH] = 6.25×10^{-8} M, and [H₂O₂] = 1.2×10^{-3} M. (e) TOC change in the degradation of RhB (1.25×10^{-4} M) in the presence of CDH (6.25×10^{-7}) and H₂O₂ (1.2×10^{-2} M) at pH 4.9. The light intensity was 48 mW/cm².

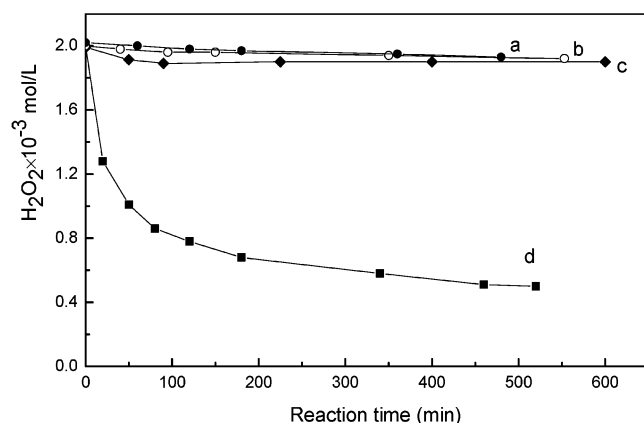


Figure 3. Decomposition of H₂O₂ for the RhB/CDH system under visible light irradiation: (a) H₂O₂/CDH, visible light; (b) RhB/H₂O₂, visible light; (c) RhB/H₂O₂/CDH, in the dark; (d) RhB/H₂O₂/CDH, visible light. Initial conditions: [RhB] = 2.5×10^{-5} M, [CDH] = 1.25×10^{-7} M, pH 4.9.

TOC measurements in our reaction system. The mineralization yield of RhB in the CDH/H₂O₂ system is much greater than that in the FePcS/H₂O₂ system, in which the removal of the TOC was only 30% after 8 h of reaction.⁴

Other types of organic pollutants such as cationic dyes (Malachite Green, Crystal Violet), anionic dyes (Orange II, Sulforhodamine B), and small molecular organic compounds (salicylic acid, *N,N*-dimethylamine) were also examined in an aqueous CDH/H₂O₂ system under visible light irradiation. All these compounds could be degraded rapidly in the present systems. The investigation of RhB and DCP will be described in detail.

Figure 3 shows the decomposition of H₂O₂ in the reaction processes under different conditions. The concentration of H₂O₂ remained virtually unchanged for the CDH/H₂O₂ (curve a) and RhB/H₂O₂ (curve b) systems under visible light irradiation and for the RhB/CDH/H₂O₂ (curve c) system in the dark. However, a rapid decomposition of H₂O₂ occurred for the RhB/CDH/H₂O₂ (curve d) system under visible light irradiation. During the irradiation, the decrease of H₂O₂ became slower and slower accompanied by the degradation of RhB. It indicates that the undesirable decomposition of H₂O₂ can be effectively suppressed, and the oxidant is consumed only during the photo-

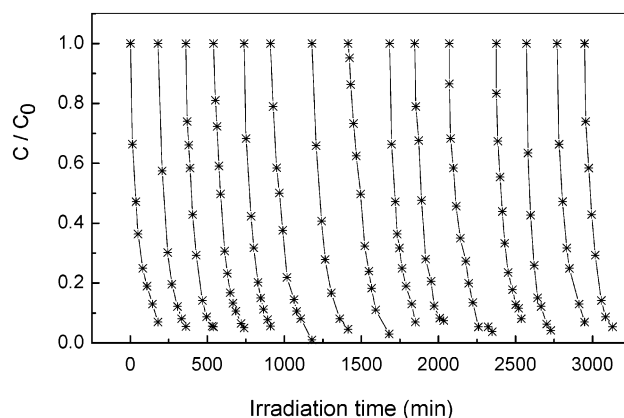


Figure 4. Changes in the concentration of RhB during the multicycle degradation process in the presence of CDH (6.25×10^{-8} M) under visible light irradiation at pH 4.9 (addition of RhB, 1.25×10^{-5} M/run, and H₂O₂, 8.2×10^{-4} M/run).

oxidation of RhB. This is an important finding because other advanced oxidation methods, such as Fenton and photolike Fenton reactions,^{15,16} suffer from rapid H₂O₂ decomposition regardless of the presence of organic substrates. For the photocatalytic reaction, the required ratio of catalyst to substrate is only 0.005:1, indicating that CDH is an effective catalyst for the degradation of pollutants in aqueous media under visible irradiation.

