

Preparation of a μ -N-bridged Binuclear Fe(III) Schiff-base Complex as Catalyst for the Degradation of Emerging Contaminants Dibutylphthalate (DBP)

Haoyu Shen^{*}, Yufei Wang, Leyi Weng, Zhehao Jiang and Qi Jiang
Ningbo Institute of Technology, Zhejiang University; Ningbo, Zhejiang, 315100, China

Keywords: Fe(III) Schiff base complex; Emerging contaminants (ECs); Dibutyl phthalate (DBP); Degradation; Fenton-like reaction.

Abstract: Schiff base ligand (ST = N, N'-tetraethylenepentaminebis (salicylideimine)) was prepared by condensation reaction of salicylaldehyde (SA) and tetraethylenepentamine (TEPA), and further coordinated with iron (III) *via* coordination reaction to form a binuclear iron (III) complex, $[\text{Fe}_2(\text{ST})(\text{H}_2\text{O})_4]\text{Cl}_4$ (abbreviated as, $\text{Fe}_2(\text{ST})$). It was characterized by elemental analysis (EA), Fourier transform infrared spectrometer (FTIR), and ultraviolet-visible spectroscopy (UV-vis), *etc.* It was used as catalyst for the degradation of emerging contaminants, *e. g.*, dibutyl phthalate (DBP) under visible light with hydrogen peroxide solution as oxidant. The results showed that at pH 3.5-8.0, with the initial concentration of $\text{Fe}_2(\text{ST})$ complex larger than $5.50 \mu\text{mol}\cdot\text{L}^{-1}$, and that of H_2O_2 larger than $8.16 \text{ mmol}\cdot\text{L}^{-1}$, the degradation of DBP at initial concentration less than $20.0 \text{ mg}\cdot\text{L}^{-1}$ can be reached to almost 100% within 10 min. The catalytic reaction system has been monitored by electronic spectrum before or after adding H_2O_2 at different time intervals. The result showed the catalytic activity site may be a μ -N-bridged binuclear Fe(III) centre and a di-Fe(III)- H_2O_2 transition-state might be formed, which was favourable to the activation of the H_2O_2 under visible light. The $\text{Fe}_2(\text{ST})$ is a potential effective and green catalyst for the degradation of DBP.

1 INTRODUCTION

Phthalate esters (PAEs) are commonly used synthetic materials and plasticizers, pesticides, *etc.* They are typical environmental hormones and Emerging contaminants (ECs) (Vrijheid et al., 2016). In recent years, PAEs residue was detected in the environmental samples, and even in food. The pollution of PAEs is becoming more and more serious (Shen, 2005). How to effectively remove the PAEs in the environment is a major challenge in the field of environmental science and technology. At present, the most effective methods for removing PAEs are advanced oxidation processes (AOPs) (Legrini et al., 1993). Among AOPs, Fenton reaction is an attractive method for effective degradation of PAEs because of its low cost, the lack of toxicity of the reagents (Hu et al., 2012). Recently, it has proved that the Fe^{3+} transition metal complex- H_2O_2 system has the advantages of high utilization rate of H_2O_2 than the conventional Fenton oxidation method (Hu and Xu, 2014). Among them, the metal Schiff-base

complex has attracted much attention due to the peculiar electronic characteristics, stable structure, and tailoring the electronic and space effect of complex accurately and easily by changing the ligand or metal ion. The iron Schiff-base can act as catalyst in lots of oxidation reactions, which not only overcome the shortcomings of high acidity requirements, but also exhibit some characteristics of biomimetic reactions. At present, iron Schiff-base complexes have been reported about the selective catalytic oxidation of different group mainly in homogeneous reaction, but few research pays attention to the heterogeneous photocatalytic performance in water treatment of toxic organic pollutants under visible light.

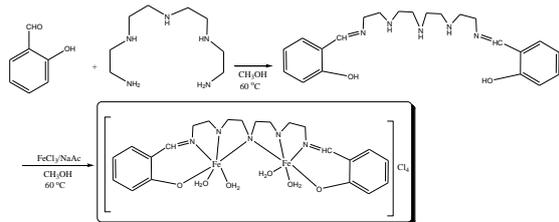
In this work, a novel binuclear iron (III) complexes with Schiff base $[\text{Fe}_2(\text{ST})(\text{H}_2\text{O})_4]\text{Cl}_4$ (abbreviated as: $\text{Fe}_2(\text{ST})$) was synthesized and characterized. It was used for the catalytic degradation of DBP. The effects of the solution pH value, the concentration of H_2O_2 in the system, $\text{Fe}_2(\text{ST})$ and the initial concentration of DBP were

investigated. The presumed degradation mechanism was deeply investigated in present work.

