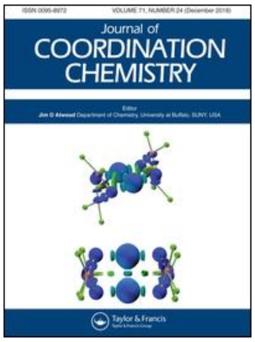


Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: https://www.tandfonline.com/loi/gcoo20

Synthesis of a simplified iron(III) tetraamido macrocyclic ligand (Fe^{III}-TAML) catalyst and its catalytic activity for degradation of dye wastewater by H_2O_2

Shunlai Li, Liaoyuan Wang, Run Zhou, Cheng Zhou & Hongguang Du

To cite this article: Shunlai Li, Liaoyuan Wang, Run Zhou, Cheng Zhou & Hongguang Du (2020): Synthesis of a simplified iron(III) tetraamido macrocyclic ligand (Fe^{III}-TAML) catalyst and its catalytic activity for degradation of dye wastewater by H_2O_2, Journal of Coordination Chemistry, DOI: 10.1080/00958972.2019.1710138

To link to this article: https://doi.org/10.1080/00958972.2019.1710138

JOURNAL OF COORDINATION CHEMISTRY
https://doi.org/10.1080/00958972.2019.1710138

Taylor & Francis
Taylor & Francis Group

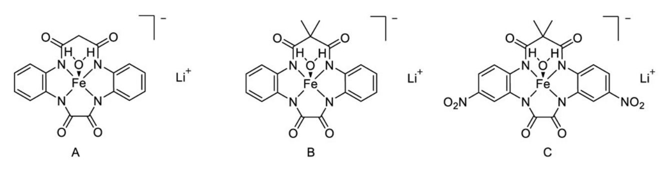
Synthesis of a simplified iron(III) tetraamido macrocyclic ligand (Fe^{III}-TAML) catalyst and its catalytic activity for degradation of dye wastewater by H_2O_2

Shunlai Li, Liaoyuan Wang, Run Zhou, Cheng Zhou and Hongguang Du

College of Chemistry, Beijing University of Chemical Technology, Beijing, China

ABSTRACT

To reduce the cost of water treatment reagents, a simplified iron(III) tetraamido macrocyclic ligand compound (Fe^{III}-TAML) was synthesized with a total yield of 53.3%. For comparison, two second generation Fe^{III}-TAML catalysts were synthesized. The synthetic route was optimized, and the total yield increased from 30.1% to 49.5%. The catalytic activity of the simplified catalyst for degradation of dye wastewater by hydrogen peroxide was tested and compared with that of the second generation Fe^{III}-TAML catalysts. The experimental results show that the simplified catalyst has good catalytic activity. At 25 °C, pH = 8, $C_{\text{Fe-TAML}} = 50\,\text{mg/L}$, and $C_{\text{hydrogen peroxide}} = 1.5\,\text{g/L}$, the decolorization and chemical oxygen demand removal of methylene blue, methyl orange, neutral red, and Rhodamine B dye wastewater were 74.8%–96.1% and 46.9%–63.7%, respectively.



ARTICLE HISTORY
Received 19 August 2019
Accepted 16 December 2019

KEYWORDS
Tetraamido macrocyclic ligand; water treatment; dye degradation; COD

1. Introduction

Environmental pollution is becoming more serious. In industrial production, especially in printing, dyeing, and textile fields, large amounts of wastewater are discharged every year, containing toxic organic matter. If discharged directly without treatment, it causes serious damage to the natural ecology [1]. Therefore, it is necessary to study how to treat organic matter in industrial sewage more efficiently.

At present, the commonly used chemical treatment technologies of organic wastewater are ozone oxidation, chlorine oxidation, and Fenton oxidation [2, 3]. Ultraviolet irradiation is a common method in ozonation, which can destroy the unsaturated

CONTACT Hongguang Du dhg@mail.buct.edu.cn

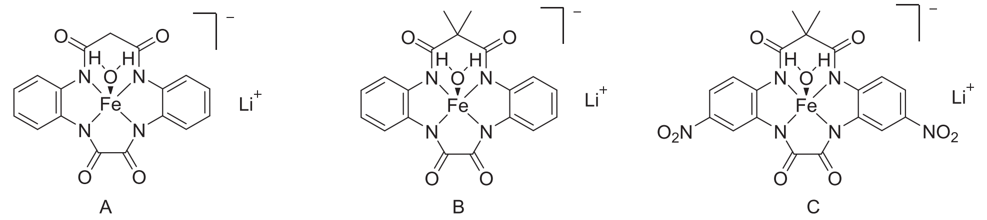


Figure 1. The structures of three Fe^{III}-TAML catalysts A, B, and C.

bonds of organic compounds and directly oxidize organic compounds to form small molecules. The method has the characteristics of wide application range, high reaction efficiency, and no secondary pollution. The disadvantages are that ozone is unstable and its utilization rate is low; also producing ozone consumes a lot of electricity.

Sodium hypochlorite, chlorine, and chlorine dioxide are used in chlorine oxidation processes [4]. These technologies have the advantages of low cost and simple operation. However, its disadvantage is high toxicity, which may produce chlorinated organic compounds with high toxicity and cause secondary pollution to the environment.

The Fenton reaction was discovered by British scientist Fenton. It mixed hydrogen peroxide with iron salts to form a strong oxidation system, which can degrade organic matter in wastewater. With the development of the Fenton method, optical Fenton method [5–9] and electro Fenton method [10–14] appeared. The Fenton method can degrade refractory substances with fast reaction speed and mild conditions. The disadvantage of the Fenton reaction is that it needs strong acidic conditions. Alkali should be adjusted after the reaction to make iron ion precipitation flocculate, and acid-base consumption is high. A large amount of ferric hydroxide sludge is produced after the reaction.

