

Green Oxygenation Degradation of Rhodamine B by Using Activated Molecule Oxygen

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Abstract: Iron(II) tetra-(1,4-dithin)-porphyrzine, (FePz(dtn)₄) is able to activate molecule oxygen for oxygenation degradation of rhodamine B (RhB) in an extensive pH region without light excitation. Experiments indicate that the RhB can be degraded nearly 52% in alkaline aqueous solution, bubbling with dioxygen for seven hours in the presence of FePz(dtn)₄ and the hydrogen peroxides as an active intermediate were determined by DPD method. The catalyst is recyclable and the catalyst activity was maintained after 10 recycles.

Keywords: Activation of molecule oxygen, iron(II) tetra(1,4-dithin)porphyrzine, oxidative degradation of pollutants, rhodamine B.

For most chemical processes, the hypothetical zero-waste level will not be reached in the near future. Furthermore, if the products could not be recycled or biodegraded, they will turn to the wastes at the end of use. Some new efficient catalytic methods therefore have to be developed to eliminate poorly biodegradable chemicals in industrial sites, which can damage the environment. To mimic the high efficiency oxidative characteristics of iron-containing oxygenase enzymes, several synthetic analogues have been developed in the non-biodegradable pollutants treatment. For example, Sen Gupta *et al.* reported a new oxidative cleaning method for chlorinated phenols, by using hydrogen peroxide and iron-containing hetero-cyclic (Fe-TAML) catalyst², in which nearly full conversions of chlorinated phenols were obtained within a few minutes. Recently, a new complex photo-catalysis system with iron (II) bipyridine carried on ion-exchanged resin has also been successfully developed, which allows directly use of molecule oxygen, the most environment friend oxidant dissolved in the water with visible light irradiation at ambient temperature for pollutants treatment³.

In this letter, we would like to report a novel green catalyst, iron(II) tetra-(1,4-dithin)-porphyrzine (abbreviated to FePz(dtn)₄), which is able to directly activate molecule oxygen for oxygenation non-biodegradable organic pollutants such as rhodamine B (RhB) in an extensive pH region without light excitation.

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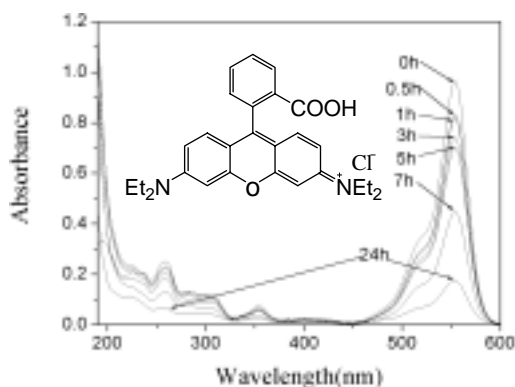
Experimental

The synthesis and characterizations of the FePz(dtn)_4 have been reported⁴. 10.0 mg of FePz(dtn)_4 carried on the ion-exchanged resin (Amberlite resin type CG400, size 200 mesh, $\text{FePz(dtn)}_4/\text{resin} = 0.7\%$, w/w) was mixed with 5 mL of buffer (phosphate pH 6.86, citrate pH 3, or borate pH 9.2 were used, respectively) with 5 mL RhB aqueous solution (1.0×10^{-5} mol/L). The reaction mixtures were bubbled with nitrogen for adsorption equilibration in the first 30 min., and then, the oxygenation reaction carried out at ambient temperature and in different pH conditions with constant bubbling dioxygen. Reaction processes were monitored by UV/Vis spectroscopy (Perkin Elmer USA, Lamberda-Bio35) and HPLC (Hitachi L7000, Turner C18 column, Japan) after filtration of the catalyst carried on the ion-exchanged resin in the different time intervals.

Figure 1 shows the oxidative degrading trend of RhB described by UV-Vis spectral changes with different dioxygen bubbling time intervals under the presence of FePz(dtn)_4 in borate buffer, during which the absorption peak at 550 nm was decreasing gradually in the first 5 hours, and an obvious dropping of this peak was observed after 7 hours, while the absorption peak around 200 nm rapidly increased with decreasing the peak at 550 nm. It means that the aromatic ring of the RhB has been broken during the dioxygen bubbling and the formed smaller molecules have a large absorbance around the 200 nm. The further drop of the peak around 200 nm during the dioxygen bubbling shows the degraded species in mineralizing. The mineralization rate of RhB determined by chemical oxygen demand values (COD_{Cr} method⁵) is about 12 % after reacting for 24 hours⁶.

Comparing the variations of relative concentration of RhB *versus* different dioxygen-bubbling time interval in the absence and presence of FePz(dtn)_4 in the buffer with different pH conditions (base-borate, neutral-phosphate, acid-citrate) indicate that there is no detectable degradation of RhB in the absence of FePz(dtn)_4 , but in the presence of FePz(dtn)_4 the degradation rates calculated from the variations of relative concentration of RhB with initial concentration $= 1 \times 10^{-5}$ mol/L are about 20~22% in acid and neutral aqueous and 52% in basic aqueous solution for 7 hours dioxygen-bubbling.

Figure 1 UV-Vis spectral changes of rodamine B (1×10^{-5} M) as a function of different dioxygen-bubbling time interval in the presence of catalyst FePz(dtn)_4 .



It demonstrates that the FePz(dtn)_4 as a kind of green catalyst is able to oxygenate degradation of organic pollutants efficiently in an extension pH conditions.