2 EXPERIMENTAL

2.1 Preparation of Fe₂(ST)

0.2 mmol (37.9mg) of TEPA and 0.4 mmol (48.8mg) of SA was dissolved in 10 mL methanol, respectively. SA methanol solution was added to the TEPA solution dropwise under vigorous stirring. The reaction was continued at 60 °C for 2 hrs. After the mixture solution was cooled down, the yellow colour Schiff base ligand, in which ST is the N, N'-tetraethylenepentamine-bis (salicylide-imine), was obtained. The yellow crystals of ST were collected by filtering under vacuum, washed with a small amount of water and methanol for three times, and dried under vacuum at 60 °C for 12 hrs, yield: 96.5%. 0.2 mmol (54.6 mg) of FeCl₃·6H₂O and 0.1 mmol (35.2 mg) of ST was dissolved in 10 mL methanol, respectively. FeCl₃·6H₂O methanol solution was added to the ST solution dropwise under vigorous stirring. The 0.1 mol·L⁻¹ NaAc solution at was then added dropwise to adjust the mixture solution pH to 8-9. The reaction was continued at 60 °C for 2 hrs. After the mixture solution was cooled down, the brown microcrystalline product was obtained, and collected by filtering under vacuum, washed with a small amount of water and methanol for three times, and dried under vacuum at 60 °C for 12 hrs, yield: 89.6%. The overall preparation procedure was shown in Scheme 1.



Scheme 1: Preparation of Fe₂(ST).

2.2 Catalytic Degradation of DBP by Fe₂(ST)

Catalytic degradation experiments were carried out in 150 mL stoppered flasks, each of which contained 25.00 mL of DBP acetonitrile solution at concentration of 20 mg·L⁻¹, 40 μL of Fe₂(ST) acetonitrile solution at concentration of 4.0 mg·L⁻¹ was added, followed adding 20 uL of 30% H₂O₂. The

mixture was shaken at 150 rpm in a thermostatic shaker, sampling at every 1 min, followed by adding 1 drop of 10% Na₂SO₃ solution to stop the reaction. The experiments of traditional Fenton system was carried out similarly by replacing Fe₂(ST) with FeSO₄ acetonitrile solution of at concentration of 4.0 mg·L⁻¹. HPLC method was applied for the determination of the residue concentrations of DBP. The degradation rates of DBP under different loading amount and different pH conditions were calculated according to Eq. (1):

$$D = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

Where D is the degradation rate of DBP; A_t and A_0 are the HPLC peak area of DBP at time t and at time 0, respectively.

The effects of initial pH value, usage amount of H₂O₂, initial concentration of Fe₂(ST) DBP concentration on the degradation of DBP were investigated.

3 RESULTS AND DISCUSSION

3.1 Characterization of Fe₂(ST)

Fe₂(ST) was characterized by EA, TG/DTG, UV/Vis and FTIR, *etc.* The EA results showed that the elemental percentage of Fe₂(ST) were (experimental (theoretical), %): C: 36.58 (36.65), H: 5.25 (5.17), O: 13.52 (13.31), N: 9.52 (9.71) and Fe: 15.22 (15.49), respectively. The molar conductivity of Fe₂(ST) was determined by using acetonitrile as a solvent. It was found that Fe₂(ST) is a 1: 4 type electrolyte (Geary, 1971). The concentration of chlorine ion (Cl⁻) was obtained by titration of the Fe₂(ST) solution in acetonitrile with AgNO₃ solution, and found to be 19.96% (19.67%, theoretically). TG/DTG (Figure 1) shows that Fe₂(ST) has 10.2% weight lose at ~120°C, which would be relevant to 4 molecular of water (theoretical data: 9.99%). Combined with the results of its conductivity and Cl⁻ content, it would be deducted that the four water molecules might be in the inner boundary of the Fe₂(ST) and coordinated with Fe (III), while the four Cl⁻ ions are in the outlay of the complex.

