SCIENCE CHINA
Chemistry

• ARTICLES •

doi: 10.1007/s11426-014-5238-0

# Hemin associated to cetyltrimethylammonium broide micelles: a biomimetic catalyst for 2,4,6-trichlorophenol degradation

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Received August 29, 2014; accepted October 15, 2014

For the first time, an efficient, green, economical biomimetic catalyst (hemin-cetyltrimethylammonium bromide micelles) was discovered to degrade 2,4,6-trichlorophenol (TCP). The degradation experiments indicate that pH, temperature, the addition of 2-methylimidazole, and the amount of hydrogen peroxide influence the degradation process. Test of reusability revealed that CTAB micelles can protect hemin from destruction by $H_2O_2$ and that the materials can be recycled. This material can be of great use for waste-water treatment.

**hemin-CTAB micelles, biomimetic catalyst, degrade, TCP, recycle**

## 1 Introduction

Polychlorinated phenols such as 2,4,6-trichlorophenol (TCP) have been widely used as herbicides, fungicides, pesticides, insecticides, pharmaceuticals and dyes. Due to their high toxicity, carcinogenic properties, and persistence in the environment, they have been listed as a group of priority pollutants by the US Environmental Protection Agency [1]. Therefore, an efficient chemical treatment process is needed in order to effectively degrade chlorophenols. Recently, an advanced oxidation process (AOP) has been developed. During AOP, highly reactive hydroxyl radicals are produced that can oxidize most of the organic pollutants; therefore, AOP technique has been widely used for degradation of many persistent contaminants [2–5]. As one of the AOPs, the Fenton process (FP) has been used in the degradation of phenols and chlorophenols [6–9]. Compared to other AOPs, FP has several advantages. First, $H_2O_2$ is used as the stoichiometric oxidant, which gives water as the only by-product [10,11]. The degradation process is therefore environmentally friendly. Second, FPs can be conducted under mild conditions [12–14].

$H_2O_2$ does not oxidize TCP in the absence of catalysts, however. Previous studies have shown that, using hydrogen peroxide as the oxidant, horseradish peroxidase (HRP) [15–17], the extracellular lignin peroxidases of phanerochaete chrysosporium [18], myoglobin (Mb) under conditions of oxidative stress [19], and chloroperoxidase (CPO) from caldariomyces fumago [20,21] could mediate the oxidation of chlorinated phenols. The iron complexes of porphyrins (e.g. hemin) are known to form the active sites of a variety of systems such as HRP, Mb and CPO. Studies have shown that hemin can be used to mimic the functions of natural enzyme [22–33]. However, a hemin molecule in the absence of a protein matrix easily undergoes dimerization in aqueous solution, which has limited its utility for the degradation of contaminants in waste-water.

To stabilize the monomeric form of hemin, it is immobilized on various substrates such as methacrylamide-ethylene glycol dimethacrylate copolymer [34], ß-cyclodextrin [35], and the surface of a glassy carbon electrode to degrade TCP [36]; 2,6-dichlorobenzo-quinone (DCQ) is the main product of these approaches (Scheme 1). However, these immobili-

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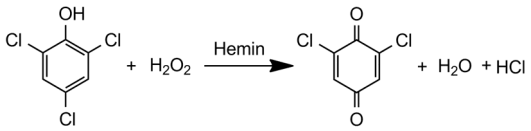
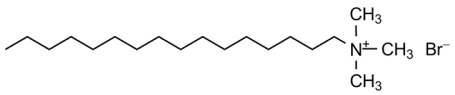



**Scheme 1** Fenton oxidation of TCP to form quinone product by a hemin-$H_2O_2$ system.

zation processes are generally so complicated as to increase the degree of difficulty in practical application. Moreover, during these immobilization processes, only a small part of the hemin could be adsorbed to the substrate. It is therefore necessary to develop an efficient, environmentally friendly, and economical biomimetic catalyst [26].