With the development of water treatment research, enzymatic catalyst has gradually developed. Enzyme-mimetic catalyst mainly simplifies the structure of natural enzymes, extracts the key parts of natural enzymes, and makes them have similar catalytic activity as natural enzymes. These mimetic enzymes are usually characterized by mild reaction conditions, a small amount of catalysts and high activity. Common catalysts include metal porphyrins, metal phthalocyanines [15–17], and Schiff bases [18–20]. The second generation of iron-tetraamido macrocyclic ligand catalyst (Fe^{III}-TAML) [21, 22] designed by Carnegie Mellon University in the United States is a hydrogen peroxide mimetic enzyme. It has been reported that it has high catalytic activity for hydrogen peroxide [23, 24] and can be used as a sewage treatment reagent [25–27]. On the basis of its structure, the two methyl substituents at the tail were removed. A simplified Fe^{III}-TAML catalyst A (Figure 1) was synthesized. Since the two methyl groups were removed, 2,2-dimethylmalonyl chloride, one of the raw materials for the synthetic catalyst, was replaced with dimethyl malonate, and the cost of the synthesis of the new catalyst was nearly 10,000 times lower than that of the original catalyst.

At the same time, two other Fe^{III}-TAML catalysts with known structures (Fe^{III}-TAML catalyst B and Fe^{III}-TAML catalyst C, also shown in Figure 1) were synthesized, and the synthetic route of catalyst B was redesigned and optimized. In this article, the catalytic activity of catalyst A was investigated to determine the optimal conditions for its

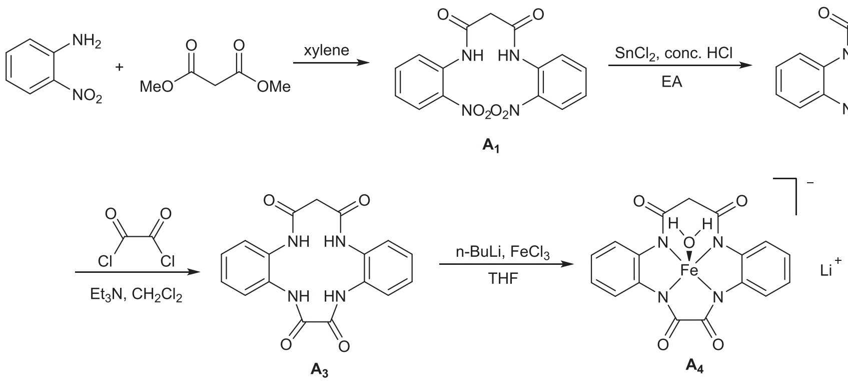


Figure 2. Synthetic route of dihydrogen Fe^{III}-TAML catalyst A.

reaction. The activities of catalysts were compared by treating methylene blue, methyl orange, neutral red, and Rhodamine B simulated dye wastewater.

2. Materials and methods

2.1. Materials

All reagents were analytical pure and solvents were dried by standard procedures before use. IR spectra were recorded on a Bruker Vector22 spectrophotometer. The ^1H (400 MHz) and $^{13}C\{^1H\}$ (100 MHz) NMR spectra were recorded on a Bruker AVANCE AV 400 MHz spectrometer in DMSO-d_6 or $CDCl_3$. The HRMS were recorded with an Agilent Q-TOF-6540 high resolution mass spectrometer. The dye absorbance was measured using a 722 spectrophotometer. The elemental analyses (C, H, N) were performed on a Elementar Vario EL CUBE.

2.2. Synthesis of dihydrogen Fe^{III}-TAML catalyst A

The synthesis of dihydrogen Fe^{III}-TAML catalyst A is shown in Figure 2. 2-Nitroaniline (10.0 g, 72.4 mmol) was dissolved in xylenes (50 mL) in a 100 mL round-bottom flask. Dimethyl malonate (0.5 eq, 4.78 g, 4.14 mL, 36.2 mmol) was added. The temperature of the system was raised to 180 °C. By controlling the temperature at the top of the column to lower than 100 °C, the distillate can be steamed out slowly in the branch pipe of the column. After heating for 12 h, the reaction was stopped and yellow solids precipitated after cooling to room temperature. After vacuum filtration, the solid was recrystallized with anhydrous ethanol. Yield: 86% (10.71 g). ^1H NMR (DMSO-d_6): 11.09 (s, 2 H, CONH), 8.80 (d, $J = 4.4$, 2 H, ArH), 8.26 (d, $J = 8.4$, 2 H, ArH), 7.72 (t, $J = 7.6$, 2 H, ArH), 7.29 (t, $J = 4.4$, 2 H, ArH), 3.76 (s, 2 H, CH_2). ^{13}C NMR (DMSO-d_6): 165.0, 137.2, 135.9, 133.7, 125.8, 124.2, 122.8, 47.0.