Good stability of the catalyst is very important for the treatment of pollutants. To investigate the stability of CDH catalyst in the photocatalytic reaction, we subjected the CDH/RhB/H₂O₂ catalytic system to several repeated experiments. The results are shown in Figure 4.

Under the experimental conditions, the first cycle finished within the initial 180 min. The next cycle for the degradation of RhB became slightly faster than the previous cycle (after the initial RhB had been degraded, a definite amount of RhB and H₂O₂, which is the same as the initial concentration of RhB and H₂O₂, was added again into the system undergoing degradation). This phenomenon was similar to that where H₂O₂ was not added for the second and third cycles. From Figure 4, it is evident that CDH catalyst can be recycled more than 15 times without any significant loss of activity. Also, no free Fe²⁺ or Fe³⁺ ions were detected using a standard spectrophotometric method.¹⁷ The HPLC peak (measured by a UV detector at 300 nm) of CDH with a retention time of 22.5 min remained unchanged during the RhB degradation process. Evidently, the CDH catalyst is highly stable with respect to self-oxidation by H₂O₂.

Measurement of Radicals. EPR spin-trapping technique is very useful for detecting the formation of short-lived radicals and for understanding the photocatalytic reaction mechanism. All the measured EPR spectra of the CDH/RhB/H₂O₂ system under in situ laser irradiation ($\lambda = 532$ nm) (see Figure 5) exhibited a four-peak spectrum with an intensity ratio of 1:2:2:1, which is the typical and characteristic EPR signal of the DMPO- \cdot OH adducts. It indicates that \cdot OH radicals are generated and participate in the photodegradation of RhB under visible irradiation. The intensity of the four peaks of DMPO- \cdot OH was significantly enhanced with increasing irradiation time. By contrast, the intensity of the EPR signals in the dark showed no change with time. It shows that the reaction for the CDH/RhB/H₂O₂ system in the dark does not lead to the formation of \cdot OH radicals. From the results of Figure 5, we find that visible irradiation can result in efficient generation of \cdot OH radicals and hence accelerates significantly the degradation of RhB. For the

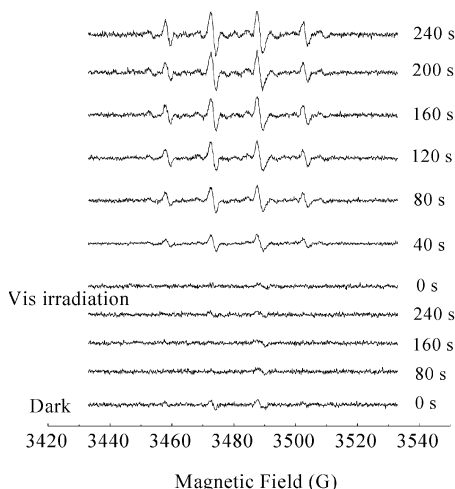


Figure 5. DMPO-trapping EPR spectra of the RhB/H₂O₂/CDH system under 532 nm laser irradiation and in the dark, pH 4.9, [RhB] = 1.0×10^{-4} M, [CDH] = 6.25×10^{-8} M, [H₂O₂] = 8.2×10^{-3} M, [DMPO] = 0.10 M.

CDH/RhB/H₂O₂ system, purging with both O₂ and N₂ does not influence the degradation of RhB (CDH = 6.25×10^{-8} M, RhB = 1.25×10^{-5} M, H₂O₂ = 1.2×10^{-3} M). It can be seen that the CDH indeed mimics peroxidase, which efficiently activates H₂O₂. The active site of metal–organic complexes is at the axial position of planar molecules of the catalyst.¹⁸ It is well-known that several inorganic ions are good axial ligands for Fe–organic complexes. The effect of F[−] ions on the photodegradation of RhB in the CDH/RhB/H₂O₂ system was investigated under visible light irradiation. The results indicate that F[−] scarcely influences the degradation of RhB at various concentrations of F[−] (1.0×10^{-4} to 2.5×10^{-3} M). This case is different from that of simple metal–organic complexes.⁴ β -CD can promote effectively the activation of H₂O₂ by the catalytic center of the CDH molecule and preclude the effect of F[−] at the axial position of the catalyst.¹⁰

EDTA and methanol are known to be effective scavenging agents for hydroxyl radicals. For the RhB or DCP/CDH/H₂O₂ system under visible light irradiation, addition of EDTA (1.5×10^{-4} to 2.5×10^{-3} M) and methanol (2.5×10^{-4} to 2.5×10^{-3} M) greatly inhibited the photocatalytic reaction of the substrates. The results further prove that the photocatalytic reaction involves the generation and participation of hydroxyl radicals.