UV-Vis spectrum (Figure 2(a)) of ST and Fe₂(ST) showed that the characteristic peaks of π - π^* transition and n - π^* transition absorption of benzene ring and imine in ST appeared at 252 nm and 315 nm. After forming Fe₂(ST) complex, these two peaks were red-shifted to 260 nm and 325 nm, respectively, along with the absorption peak at 325 nm

significantly broadening, which can be attributed to the charge transfer of the $p_x(N) \rightarrow d_{xz}(Fe)$ in $Fe_2(ST)$. Simultaneously, the d-d transition absorption peak of Fe(III) was observed at 512 nm. The FTIR of ST and $Fe_2(ST)$ (Figure 2(b)) showed that typical peaks at 1642 cm^{-1} and 1585 cm^{-1} assigned to the absorption of imine and amino groups of ST appeared. After coordination with Fe(III), these two peaks were red-shifted to 1635 cm^{-1} and 1445 cm^{-1} , respectively, with a large broadening. New peaks at 620 cm^{-1} and 525 cm^{-1} , attributed to the characteristic absorption peaks of Fe-N and Fe-O bonds appeared (Mao et al., 2009), indicating the successful formulation of $Fe_2(ST)$ complex.

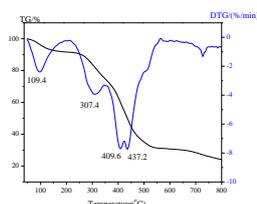


Figure 1: TG-DTG curves of $Fe_2(ST)$.

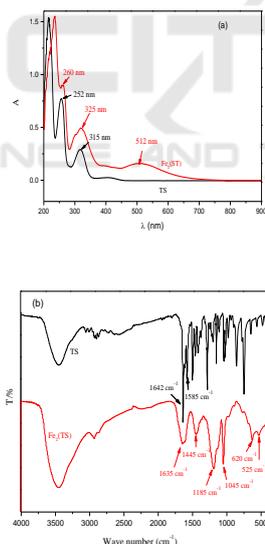


Figure 2: (a) UV and (b) FTIR spectra of ST and $Fe_2(ST)$.

3.2 Degradation of DBP by $Fe_2(ST)$

Figure 3(a) shows the degradation of DBP by $Fe_2(ST)$ in H_2O_2 /visible light system. With the increasing of the reaction time, the degradation rate of DBP increased from 75.6% to 99.8% within 10 min. The experimental results of traditional Fenton system are

shown in Figure 3(b). With the reaction time increasing, the degradation rate of DBP decreases from 30.2% to less than 0.5% in 8 mins. This might be due to the fact that $\cdot OH$ free radical is easily deactivated generated by the traditional Fenton system. It can be seen that the $Fe_2(ST)/H_2O_2$ /visible light system has higher catalytic degradation performance for DPB than that of the traditional Fenton system. The high catalytic degradation efficiency under visible light conditions might be contributed to the μ -N-bridged binuclear Fe(III) centre of the $Fe_2(ST)$.

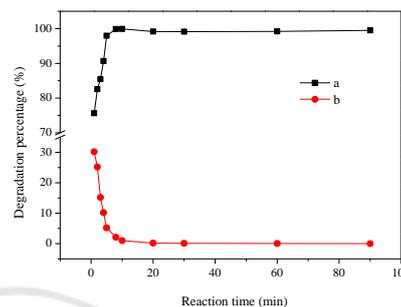


Figure 3: Degradation extent of DBP under (a) $Fe_2(ST)/H_2O_2/vis$, (b) traditional Fenton catalytic systems.

The electronic spectra of DBP solution before and after the addition of $Fe_2(ST)/H_2O_2$ are shown in Figure 4. With the addition of H_2O_2 (c, 0 min; d, 1 min; e, 5 min; f, 10 min), the intensity of the characteristic peak of the charge transfer of the $p_x(N) \rightarrow d_{xz}(Fe)$ of $Fe_2(ST)$ at about 325 nm gradually increased and broadened. This might be due to the fact that the formation of an μ -N-bridged binuclear Fe(III)- H_2O_2 transition states during the catalytic process (Mao et al., 2009), shown in Figure 5. When H_2O_2 was added into the $Fe_2(ST)$, a H_2O_2 bridged transition state might be formed, which might be favourable to the activation of H_2O_2 , leading the produce of $\cdot OH$ free radicals, under visible light, the DBP was mineralized to CO_2 and H_2O . As shown in Figure 4, the characteristic absorption peaks of DBP at 230 nm and 275 nm disappeared, indicating a significant degradation of DBP (Figure 4b). The COD of the post-degradation solution was tested according to HJ 828-2017 method and the result was at 15 mg/L, indicating the mineralization of the DBP.

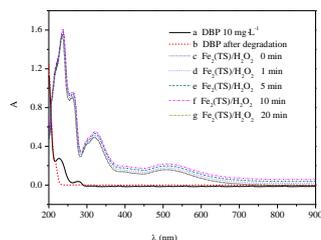


Figure 4: UV spectra of DBP before (a) and after (b) adding Fe₂(ST)/H₂O₂ at different reaction time (c-g).