A_1 (5.0 g, 14.5 mmol) was dissolved in 30 mL ethyl acetate in a 250 mL round-bottom flask. Stannous chloride (6 eq, 19.66 g, 87.1 mmol) in 4.8 mL of concentrated hydrochloric acid was slowly dropped into the reaction system. After stirring for 4 h at room temperature, the yellow solution gradually became colorless and a white precipitate was formed. The acid was neutralized with ice cold aqueous NaOH and the pH of the aqueous layer

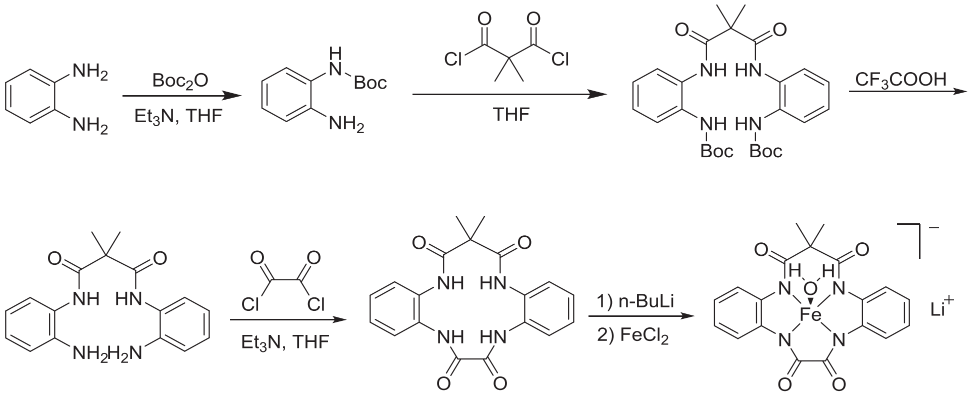


Figure 3. A reported synthetic route of Fe^{III}-TAML catalyst B.

was adjusted to 9–10, and the organic and aqueous layers were separated. The aqueous layer was extracted three times with EA (20 mL each). All organic layers were combined, dried over Na_2SO_4, and the solvent removed by rotary evaporation to afford white solid A_2. Yield: 92% (3.8 g). ^1H NMR (DMSO-d_6): 9.38 (s, 2 H, CONH), 7.15 (d, $J = 8.0$, 2 H, ArH), 6.94 (t, $J = 8.0$, 2 H, ArH), 6.73 (dd, $J_1 = 8.0$, $J_2 = 1.2$, 2 H, ArH), 6.55 (td, $J_1 = 7.6$, $J_2 = 1.2$, 2 H, ArH), 4.96 (s, 4 H, NH_2), 3.50 (s, 2 H, CH_2). ^{13}C NMR (DMSO-d_6): 166.1, 142.6, 126.4, 125.9, 122.7, 115.9, 115.4, 44.2.

A_2 (0.5 g, 1.76 mmol) was dissolved in CH_2Cl_2 (150 mL) in a 250 mL round-bottom flask. Triethylamine (2.2 eq, 392 mg, 0.54 mL, 3.87 mmol) was added with stirring. Oxalyl chloride (1 eq, 223 mg, 1.76 mmol) dissolved in CH_2Cl_2 (10 mL) was added dropwise to the solution in a dropping funnel with rapid stirring in an ice bath. During the reaction, a white solid was produced. Stirring was continued for 6 h, the liquid was filtered and the filtrate was evaporated. The obtained solid was recrystallized from acetonitrile and isopropyl alcohol. Yield: 71% (0.42 g). ^1H NMR (DMSO-d_6): 10.16 (s, 2 H, CONHR), 9.65 (s, 2 H, CONH), 7.88 (m, 4 H, ArH), 7.19 (m, 4 H, ArH), 3.18 (s, 2 H, CH_2). ^{13}C NMR (DMSO-d_6): 170.6, 159.2, 127.4, 126.6, 126.2, 125.3, 38.6.

A_3 (0.5 g, 1.48 mmol) was dissolved in freshly distilled THF (50 mL) under nitrogen; the solubility of the ligand was not good, and the solution was turbid. Under ice bath, n-BuLi (4 eq, 2.19 mL, 5.91 mmol) was added slowly to the system. The ligand was gradually dissolved. After stirring for 15 min, $FeCl_3$ (1 eq, 240 mg, 1.48 mmol) dissolved in freshly distilled THF (2 mL) was added to the system and the color of system became dark purple. After stirring for 8 h at room temperature, the solution was concentrated to 10 mL and then poured into 100 mL hexane to give a brown solid. Yield: 95% (0.42 g). FTIR (film, cm^{-1}): 3379 (Ph-H), 2955 (R-CH_2-R), 2858 (R-CH_2-R), 1685 (R-CO-NR_2), 1602 (Ph), 1540 (Ph), 1437, 1386, 1040, 865, 757, 516. ESI-HRMS $[M\text{-}18]^-$ m/z: calcd for $C_{17}H_{10}FeN_4O_4^-$ 390.1245, found 390.1240. Anal Calcd: C, 49.83; H, 2.49; N, 13.38; Found: C, 49.19; H, 2.91; N, 13.50.

2.3. Redesign and synthesis of Fe^{III}-TAML catalyst B

The synthesis of Fe^{III}-TAML catalyst B has been reported [21, 22], but its synthesis route is complex (Figure 3), involving the protection and deprotection of amino groups, which increases the cost of synthesis. To simplify the route and reduce the cost, we redesigned