FTIR Analyses during the Degradation of RhB. The infrared spectra of the intermediates produced at different reaction periods for the degradation of RhB using CDH as the catalyst and H₂O₂ as the oxidant were recorded (Figure 6). Three characteristic bands around 1592, 1341, and 1181 cm^{−1} in the IR spectra of the RhB are due to the stretching vibrations of the molecular frame, the stretching vibration of the C–CH₃ bond, and the stretching vibration of the Ar–N bond, respectively. The peaks at 1470 (1646), 1411, 1078, and 685 cm^{−1} are attributed to the stretching vibration of the phenyl ring (–C=C–), the C=O band stretching vibration of carboxylic acids, the stretching vibration of the C–O–C band, and the stretching vibration of Ar–H bonds. Initially, both RhB and CDH are present (0 min, curve b), and the characteristic peaks closely resemble that of pure RhB. The infrared region from about 1000 to 1200 cm^{−1} corresponding to the ring vibration of the CDH frame becomes much broader. A new peak at 485 cm^{−1} also shows up, which is attributed to the characteristic infrared spectrum of the CDH catalyst.

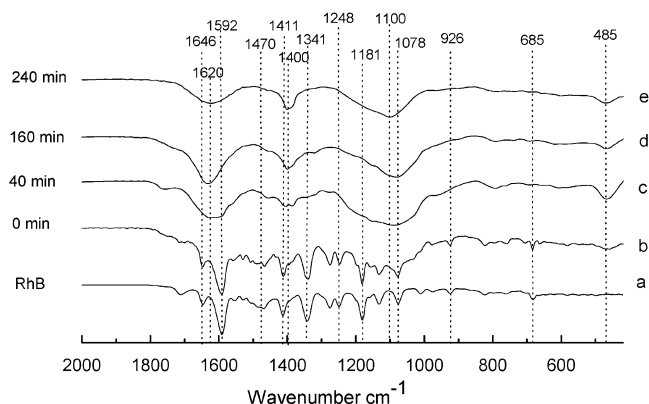


Figure 6. IR spectrum of the intermediates during the degradation of RhB (1.25×10^{-5} M) in the H₂O₂ (1.2×10^{-3} M)/CDH (6.25×10^{-8} M) system under visible light irradiation at pH 4.9: (a) RhB; (b) 0 min reaction time; (c) 40 min reaction time; (d) 160 min reaction time; (e) 240 min reaction time.

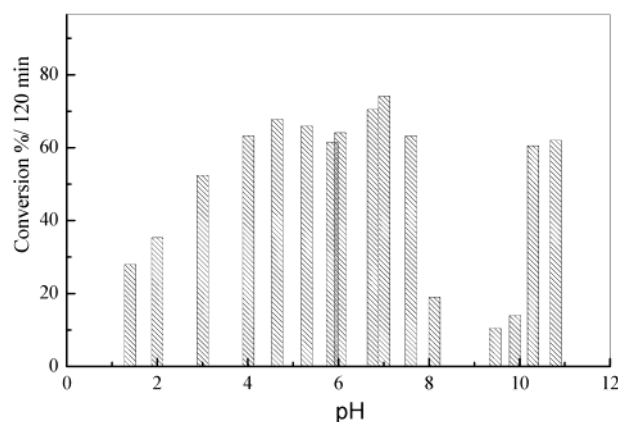


Figure 7. Effect of pH on the degradation of RhB (1.25×10^{-5} M) in the presence of CDH (6.25×10^{-8} M) and H₂O₂ (1.2×10^{-3} M) under visible irradiation.