The fragmental species of the RhB in oxygenation degradation after 24 h are detected by the analysis of GC-MS and IR ⁶. Nine peaks of degraded small molecules and some substituted benzene from the RhB, appeared such as 1-isocyano-4-methylbenzene (the retention time $t_r = 5.57$ min), 5-pyrrolidin-2-ylidenemethyl-3,4-dihydropyrrol-2-one ($t_r = 6.21$ min), 2-furancarboxylic acid ($t_r = 6.65$ min), 2-methyl-3-oxocyclohex-1-enyloxy acetic ethanol ester ($t_r = 9.16$ min), 4-methyl-2H-1-benzopyran-2-one ($t_r = 12.25$ min), 3-methyl-3-phenyl-2-propenal ($t_r = 14.36$ min), *o*-methyloxime-cyclohexanone ($t_r = 14.78$ min), 2-cyanohexanoic ethyl ester ($t_r = 16.00$ min), and 5-hydroxy-1H-indole-3-ethanol ($t_r = 20.24$ min). These data indicated that the oxygenation degradation of RhB had proceeded in the presence of $\text{FePz(dtn)}_4 / \text{O}_2$ without light irradiation with breaking the pyran and benzene rings to form small molecular species.

In the course of degradation, hydrogen peroxide as an active intermediate has been demonstrated by DPD method ⁷ in our laboratory. The survival of the hydrogen peroxide was observed in the oxygenation degradation of *p*-nitrobenzoic acid ⁶ as showing in **Figure 2**, in which the increasing of the concentration of H_2O_2 and organoperoxides appeared obviously after bubbling with dioxygen for 5 hours in borate buffer in the presence of FePz(dtn)_4 (curve 1); After adding some catalase, which can remove the H_2O_2 , a little peroxide is detected (curve 2); it means that the main peroxide detected is H_2O_2 . The curve 3 shows H_2O_2 determined in triple distill water.

The effect of the resin supporting catalyst on the catalyst activity was also studied under different pH condition. The stronger adsorption ability of the cation resin to the substrate with anion in alkaline aqueous caused high degradation rate of RhB, due to it facilitated the substrate to contact closely with the catalyst, so that the molecule oxygen was activated by the catalyst adsorbed on the same carrier more easily. However, the lower degradation rate was observed in acid and neutral aqueous solution, in which RhB molecule appeared the species with positive charge, which block up the close contact with the catalyst carried on the supporting resin to decrease the adsorption rate. Therefore, the degrading rates of RhB under different pH conditions also correspond to the adsorption ability of the resin to RhB.

The adsorption effect on degradation rate, on the other hand, has also been demonstrated that with unreactivated reused catalyst, the catalyst activity rapidly reduced (as showing in **Figure 3**). The reaction rate decreased to one of the fifth of the initial after 4 to 6 cycles. In the results, the overload of RhB on the resin inhibited activation of molecule oxygen by the catalyst. However, the catalytic activity of the FePz(dtn)_4 in the degradation of RhB can be maintained in 6th run, if the catalyst was reactivated by a procedure of filtration, washing with mixture of water and ethanol, and then drying. The IR spectra of the reactivated catalyst appeared no changes before and after 10 cycle runs. It means that the FePz(dtn)_4 carried on the resin is stable and can be reused, it can strongly adsorb on the carrier without obvious desorption during the oxygenating degradation and reactivating processes.

Figure 2 Detections of hydrogen peroxide by adding DPD and POD into the oxygenation degraded aqueous solution of *p*-nitrobenzoic acid (1×10^{-3} mol/L) after dioxygen-bubbling for 5 hours in borate buffer in the presence of $\text{FePz}(\text{dtn})_4$

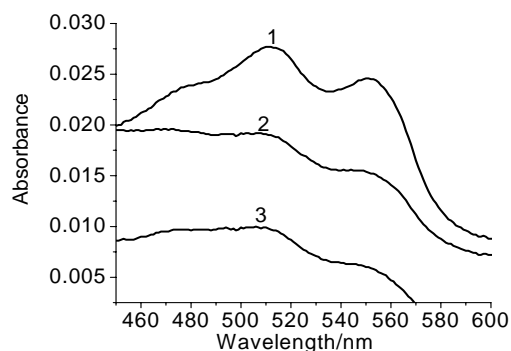
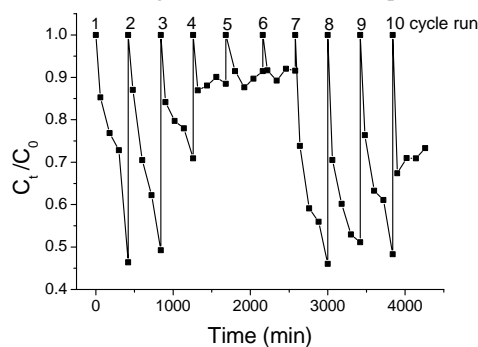


Figure 3 Cycle runs in the degradation of RhB in the presence of $\text{FePz}(\text{dtn})_4$.



In conclusion, a green sulf-containing iron-porphyrzine catalyst, $\text{FePz}(\text{dtn})_4$, as biomimetic oxygenase enzyme is able to activate molecule oxygen for oxygenating degradation toxic organic pollutants efficiently without light irradiation in an extensive pH regions in aqueous solution.

Acknowledgments

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