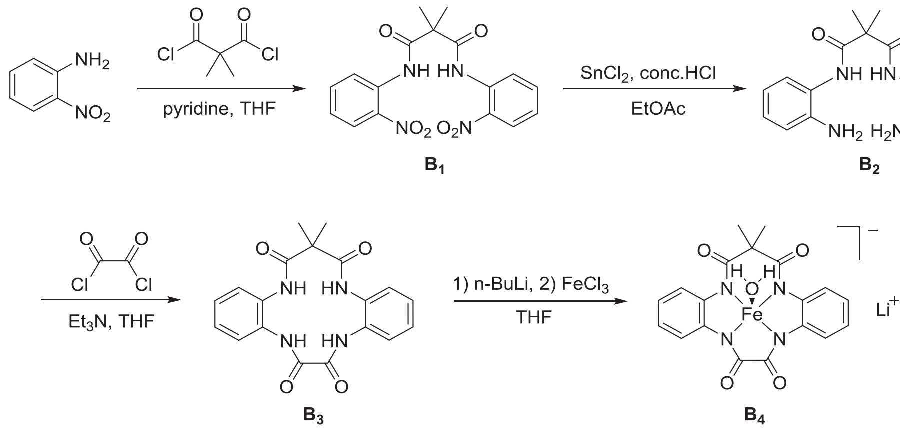


Figure 4. Improved synthesis of Fe^{III}-TAML catalyst B.

the synthetic route (Figure 4). The improved route uses 2-nitroaniline as a raw material, and 2-nitroaniline reacts with dimethylmalonyl dichloride to form amide intermediate B_1. The two nitro groups of B_1 are reduced to the amino group, and the resulting intermediate B_2 is further reacted with oxalyl chloride to give TAML (B_3). Finally, TAML complexes with the iron salt in the presence of n-BuLi to form Fe^{III}-TAML (B_4). The total yield of the improved synthetic route was increased from 30.1% to 49.5% compared with the reported route.

2-Nitroaniline (5.0 g, 36.2 mmol) was dissolved in freshly distilled THF (100 mL) in a 250 mL round-bottom flask. Pyridine (2.2 eq, 6.3 g, 6.43 mL, 79.6 mmol) was added. The temperature of the system is raised to 50 °C. Dimethylmalonyl dichloride (0.5 eq, 3.06 g, 1.38 mmol) dissolved in freshly distilled THF (10 mL) was added dropwise to the solution in a dropping funnel with rapid stirring in an ice bath. After 6 h, the mixture was cooled to room temperature and suction filtered, giving a yellow oily liquid by evaporation. Adding 20 mL of methyl tert-butyl ether and sonicating for 5 min to precipitate a large amount of yellow solid. The liquid was filtered, and the solid was washed with a small amount of methanol. Yield: 86.7% (5.84 g). ^{1}H NMR ($CDCl_3$): 11.15 (s, 2 H, CONH), 8.79 (dd, $J_1 = 1.2$, $J_2 = 8.4$, 2 H, ArH), 8.23 (dd, $J_1 = 1.6$, $J_2 = 8.4$, 2 H, ArH), 7.67 (td, $J_1 = 1.2$, $J_2 = 7.2$, 2 H, ArH), 7.22 (m, 2 H, ArH), 1.79 (s, 6 H, CH_3). ^{13}C NMR ($CDCl_3$): 171.7, 137.0, 136.0, 134.3, 125.8, 123.9, 122.6, 53.2, 23.7.

B_1 (0.5 g, 1.34 mmol) was dissolved in ethyl acetate (20 mL) in a 100 mL round-bottom flask. Stannous chloride (6 eq, 1.53 g, 8.06 mmol) in 1.6 mL of concentrated hydrochloric acid was slowly dropped into the reaction system. After stirring 4 h at room temperature, the yellow solution gradually became colorless and a white precipitate formed. The acid was neutralized with ice cold aqueous NaOH, the pH of the aqueous layer was adjusted to 9–10, and the organic and aqueous layers were separated. The aqueous layer was extracted three times with EA (20 ml each). All organic layers were combined, dried over Na_2SO_4, and solvent removed by rotary evaporation to afford white solid B_2. Yield: 96.1% (0.4 g). ^{1}H NMR (DMSO-d_6): 9.00 (s, 2 H, CONH), 6.95 (td, $J_1 = 8.8$, $J_2 = 0.8$, 4 H, ArH), 6.72 (dd, $J_1 = 0.8$, $J_2 = 8.0$, 2 H, ArH), 6.55 (td, $J_1 = 1.2$, $J_2 = 7.6$, 2 H, ArH), 4.89 (s, 4 H, NH_2), 1.57 (s, 6 H, CH_3). ^{13}C NMR (DMSO-d_6): 172.8, 144.1, 127.5, 126.8, 122.7, 115.8, 115.4, 50.7, 23.5.

B_2 (0.5 g, 1.6 mmol) was dissolved in freshly distilled THF (100 mL) in a 250 mL round-bottom flask. Triethylamine (2.2 eq, 356.3 mg, 0.49 mL, 3.52 mmol) was added with stirring. Oxalyl chloride (1 eq, 203 mg, 0.135 mL, 1.6 mmol) dissolved in freshly distilled THF (10 mL) was added dropwise to the solution in a dropping funnel with rapid stirring in an ice bath. During the reaction, a white solid was produced. Stirring was continued for 6 h, the liquid was filtered and the filtrate was evaporated. The obtained solid was recrystallized from acetonitrile and isopropyl alcohol. Yield: 64.3% (0.38 g). ^{1}H NMR (DMSO-d_6): 10.18 (s, 2 H, CONHR), 9.56 (s, 2 H, CONH), 7.51 (d, $J = 8.0$, 2 H, ArH), 7.35 (d, $J = 7.6$, 2 H, ArH), 7.26 (t, $J = 7.6$, 2 H, ArH), 7.17 (t, $J = 8.0$, 2 H, ArH), 1.58 (s, 6 H, CH_3). ^{13}C NMR (DMSO-d_6): 172.5, 161.8, 131.7, 130.7, 127.2, 126.5, 126.0, 125.4, 51.2, 23.3.