As the reaction proceeds, all the characteristic peaks of RhB gradually decrease. In particular, the peaks at 1470, 1341, and 685 cm^{−1} eventually disappear. The new peaks at 1100 and 1400 cm^{−1}, which are due to the stretching vibrations of –C–NH₂ and the stretching vibration of the carbonyl group, respectively, emerge and become stronger with time. This indicates that Ar–N(C₂H₅)₂ and –C–O–C– are completely destroyed and primary amines and carboxylic acid products are generated during the photocatalytic degradation of RhB. Moreover, the peaks at 1592 and 685 cm^{−1} and 926 and 975 cm^{−1}, which correspond to the phenyl group, gradually disappeared. Meanwhile, a new intense peak at 1620 cm^{−1} shows up, which is due to the stretching vibration of C–NH₂. From the IR results, it can be concluded that the conjugated structure and phenyl rings of the RhB molecule are completely destroyed during the photocatalytic oxidation process under visible light irradiation. Carboxylic acids and primary amines are the main intermediate products.

Effect of pH. Natural enzyme proteins are most active at pH 6.8–7.2. Figure 7 presents the effect of pH on the photooxidative degradation rate of RhB in the CDH/H₂O₂ system under visible light irradiation. The results showed that CDH catalyst exhibited excellent photocatalytic properties over a wide pH range from 1.5 to 11.0. Interestingly, the best photocatalytic activity of CDH occurred at two pH regions, 3.8–7.4 and >10. This is significantly different from the photo-(like) Fenton reaction,¹⁹ where the Fenton reagent loses its

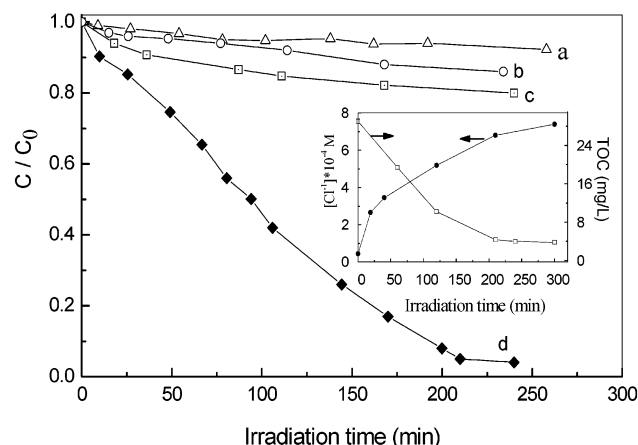


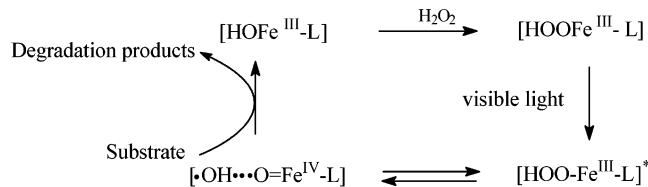
Figure 8. Photodegradation of DCP under different conditions: (a) DCP/CDH, visible light; (b) DCP/H₂O₂, visible light; (c) DCP/H₂O₂/CDH, dark; (d) DCP/H₂O₂/CDH, visible light. Inset: Change of TOC and evolution of the Cl⁻ ions during the degradation of DCP in the DCP/H₂O₂/CDH system. The reactions were done at pH 4.9, [DCP] = 4.0×10^{-4} M, [CDH] = 4.0×10^{-7} M, and [H₂O₂] = 5.0×10^{-2} M.

activity owing to precipitation of Fe³⁺ at pH greater than 3. It is well-known that the binding sites of natural enzymes influence the microenvironment of enzyme reactions, which results in the enzyme exhibiting a greater activity at natural pHs. The supramolecular structure of the CDH also provides an appropriate microenvironment for the active catalytic sites and leads to the high photocatalytic activity of the CDH at neutral pHs.

Degradation of DCP. Chlorinated phenols are good targets for the evaluation of new catalytic oxidation systems that use metal-organic complexes as catalysts.²⁰ Meanwhile, a study on the degradation of small organic molecules which have no absorption in the visible region can provide further insights into the photocatalytic reaction mechanism under visible light irradiation.