The surfactant molecule is usually composed of two parts: a long-chain hydrocarbon "tail" and a polar "head". The two polar head groups undergo a repulsive electrostatic interaction to form micelles above a well-defined threshold concentration (i.e. the critical micelle concentration, CMC). At CMC, the long-chain hydrocarbon tails meet at a common center space and the charged polar groups form a multicharged surface. Micelles, which are usually spherical in shape, can be cationic, anionic, or nonionic. Cetyltrimethylammonium bromide (CTAB) is one kind of cationic surfactant (Sheme 2). Generally, the CMC of CTAB is 0.0009 mol/L in water, and the aggregation number of one spherical micelle is 62 at 25 °C. In a solution containing surfactants, an organic molecule is usually located in the hydrophobic center of the micelles and could increase the concentration of dissolved organic matter in the solution [37–43]. For example, the insoluble porphyrins are highly soluble in water in the presence of detergents such as CTAB (Figure 1).

As we know, the catalytic efficiency of hemin is low in comparison with natural peroxidase enzyme due to the lack of hydrophobic polypeptide and amino acid residues such as histidine-170 and histidine-42 [44–51]. The imidazole group in these two forms of histidine is generally considered to be the essential functional group in the catalytic oxidation process of HRP. The objective of this study was to form a hemin-CTAB complex to stabilize the monomeric form of hemin and utilize this composite as the catalyst to degrade TCP. Some imidazole bases were used to mimic the function of amino acid residues. In addition, we conducted a recycling experiment to test the stability of this new material.




**Scheme 2** Chemical structure of CTAB.

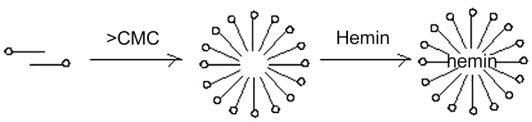



**Figure 1** The formation of monomeric hemin intercalated in CTAB micelles.

## 2 Experimental

### 2.1 Chemicals

Hemin, CTAB, imidazole (Im), 2-methylimidazole (2-MeIm), 4-methylimidazole (4-MeIm), histamine, and TCP were purchased from Sigma-Aldrich (USA). Methanol (MeOH), acetonitrile ($CH_3CN$), and acetic acid (HAC) were of HPLC grade and purchased from Tedia (USA). $C_6H_5Na_3O_7 \cdot 2H_2O$, $Na_2HPO_4 \cdot 7H_2O$, $NaH_2PO_4 \cdot 2H_2O$, $CH_3COONa \cdot 3H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, sodium hydroxide, boric acid, citric acid, dimethyl sulfoxide (DMSO), and $H_2O_2$ (30%) were of all analytical grade and obtained from Nanjing Chemical Corporation (China). All of the chemicals were used as received.

Hemin stock solution (5 mmol/L) was prepared by dissolving hemin in 1 mL of DMSO and shaking until fully dissolved. TCP stock solution (5 mmol/L) was prepared in methanol. Im, 2-MeIm, 4-MeIm, and histamine were dissolved in methanol to prepare 5 mmol/L of solution. $H_2O_2$ (3%) was obtained by diluting $H_2O_2$ (30%) by ultrapure water. Various pH buffers were made from the corresponding salts, acids, and bases. Sodium citrate-sodium phosphate was used for pH 3.0, sodium acetate buffer for pH 4.0–5.0, and sodium phosphate buffer for pH 6.0–7.0.

### 2.2 Preparation of CTAB micelles and hemin-CTAB micelles

When the concentration is below its CMC, CTAB molecules exist as the monomer in aqueous solution [52–56]. When the initial CTAB concentration is greater than its CMC [57–59], CTAB micelles form in the solution. In our study, 24 mg of CTAB was added to 30 mL of acetic buffer (pH 4) to obtain CTAB micelles (the concentration of CTAB is 2.2 mmol/L, larger than its CMC of 0.9 mmol/L). Then, 180 μL of hemin (5 mmol/L) was added into the solution of CTAB micelles until the concentration of hemin was 30 μmol/L. The hemin-CTAB micelles were used as the catalyst for the degradation of TCP by $H_2O_2$.

### 2.3 Batch degradation assays

The concentrations of TCP during the degradation process were monitored by a high-performance liquid chromatography (HPLC, Waters Alliance, USA) instrument equipped with a Symmetry C18 column. The mobile phase was composed of 15% acidified water (0.5% acetic acid) and acetonitrile (15:85, *v*/*v*) at a flow rate of 1.0 mL/min. The UV

detector was operated at a wavelength of 220 nm; the injection volume was 20 μL. The column temperature was set at 30 °C. The total analysis time was 5 min; the elution time of the TCP was 3.9 min. The standard curve of the TCP concentrations is provided in Figure S1 (see Supporting Information online). Ratio of $H_2O_2$/TCP, reaction pH, molar ratio of substrate-to-catalyst, effect of imidazole structure, and temperature were optimized for the degradation of TCP. Last, the degradation kinetic of TCP was carried out in these optimum conditions and the results were compared to those in ordinary conditions.