B_3 (0.5 g, 1.36 mmol) was dissolved in freshly distilled THF (50 mL) under nitrogen; the solubility of the ligand was not good, and the solution was turbid. Under ice bath, n-BuLi (4 eq, 1.37 g, 2.02 mL, 5.46 mmol) was added slowly to the system. The ligand gradually dissolved. After stirring for 15 min, $FeCl_3$ (1 eq, 221.4 mg, 1.36 mmol) dissolved in distilled THF (2 mL) was added to the system and the color of system became dark purple. After stirring for 8 h at room temperature, the solution was concentrated to 10 mL and then poured into 100 mL hexane to give a brown solid. Yield: 92.5% (0.53 g). FTIR (film, cm^{-1}): 3415 (Ph-H), 2956 (R-$(CH_3)_2$), 2872 (R-CH_3), 1640 (R-CO-NR_2), 1602 (Ph), 1570 (Ph), 1472, 1398, 1354, 1039, 754, 593. ESI-HRMS [M-18]$^-$ m/z: calcd for $C_{19}H_{14}FeN_4O_4^-$ 418.3082, found 418.3086.

2.4. Synthesis of Fe^{III}-TAML catalyst C

Fe^{III}-TAML catalyst C is based on the structure of Fe^{III}-TAML catalyst B, adding two nitro groups. According to relevant literature, introducing electron-withdrawing groups into Fe^{III}-TAML can improve the catalytic activity and stability of Fe^{III}-TAML. In this article, we synthesized it according to the methods reported [21, 22]. Yield 38.8%. FTIR (film, cm^{-1}): 3432, 2925, 2863, 1625, 1537, 1508, 1470, 1394, 1335, 737, 593. ESI-HRMS [M-18]$^-$ m/z: calcd for $C_{19}H_{12}FeN_6O_8^-$ 508.0072, found 508.0072.

2.5. Activity test method of Fe^{III}-TAMLs

A 100 mL dye sewage solution with a mass concentration of 30 mg/L was prepared and the initial absorbance was measured as A_0. The pH was adjusted with Na_2CO_3/$NaHCO_3$ buffer. An appropriate amount of Fe^{III}-TAML catalyst was added and mixed well. With the reaction temperature controlled by a water bath, a certain amount of H_2O_2 was added to initiate the reaction. After 30 min, the absorbance was measured and the decolorization was calculated.

$$\text{Decolorization} = \frac{A_0 - A_t}{A_0} \times 100\%$$

The method for measuring chemical oxygen demand (COD) was carried out in accordance with the national standard GB 11914-89 (Determination of COD in water quality). Deionized water (20 mL) was added to a 500 mL reaction flask, followed by $HgSO_4$ (0.4 g), standard potassium dichromate solution (10 mL), and standard H_2SO_4-

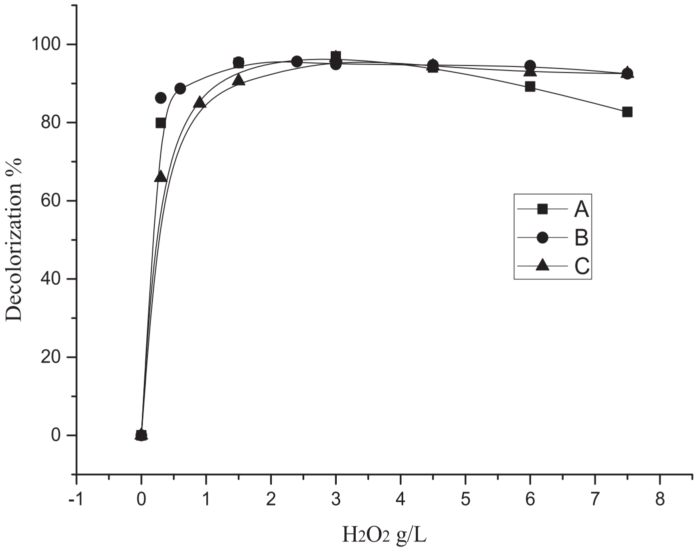


Figure 5. Influence of hydrogen peroxide dosage on decolorization.

Ag_2SO_4 solution (30 mL). After heating to reflux for 2 h, the solution was cooled to room temperature, and 3 drops of Ferroin solution was added as an indicator. The system was titrated with a solution of ammonium ferrous sulfate, and the volume of the consumed ammonium ferrous sulfate was recorded as V_0. The water sample to be tested is treated as described above, and the volume of the consumed ammonium ferrous sulfate is recorded as V_1.

$$\mathrm{COD_{Cr}} = \left[(V_0 - V_1) \times c \times 8 \times 1000\right]/V$$

In the above formula, V is the water sample volume (mL) and c is the concentration of ammonium ferrous sulfate (mol/L).

3. Results and discussion

3.1. Effect of hydrogen peroxide dosage in the reaction

Fe^{III}-TAML catalysts A, B, and C were selected to test the treatment of methylene blue simulated wastewater. The effect of hydrogen peroxide dosage on the degradation of dyes was studied at 25 °C, $C_{Fe\text{-}TAML} = 25$ mg/L, and pH = 8. The reaction results are shown in Figure 5. The decolorization increases with increase of hydrogen peroxide. Increasing the concentration of hydrogen peroxide can increase the concentration of high valent iron and·OH in the reaction system, which can degrade dyes more quickly. However, it was also observed that the decolorization decreased if the amount of hydrogen peroxide continued to increase. This is because excessive hydrogen peroxide competes with substrates and combines with high valent iron produced in the reaction process, resulting in lower reaction rate and decolorization. Considering the experimental results and the cost of reagents, we consider that the optimal amount of hydrogen peroxide used in the catalytic reaction is 1.5 g/L.