The degradation of DCP (4.0×10^{-4} M) as the target compound in the presence of CDH (4.0×10^{-7} M) and H₂O₂ (5.0×10^{-2} M) was investigated by HPLC analysis with an ultraviolet detector at 283 nm under visible light irradiation in aqueous media (pH 4.9). DCP decreased about 96% after photoreaction for 210 min. It was also found that DCP was not degraded in the presence of CDH alone or H₂O₂ alone, or when both were present in the dark. Under experimental conditions, visible illumination can significantly lead to the degradation of DCP although DCP has no absorption in the visible range. This result reveals that the photocatalytic degradation process is initiated by the photoexcitation of the CDH catalyst with visible light, rather than by the excitation of DCP, and the photosensitization process induced by the photoexcitation of the substrates does not play a major role. Removal of TOC and formation of chloride ions are displayed in the inset in Figure 8. Removal of TOC was about 59% and 85% after 120 and 210 min, respectively. The TOC data indicate that about 85% of the initial carbon atoms of DCP are mineralized into CO₂ and H₂O. About 81% of the chlorine atoms of DCP are released in the reaction solution as free chloride after 210 min of photocatalytic reaction. It further suggests that formation of free Cl⁻ ions is the result of ring cleavage and mineralization of DCP in the CDH/DCP/H₂O₂ system under visible irradiation. Turnover numbers (ratio of DCP to catalyst) reached 1000 under the experimental conditions. Meunier²¹ reported that 2,6-dichloro-2,4-benzoquinone is an intermediate produced in the degradation of DCP and cannot be further destroyed using metalloporphyrins as catalysts in the dark. FePcS as catalyst

SCHEME 1: Proposed Photodegradation Mechanism of Organic Pollutants in the Aqueous H₂O₂/CDH System under Visible Light Irradiation



cannot degrade DCP using H₂O₂ as oxidant in aqueous media under visible irradiation.⁴ The above experimental results showed that CDH exhibited high catalytic activity for the oxidation of DCP under visible light irradiation at natural pHs. The catalyst CDH can be easily excited to an excited state which provides high catalytic activity to activate H₂O₂; β -CD exhibits excellent functions for strengthening the interaction between the catalytic center and the substrate. To further examine the role of visible light irradiation, DMPO-trapping EPR signals were measured for the DCP/CDH/H₂O₂ system with 532 nm laser irradiation. The EPR signal intensity of the DMPO- \bullet OH adducts was enhanced gradually with increasing illumination time. No signals of DMPO- \bullet OH adducts were observed in the dark under conditions otherwise identical to those of the photoreaction. This further clarifies the photocatalytic mechanism of CDH under visible light irradiation.

Reaction Mechanism. CDH contains a binding site (β -CD) and next to it a catalytically active iron porphyrin molecule. β -CD plays an important role in the photocatalytic reaction. There are several reasons for this:^{9,10,22} (1) It depresses aggregation of iron porphyrin molecules. (2) The hydrophobic inner cavity efficiently envelops substrates to approach the active center of the catalyst. (3) Polyhydroxyl groups in β -CD create a soft and electron-donating microenvironment and contribute to both activate oxidant and enhance the electrophilicity in the catalytically active species.^{9,10} So, CDH exhibits excellent properties in both catalytic activity and stability. On the basis of all the experimental results and considerations, a possible mechanism for the degradation of organic pollutants for the H₂O₂/CDH system under visible light irradiation is illustrated in Scheme 1.

When H₂O₂ is present in aqueous media, the aqueous complex [HOFe^{III}-L] converts into the [HOOFe^{III}-L] complex,^{4,23,24} where L represents ligands with Fe^{III} in a CDH molecule. Upon visible light irradiation, [HOOFe^{III}-L] is excited to an excited state, which subsequently undergoes, with the assistance of β -CD, an electron transfer (MLCT) to form [O=Fe^{IV}-L]^{25,26} and \bullet OH. The formation of \bullet OH radicals has been evidenced by EPR experiments. Because the oxidative activity of \bullet OH radicals is much higher than that of high-valence iron-oxo species, the photooxidative reaction with \bullet OH radicals should be predominant in the present system. In the presence of substrates, the \bullet OH radicals generated by the CDH-induced photoactivation of H₂O₂ react immediately with organic substrates and degrade them effectively. However, if there were no substrates in the system, the \bullet OH radicals would recombine rapidly with the iron-oxo species,²⁷ which can explain the results of Figure 3.

Conclusion

An environmentally friendly photooxidation system for the degradation of toxic organic pollutants, such as organic dyes and chlorophenols, has been developed. The new CDH complex

photocatalyst is able to activate H₂O₂ efficiently to oxidize and mineralize organic pollutants in aqueous media over a wide pH range under visible light irradiation. The catalytic reaction mechanism is different from that in the dark. The CDH catalyst exhibits high catalytic activities with high turnover numbers (substrate:catalyst ratios), a high capacity to cleave the ring of aromatic derivatives such as RhB and DCP, and very high stability in the photocatalytic reaction. The proposed catalytic system may open new doors for the design of solar-energy-based treatment of toxic, nonbiodegradable, and trace organic pollutants in water.

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