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Efficient degradation of dye pollutants using dioxygen mediated by iron(II) 2,2'-bipyridine loaded layered clay catalyst under visible irradiation

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Abstract The organic-inorganic layered solid catalyst $\text{Fe}(\text{bpy})_3^{2+}$ -laponite was able to photodegrade Rhodamine B (RhB) by activation of dioxygen under visible irradiation ($\lambda > 420 \text{ nm}$), while the homogeneous aqueous solution $\text{Fe}(\text{bpy})_3^{2+}$ showed no photoactivity. The catalyst could be repeatedly used and retained its reactivity. The hybrid catalyst could be separated from the suspension by centrifugation or sedimentation. The TOC removal yield of RhB was measured. Reactive oxygen species (ROS) formed during degradation was detected by EPR. A possible mechanism was proposed on the basis of the experimental results.

Keywords: laponite, Rhodamine B, molecular oxygen, visible light.

Heterogeneous photocatalyst has been brought into wide application in wastewater treatment due to its long life time, facile recovery and easy separation^[1-5]. Green chemical technology suggests the use of hydrogen peroxide or molecular oxygen as the oxidant^[6]. The abundant and cheap molecular oxygen makes green chemical technology a widely applicable method for wastewater treatment. We have reported in our previous work that $\text{Fe}(\text{bpy})_3^{2+}$ anchored on resin could effectively degrade organic pollutants under visible irradiation^[7]. However, its application encounters great limit in that it will be destroyed at high temperature, in strong acidic or basic media, and in organic solvents.

In this report, a layered photocatalyst was prepared by intercalation of $\text{Fe}(\text{bpy})_3^{2+}$ into laponite clay. The catalyst was able to degrade organic dyes with dioxygen under visible irradiation.

1 Experimental

1.1 Materials

The laponite clay was supplied by Fernz Specially Chemicals, Australia, and used as received. The clay powder has a cation exchange capacity (CEC) of 55 meq/100 g of clay. Rhodamine B (RhB) was chosen as target pollutant. Ultrapure water was used throughout this study.

1.2 Preparation of the photocatalyst

Before immobilization, the laponite clay (1 g) was first put in a 250 mL beaker and allowed to dissolve by vigorous stirring. Then $\text{Fe}(\text{bpy})_3^{2+}$ was put into the beaker and the dispersion was vigorously stirred for 24 h. The carmine floccules of $\text{Fe}(\text{bpy})_3^{2+}$ intercalated laponite were formed. The supernatant solution was removed and the catalyst was washed with ultrapure water till no $\text{Fe}(\text{bpy})_3^{2+}$ was detected spectrophotometrically in the solution. The clay was finally dried in a vacuum oven at 50°C for 10 h. The catalyst was obtained after being pulverized into powder, which we name FeBL. Following this procedure, the catalysts with different loadings of 20%, 40%, 50%, 70%, and 100% CEC were prepared and then applied in the photodegradation of RhB. Since the clay loaded with 50% CEC of $\text{Fe}(\text{bpy})_3^{2+}$ (0.275 mmol of $\text{Fe}(\text{bpy})_3^{2+}$ / 1 g laponite) exhibited the highest activity, this catalyst was used for the following experiments.

1.3 Photoreactor and light source

The irradiation source was a 500 W halogen lamp (Institute of Electric Light Source, Beijing). A cut off filter was placed outside the water jacket to remove wavelengths below 420 nm to ensure complete visible light irradiation. For detailed information see ref. [2].

1.4 Procedures and analyses

The photoreaction was performed in a cylindrical Pyrex vessel at a solution volume 50 mL, initial pH 2.7 and catalyst dosage 5 mg. The degradation of RhB was carried out after overnight dark stirring to access the adsorption/desorption equilibrium between RhB and the catalyst. The change of the concentration of RhB was monitored spectrophotometrically by a Hitachi U-3010 spectrophotometer. The active species was detected on a Bruker Model EPR 300E spectrometer. The content of TOC was assayed by using an Apollo 9000 TOC analyzer (Terkmar Dohrmann Co.).

2 Results and discussion

Fig. 1 shows the changes of the concentration of RhB under various conditions. At current reaction

conditions, homogenous $\text{Fe}(\text{bpy})_3^{2+}$ aqueous solution shows no reactivity toward the activation of O_2 under visible irradiation. Whereas, after anchoring of $\text{Fe}(\text{bpy})_3^{2+}$ on laponite, it shows significant reactivity in that 87% of RhB is degraded in 300 min by the solid catalyst with O_2 under visible irradiation, which is confirmed by the UV-Vis spectra changes of RhB (inset). TOC measurement shows that 36% of RhB is transformed into CO_2 . The catalyst does not react with RhB in the dark, revealing the accelerating effect of light on the degradation of RhB by FeBL. These results evidence that the clay changes greatly the photochemical properties of $\text{Fe}(\text{bpy})_3^{2+}$, leading to its photocatalytic activity to activate O_2 .