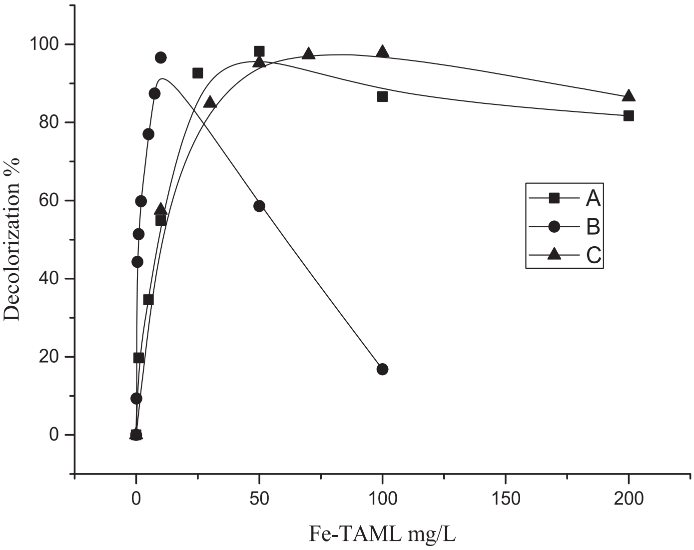


Figure 6. Influence of Fe^{III}-TAMLs dosage on decolorization.

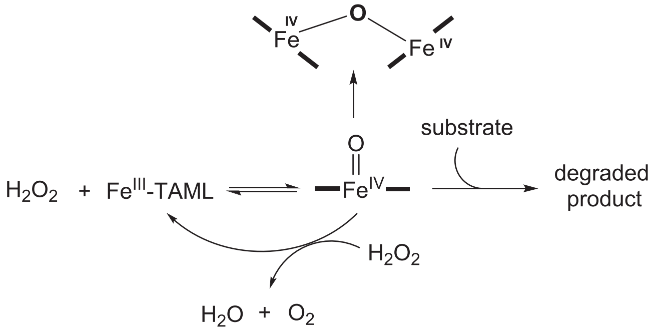


Figure 7. Catalytic reaction process.

3.2. Effect of Fe^{III}-TAMLs concentration on the reaction

Fe^{III}-TAML catalysts A, B, and C were selected to test the treatment of methylene blue simulated wastewater. The effect of Fe^{III}-TAMLs concentration on the degradation of dyes was studied at 25 °C, $C_{\text{hydrogen peroxide}} = 1.5$ g/L and pH = 8. The reaction results are shown in Figure 6. Decolorization increases with increase of catalyst concentration in a certain range, because the increase of catalyst concentration accelerates the formation of active intermediates. However, if the catalyst concentration continues to increase, the decolorization decreases. This is because the reaction rate of catalyst with hydrogen peroxide to produce active intermediates is faster than that of active intermediates and substrates, which results in the loss of some active intermediates during the reaction process, so the decolorization decreases. The reaction process is shown in Figure 7 [28]. Considering the experimental results and the cost of reagents, we consider that the optimal dosage of three Fe^{III}-TAML catalysts A, B, and C is 50 mg/L, 10 mg/L, and 50 mg/L, respectively.

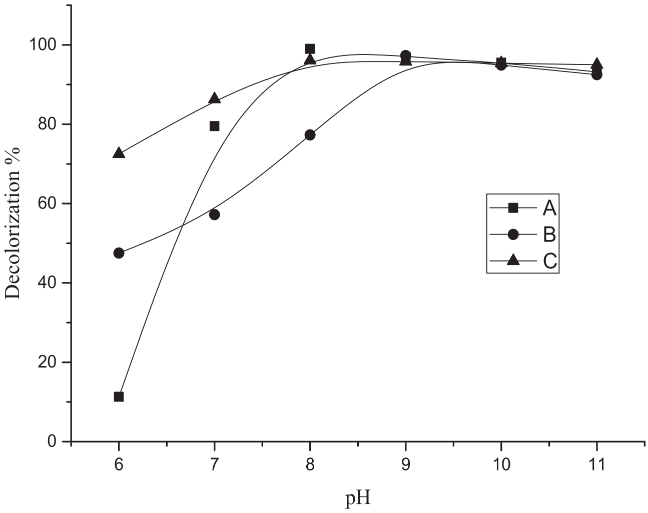


Figure 8. Influence of pH on decolorization.

3.3. Effect of pH in the reaction

Fe^{III}-TAML catalysts A, B, and C were selected to test the treatment of methylene blue simulated wastewater. The effect of pH on the degradation of dyes was studied 25 °C, $C_{\text{hydrogen peroxide}} = 1.5\,\text{g/L}$ and $C_{\text{Fe-TAML}} = 25\,\text{mg/L}$. The reaction results are shown in Figure 8. Decolorization of the reaction is low under acidic conditions because the catalyst is not stable at low pH. The hydrogen ion attacking the nitrogen causes the Fe-N bond to break and the catalyst loses its activity. With increase of pH, the decolorization increased gradually. When the reaction pH exceeded 9, the decolorization began to decrease, because hydrogen peroxide is a weak acid, which decomposes rapidly in strong alkaline environment. The results show that the optimum reaction pH of Fe^{III}-TAML catalyst A and Fe^{III}-TAML catalyst B is 8, and that of Fe^{III}-TAML catalyst C is 9.