### 2.4 Test of reusability

The test for reusability of hemin-CTAB-micelle catalyst was conducted under the optimized conditions described above. The initial concentration of TCP was 90 μmol/L and the radio of hydrogen peroxide to the substrate was 5:1. This test revealed that most of the TCP was degraded in 2 h. Therefore, we calculated the degradation efficiency by the remaining concentration of TCP determined by HPLC after 2 h. Next, the amount of TCP was replenished to maintain the initial concentration and the same amount of $H_2O_2$ was added to initiate the reaction. After another 2 h, the degradation efficiency was obtained for the second cycle, which allowed us to calculate the reusability of the materials.

## 3 Results and discussion

### 3.1 UV-Vis scan of the hemin-CTAB micelles

Metal porphyrins are not soluble in neutral and acidic aqueous solution. They also have a marked tendency to aggregation to dimers and oligomers in alkaline solution, which has little or no activity. However, they are highly solubilized as the active monomer in the presence of detergents such CTAB (see Introduction). The UV-Vis absorption of hemin in CTAB micelles solution has a Soret peak at 396 nm, which indicates that monomer is the predominant form (Figure 2). The molar extinction coefficient for the hemin-CTAB micelles system is $0.42\times10^5$ L/(mol cm).

The color of the hemin-CTAB micelles solution is reddish. Simplicio *et al.* [41] discovered that intercalated hemin is associated with an acid-base equilibrium between a red diaquo form ($M(H_2O)_2\cdot$Micelles) and a green monoaquomonohydroxy form (Me(OH)·Micelles):

$$M(H_2O_2)\cdot\text{Micelles} \rightleftarrows \text{Me(OH)}\cdot\text{Micelles}+H^+$$

The p$K_a$ of this equilibrium is 5.5; the green (Me (OH)·Micelles) changes to a reddish $M(H_2O)_2\cdot$Micelles below pH 5 [41]. Therefore, at pH 4, hemin mainly takes a red diaquo form ($M(H_2O)_2\cdot$Micelles).

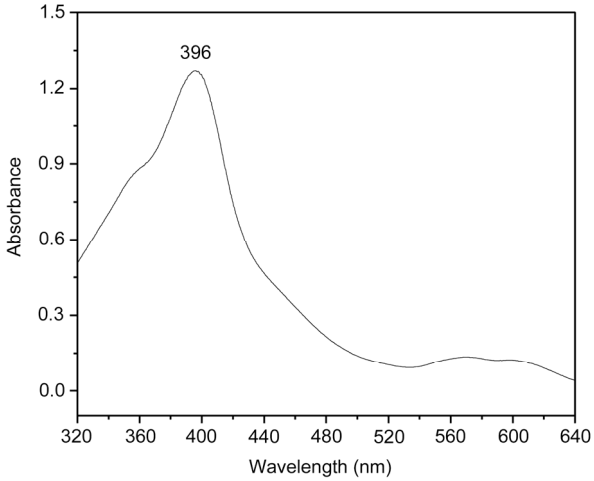



**Figure 2** UV-Vis spectra of 30 μmol/L hemin in CTAB micelles in acetate buffer (pH 4).

### 3.2 Optimization of the reaction conditions

#### 3.2.1 The ratio of $H_2O_2$/TCP

The degradation of TCP in different $H_2O_2$/TCP ratios is presented in Figure 3. It may be observed that doses of $H_2O_2$ significantly influenced the degradation of TCP. At the low ratio of $H_2O_2$/TCP (1:1), more than 50% of the initial TCP was not degraded. When we increased the ratio of $H_2O_2$/TCP to 2:1, about 93% of the TCP was degraded. At a 5:1 ratio of $H_2O_2$/TCP, about 97% of the TCP was degraded. When we continued to increase the ratio of $H_2O_2$/TCP to 10:1 and 15:1, there was no obvious change in the degradation of TCP. However, we must consider the destruction of the catalyst-hemin in the presence of large amounts of $H_2O_2$ in the solution. To achieve the efficient removal of TCP and also recycle the catalyst, we set the optimum ratio of $H_2O_2$/TCP at 5:1.