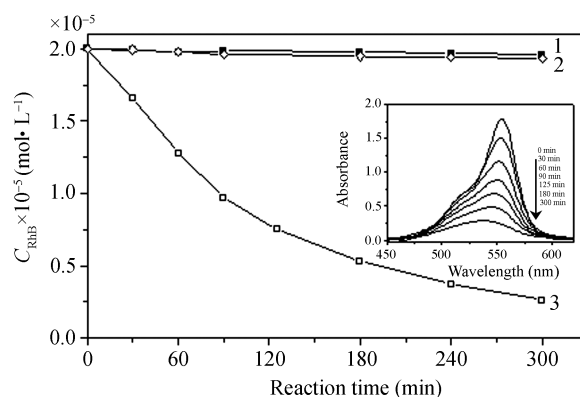


Fig. 1. Changes of RhB concentration under various reaction conditions. Curve 1, dark reaction of FeBL with RhB; curve 2, homogenous $\text{Fe}(\text{bpy})_3^{2+}$ aqueous solution with H_2O_2 under visible irradiation RhB; curve 3, reaction of FeBL with RhB under visible irradiation. $[\text{RhB}] = 2 \times 10^{-5}$ mol/L, $[\text{Fe}(\text{bpy})_3^{2+}] = 4.4 \times 10^{-5}$ mol/L, FeBL: 5 mg, pH = 2.7. Inset shows the temporal UV-Vis spectra changes of RhB as in curve 3.

Fig. 2 is the recycle of FeBL. As shown, FeBL is reused for 6 times and still retains its activity. The suspended catalyst in the system could be separated easily by centrifugation or sedimentation. It is detected that no metal ions and bipyridine or its degraded species leach into the solution. The results above show that anchoring of $\text{Fe}(\text{bpy})_3^{2+}$ on laponite greatly improves its stability.

The reaction could be accelerated by purging oxygen into the suspension while terminated with deoxygenating of the suspension, illustrating that the dioxygen is the essential oxidant for the reaction. It is de-

tected that H_2O_2 is formed during the reaction, which is a side product of the reaction.

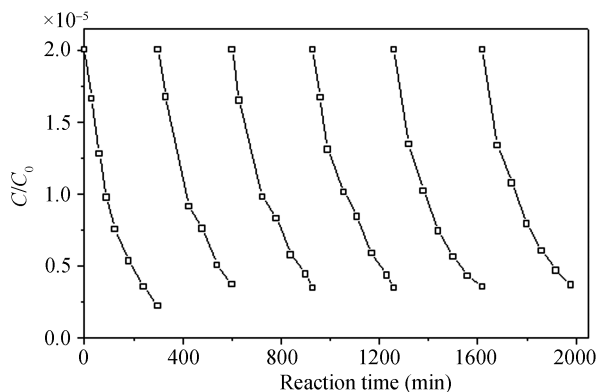


Fig. 2. Time profiles for the cyclic degradation of RhB. $[RhB] = 2 \times 10^{-5}$ (mol/L)/run, FeBL: 5 mg, pH = 2.7.

Spin-trapping EPR is an effective technique for the detection of active radicals^[8]. Activation of dioxygen could generate active oxygen species, such as singlet oxygen^[5], hydroperoxyl radical and high valent iron-oxo species^[9]. In the present FeBL/RhB system, obvious $\cdot OOH/O_2^{\cdot -}$ signals are observed under visible irradiation. What is more, the intensity increases with irradiation time (Fig. 3). Whereas no signal could be observed without light irradiation, which agrees well with the results in Fig. 1. Under visible irradiation the generated $\cdot OOH/O_2^{\cdot -}$ radicals could degrade RhB and in the dark RhB does not undergo any decomposition since there is no $\cdot OOH/O_2^{\cdot -}$ radicals. Meantime no $\cdot OH$ radicals were detected in the aqueous FeBL/RhB suspension and addition of $\cdot OH$ radical scavenger isopropanol had no effect on the degradation, implying that $\cdot OH$ radicals are not involved in the degradation of RhB.

Based on the kinetic and EPR results, a possible mechanism is proposed. Under visible irradiation, the excited $Fe(bpy)_3^{2+}$ molecules on the clay react with O_2 to form the intermediate $\{Fe(bpy)_3^{2+}O_2^{\cdot -}\}$. The species could be further converted to the high valent iron species $\{Fe(IV)(bpy)_3=O\}$. Collins' group had reported $Fe(IV)=O$ as the active intermediate based on another N-donor ligand system^[10]. The $\{Fe(IV)(bpy)_3=O\}$ species has high oxidative activity that it

can degrade the dye pollutants^[11] with itself changes to the initial state $Fe(bpy)_3^{2+}$. We propose that in the FeBL catalyzed reactions, the hydroperoxyl radicals and the $\{Fe(IV)(bpy)_3=O\}$ species are the possible oxidants that result in the degradation of RhB. Further study is needed for the detailed information of the formation and conversion of the active species and the reaction pathway.

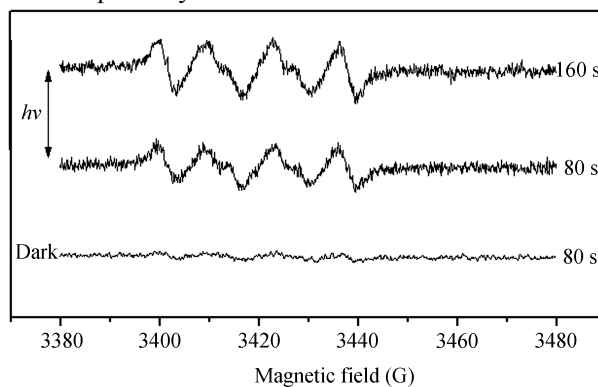


Fig. 3. EPR signals in RhB/FeBL suspension. $[RhB] = 2 \times 10^{-5}$ mol/L, FeBL: 5 mg, pH = 2.7.

3 Conclusion

FeBL is a green and stable catalyst. It provides an efficient technology for the utilization of molecular oxygen to degrade the organic pollutants.

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