3.4. Effect of temperature in the reaction

Fe^{III}-TAML catalyst A was selected to test the treatment of methylene blue simulated wastewater. The effects of temperature on catalytic reaction were investigated at $C_{\text{hydrogen peroxide}} = 1.5\,\text{g/L}$, $C_{\text{Fe-TAML}} = 25\,\text{mg/L}$, and pH = 8. The reaction results are shown in Figure 9. When the temperature increases from 20 °C to 30 °C, the reaction rate increases significantly and the decolorization increases within 30 min. This is because the temperature provides enough energy for the reaction system to accelerate the molecular motion and the rate of production of the reactive intermediates, thereby increasing the decolorization. When the temperature increases from 30 °C to 40 °C, the reaction rate at 40 °C is slightly lower than that at 30 °C. This may be due to two reasons: (1) with increase of temperature, the decomposition rate of hydrogen peroxide increases, and hydrogen peroxide cannot react with catalyst to form active intermediates, but converted into water and oxygen directly; (2) with increase of temperature, some active intermediates lose their activity before they can fully contact with organic pollutants, which leads to the decrease of decolorization.

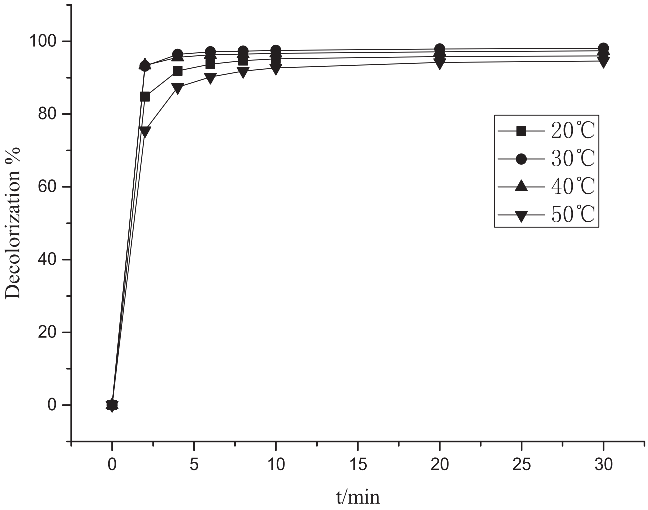


Figure 9. Effect of reaction temperature on decolorization.

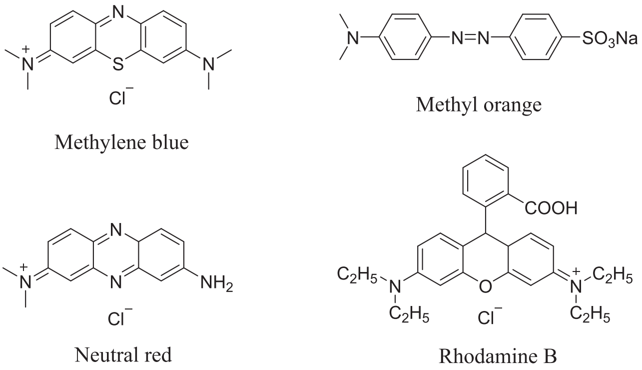


Figure 10. Structural formulas of four dyes.

Table 1. Degradation effect of catalyst A.

Dye	Methylene blue	Methyl orange	Neutral red	Rhodamine B
λ_{max} (nm)	664	464	530	554
Decolorization %	96.1	74.8	83.7	84.0
COD removal %	63.7	46.9	50.1	53.6

3.5. Treatment of four kinds of simulated dye sewage

Methylene blue, methyl orange, neutral red, and Rhodamine B (Figure 10) simulated dye wastewater were treated with the optimum reaction conditions of A, B and C. The decolorization and COD removal were determined after 30 min. The results are shown in Tables 1, 2, and 3, respectively. From the results of treating four dyes with three catalysts, there are some differences in the activity of the three catalysts. The best catalytic effect is Fe-TAML catalyst C, while the catalytic effect of Fe-TAML catalyst B is slightly better than that of Fe-TAML catalyst A.

Table 2. Degradation effect of catalyst B.

Dye	Methylene blue	Methyl orange	Neutral red	Rhodamine B
λ_{max} (nm)	664	464	530	554
Decolorization %	98.9	79.3	93.7	95.4
COD removal %	66.6	57.5	62.9	60.3

Table 3. Degradation effect of catalyst C.

Dye	Methylene blue	Methyl orange	Neutral red	Rhodamine B
λ_{max} (nm)	664	464	530	554
Decolorization %	99.6	95.6	97.2	99.6
COD removal %	71.8	62.4	65.3	76.0

The structure of the three catalysts shows that the biggest difference between Fe-TAML catalyst C and Fe-TAML catalyst B is that there are two nitro groups in the molecule. Nitro is a strong electron-accepting group, which greatly reduces the charge of iron in the molecule, and makes it easier to combine with hydrogen peroxide to form the active high valent iron, so its catalytic activity is the highest. Compared with Fe-TAML catalyst A and Fe-TAML catalyst B, there is a bare methylene in the Fe-TAML catalyst A molecule. The secondary C-H bond of the catalyst is somewhat active, and the structure of the catalyst is destroyed and inactivated in the strong oxidation environment.

Therefore, the activity of Fe-TAML catalyst A is slightly lower than that of Fe-TAML catalyst B. In general, Fe-TAML catalyst A has the activity of catalyzing hydrogen peroxide to degrade dye wastewater. Although it is not as good as Fe-TAML catalyst B and Fe-TAML catalyst C, its synthesis cost is much lower than the latter, and it has more practical value.