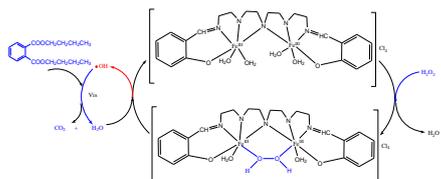


Figure 5: Presumed mechanism of μ -N bridged binuclear Fe(III)-H₂O₂ transition-state and production of OH.

3.2.1 Effect of Solution pH Values

The effect of solution pH was investigated with the pH values ranging from 3.0 to 9.0. The results (Figure 6) showed that at the pH range of 3.5-8.0, DBP can degrade almost 100% within 10 min under the Fe₂(ST)/H₂O₂/visible light catalytic system. The pH value of the DBP solution is about 6.0. Thus the catalytic degradation can be carried out without pH adjustment of the DBP solution. The reason for the wider pH range of the present catalytic system than that of the conventional Fenton reaction system may be due to the fact that the Fe(III) coordinated to the ST ligand might stable the Fe(III) active centre, leading its resistance to the effect of the solution pH varying on the degradation efficiency of DBP (Wang et al., 2007).

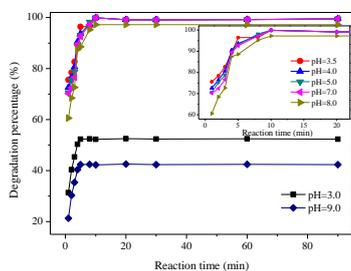


Figure 6: Effect of the solution pH on the Fe₂(ST)/H₂O₂/DEP catalytic degradation system (insert: pH=3.5-8.0 enlarged).

3.2.2 Effect of Usage Amount of H₂O₂

The effect of usage amount of H₂O₂ was investigated with the concentration of H₂O₂ in the catalytic system was in the range of 2.04 to 40.8 mmol·L⁻¹, with the initial concentration of DBP at 20 mg·L⁻¹. The results (Figure 7) showed that when the concentration of H₂O₂ was at 2.04 mmol·L⁻¹, nearly 45 mins were needed for total degradation of DBP. When the concentration of H₂O₂ at 4.08 mmol·L⁻¹, degradation of DBP can be realized within 30 mins. With the concentration of H₂O₂ increasing, the degradation rate increased gradually, and when the concentration of H₂O₂ at 8.16 mmol·L⁻¹, the degradation of DBP can be realized within 10 mins (Lee and Yoon, 2004).

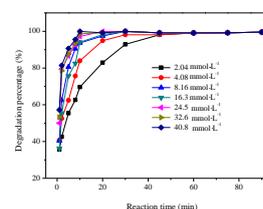


Figure 7: Effect of the usage amount of H₂O₂ on the Fe₂(ST)/H₂O₂/DEP catalytic degradation system.

3.2.3 Effect of Usage Amount of Fe₂(ST)

The effect of usage amount of Fe₂(ST) was investigated with the concentration of Fe₂(ST) in the catalytic system was at 1.10-11.0 μ mol·L⁻¹. The results (Figure 8) showed that Fe₂(ST) was found to be the key factor for the generation of the ·OH free radicals. When the usage amount of Fe₂(ST) was low, the generation rate degradation rate of DBP was very low. With the usage amount of Fe₂(ST) increasing, the generation rate of the ·OH free radicals increased, leading a increasing of degradation rate of DBP. When the usage amount of Fe₂(ST) reached 5.50 μ mol·L⁻¹, the degradation rate tends to be stable.

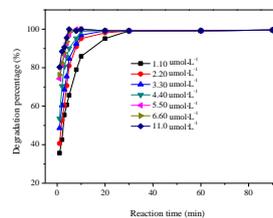


Figure 8: Effect of the usage amount of Fe₂(ST) on the Fe₂(ST)/H₂O₂/DEP catalytic degradation system.

3.2.4 Effect of the Initial Concentration of DBP

The effect of initial concentration DBP was investigated with the concentration of DBP in the catalytic system at $14.38\text{--}287.77 \mu\text{mol}\cdot\text{L}^{-1}$. The results (Figure 9) showed that when the concentration of $\text{DBP} < 71.6 \mu\text{mol}\cdot\text{L}^{-1}$ ($50\text{mg}\cdot\text{L}^{-1}$), the DBP can be totally degenerated in 10 mins. The residue concentration of DBP was at $\mu\text{g}\cdot\text{L}^{-1}$ to $\text{mg}\cdot\text{L}^{-1}$ levels in the aqueous environment, thus the present $\text{Fe}_2(\text{ST})/\text{H}_2\text{O}_2/\text{vis}$ system can be used for the treatment of the DBP in the environment.