4. Conclusion

In this article, a new simplified Fe-TAML was synthesized. Fe-TAML catalyst is a peroxidase-like complex used to catalyze the degradation of organic pollutants in water by hydrogen peroxide. The cost of synthesis is much lower than that of existing Fe-TAML catalysts, and it has practical value in this field. In addition, the synthesis of dimethyl Fe-TAML catalyst was redesigned and synthesized, which reduced the synthesis steps and costs. Next, we will continue to design new structures of Fe-TAML catalysts to further simplify its structure and enhance its stability in water.

Disclosure statement

There are no conflicts of interest to declare.

Acknowledgement

The authors gratefully acknowledge Professor Wang Qing for her contribution to this project.

Funding

This work was supported by the National Natural Science Foundation of China (No. 21272022).

ORCID

Run Zhou http://orcid.org/0000-0002-1350-5409

References

[1] P.X. Gao. *Chem. Manage.*, **30**, 191 (2018).

[2] H. Ates, M.E. Argun. *Water Sci. Technol.*, **78**, 1064 (2018).

[3] M. Srivastav, M. Gupta, S.K. Agrahari, P. Detwal. *CEE.*, **6**, 8 (2019).

[4] R.-L. Hao, X.-H. Wang, Y.-H. Liang, Y.-J. Lu, Y.-M. Cai, X.-Z. Mao, B. Yuan, Y. Zhao. *Chem. Eng. J.*, **330**, 1279 (2017).

[5] A.E.E. Sarajar, R.P. Ramadhania, P. Purwanto. *MATEC Web Conf.*, **156**, 03048 (2018).

[6] X. Guo, K. Wang, Y. Xu. *Mater. Sci. Eng., B*, **245**, 75 (2019).

[7] X.S. Nguyen, K.D. Ngo. *J. Surface Eng. Mater. Adv. Technol.*, **8**, 1 (2018).

[8] L. Clarizia, D. Russo, I.D. Somma, R. Marotta, R. Andreozzi. *Appl. Catal., B*, **209**, 358 (2017).

[9] C. Catrinescu, D. Arsene, P. Apopei, C. Teodosiu. *Appl. Clay Sci.*, **58**, 96 (2012).

[10] V. Poza-Nogueiras, E. Rosales, M. Pazos, M.Á. Sanromán. *Chemosphere*, **201**, 399 (2018).

[11] M. Labiadh, M.A. Oturan, M. Panizza, N.B. Hamadi, S. Ammar. *J. Hazard. Mater.*, **297**, 34 (2015).

[12] P.V. Nidheesh, R. Gandhimathi. *Desalination*, **299**, 1 (2012).

[13] M.-H. Zhou, Q.-Q. Tan, Q. Wang, Y.-L. Jiao, N. Oturan, M.A. Oturan. *J. Hazard. Mater.*, **215**, 287 (2012).

[14] S. Liu, X.-R. Zhao, H.-Y. Sun, R.-P. Li, Y.-F. Fang, Y.-P. Huang. *Chem. Eng. J.*, **231**, 441 (2013).

[15] A. Korkmaz, Y. Yilmaz. *MGC.*, **18**, 31 (2019).

[16] J.-Y. Zhou, F. Wu, Z.-X. Zhu, T.-F. Xu, W.-Y. Lu. *Chem. Eng. J.*, 328, 915 (2017).

[17] F. Ali, S.B. Khan, T. Kamal, Y. Anwar, K.A. Alamry, A.M. Asiri. *Carbohydr. Polym.*, **173**, 676 (2017).

[18] L. Wang, Y. Hou, X. Zhong, J. Hu, F. Shi, H. Mi. *Carbohydr. Polym.*, **208**, 42 (2019).

[19] M. Neamtu, F. Macaev, V. Boldescu, V.-D. Hodoroaba, C. Ntdejde, R.J. Schneider, A. Paul, G. Ababei, U. Pannec. *Appl. Catal., A*, **183**, 335 (2016).

[20] S. Araya, S. Quan, J. Man-Ke, M. Wan-Hong, D.M. Johnson, H. Ying-Ping. *Water Air Soil Pollut.*, **227**, 284 (2016).

[21] W.C. Ellis, C.T. Tran, M.A. Denardo, A. Fischer, A.D. Ryabov, T.J. Collins. *J. Am. Chem. Soc.*, **131**, 18052 (2009).

[22] W.C. Ellis, C.T. Tran, R. Roy, M. Rusten, A. Fischer, A.D. Ryabov, B. Blumberg, T.J. Collins. *J. Am. Chem. Soc.*, **132**, 9774 (2010).

[23] M.R. Mills, L.Q. Shen, D.Z. Zhang, A.D. Ryabov, T.J. Collins. *Inorg. Chem.*, **56**, 10226 (2017).

[24] Y. Somasundar, L.Q. Shen, A.G. Hoane, L.L. Tang, M.R. Mills, A.E. Burton, A.D. Ryabov, T.J. Collins. *J. Am. Chem. Soc.*, **140**, 12280 (2018).

[25] A.C. Weitz, M.R. Mills, A.D. Ryabov, T.J. Collins, Y.-S. Guo, E.L. Bominaar, M.P. Hendrich. *Inorg. Chem.*, **58**, 2099 (2019).

[26] P.-Y. Xu, Y.-C. Liu, X.-Y. Ma. *Indus. Water Treat.*, **36**, 44 (2016).

[27] E. Beach, R.T. Malecky, R.R. Gil, C.P. Horwitz, T.J. Collins. *Catal. Sci. Technol.*, **1**, 437 (2011).

[28] A. Chanda, A.D. Ryabov, S. Mondal, L. Alexandrova, A. Ghosh, Y. Hangun-Balkir, C.P. Horwitz, T.J. Collins. *Chem. Eur. J.*, **12**, 9336 (2006).