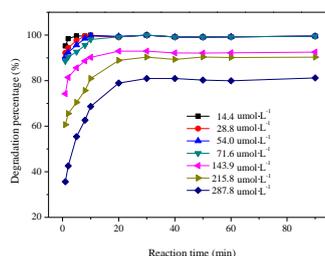


Figure 9: Effect of the initial concentration of DBP on the $\text{Fe}_2(\text{ST})/\text{H}_2\text{O}_2/\text{DEP}$ catalytic degradation system.

3.3 Reusability Investigation

The reusable of the $\text{Fe}_2(\text{ST})$ was evaluated. Results were shown in Figure 10, which indicated that $\text{Fe}_2(\text{ST})$ could be used for at least 10 cycles with degradation rate higher than 95% upon recovery on average. No obvious decrease in the degradation efficiency and iron leaching were found. Compared with literature reports, the $\text{Fe}_2(\text{ST})$ is a potential effective and reusable catalyst for the degradation of DBP with high degradation effect.

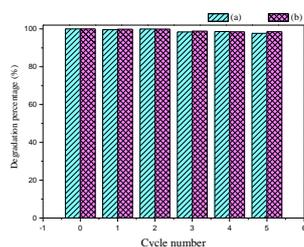


Figure 10: Recycle of the $\text{Fe}_2(\text{ST})$ catalyst (a) Method 1: re-adding DBP after rotating evaporation of the post-degeneration solution, (b) Method 2: re-adding DBP directly in the post-degeneration solution.

4 CONCLUSIONS

In this work, a binuclear iron (III) complex ($\text{Fe}_2(\text{ST})$) was prepared and characterized by EA, TG/DTG, UV/Vis and FTIR, *etc.* It was used as a catalyst for the Fenton-like reaction of the catalytic degradation of the emerging contaminants di-butyl-phthalate (DBP). It is found that under the condition of visible light, the catalytic degradation of DBP could be achieved by $\text{Fe}_2(\text{ST})/\text{H}_2\text{O}_2$ system in aqueous solution with the pH range from 3.5 to 8.0. Compared with ordinary Fenton reaction system, a wide range of pH value for the degradation of DBP achieved. The degradation of DBP was more than 99% when the concentration of $\text{Fe}_2(\text{ST})$ was larger than $5.50 \mu\text{mol}\cdot\text{L}^{-1}$, the concentration of H_2O_2 was larger than $8.16 \text{mmol}\cdot\text{L}^{-1}$, and the concentration of DBP was less than $20.0 \text{mg}\cdot\text{L}^{-1}$. With the aid of the electronic spectrum monitoring, it is found that the transition state of μ -N bridged bi-nucleus Fe(III)- H_2O_2 centre may form in the catalytic process.

ACKNOWLEDGEMENTS

We would like to thank the National Natural Science Foundation of China (51608479, 81502421), the National Natural Science Foundation of Zhejiang Province (LY14B04003), the National Natural Science Foundation of Ningbo (2018A610206), the National College Students' innovation and entrepreneurship training program (201813022009), the Xinmiao Students' innovation training program of Zhejiang Province (2018R401181) for the financial support.

REFERENCES

- Geary, W. J., 1971. *Coordination Chemistry Reviews*, 7(1): 81–122.
- Hu, M. Q. and Xu, Y. M., 2014. *Chemical Engineering Journal*, 246: 299–305.
- Hu, M. Q., Wang, Y., Xiong, Z. G., Bi, D. Q., Zhang, Y. H., Xu, Y. M., 2012. *Environmental Science & Technology*, 46: 9005–9011.
- Lee, C. H., Yoon, J., 2004. *Chemosphere*, 57:1449–1458.
- Legrini, O., Olivers, E., Braun, A. M., 1993. *Chemical Review*, 93(2): 671–698.
- Mao, C. H., Zhao, Y., Li, Y. Q. et al., 2009. *Chinese Journal of Organic Chemistry*, 29(6): 929–935.
- Shen, H. Y., 2005. *Talanta*, 66: 734–739.
- Vrijheid, M., Casas, M., Gascon, M. et al., 2016. *International Journal of Hygiene and Environmental Health*, 219: 331–342.
- Wang, B. S., Zhang, J., Huang, J. L., 2007. *Journal of Harbin Institute of Technology*, 39(2): 255-257.