#### 3.2.2 pH dependence

The degradation of TCP by Fenton reaction is greatly influenced by the pH of the system. In the literature, many researchers studied the Fenton reaction for treating wastewater and concluded that the optimal pH range of the Fenton process was between 2 and 4 [60–63]. Figure 4 shows the pH dependence of TCP oxidation by hemin-CTAB micelles solution. At pH 3–5, higher degradation of TCP was observed (>70%). However, there was little degradation at pH 6–7. At pH 4, almost all of the TCP could be degraded. Given these results above, the remainder of our experiment was carried out at pH 4.

#### 3.2.3 The substrate-to-catalyst molar ratio

The substrate-to-catalyst (S/C) molar ratio usually reveals catalytic efficiency. It is a great challenge to decrease the catalyst amount to obtain a high catalytic efficiency. The degradation of hemin-CTAB micelles toward TCP oxida-

tion at different S/C molar ratios is listed in Table 1. It could be concluded that TCP could be fully degraded by hemin-CTAB micelles solution at the S/C ratio of 3–14.

The monomeric CTAB molecules could form micelles through a self-assembly process as the concentration reaches its CMC. Then, the CTAB micelles would encapsulate the catalyst-hemin in the center and isolate it from each other to retain the monomeric form. However, because there is interspace in the CTAB micelles, the $H_2O_2$ could disperse into the hydrophobic region of the micelles to react with hemin to form a ferryl porphyrin radical cation species (Compound I). The substrate "TCP" in the micelles would then be degraded in the interspace. Such a reaction is homogenous, which is quite different from the hemin immobilized on the substrate. However, the CTAB-micelles could act as the hydrophobic center to protect the hemin from destruction by $H_2O_2$ and radical-induced damage, and could concentrate the substrate around the catalyst to facilitate the reaction.

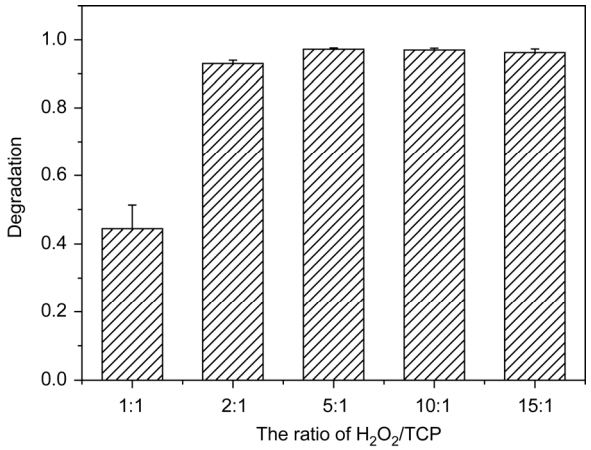



**Figure 3** The ratio of $H_2O_2$/TCP on the degradation of TCP. Reaction conditions: 30 μmol/L hemin-CTAB micelles, 100 μmol/L TCP at $H_2O_2$/TCP ratios of 1:1, 2:1, 5:1, 10:1, and 15:1.

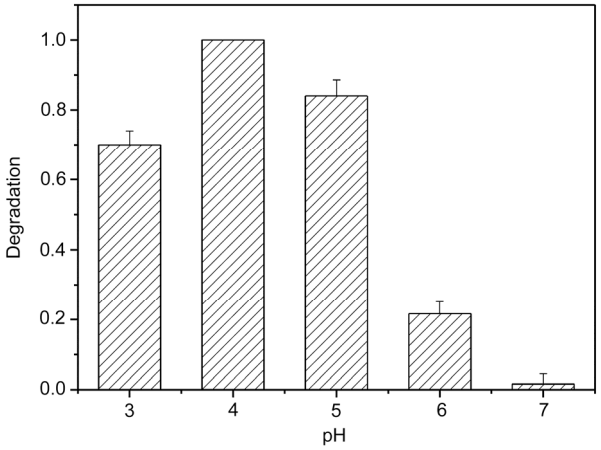



**Figure 4** pH dependence for degradation of TCP by hemin-CTAB micelles solution. Reaction conditions: 30 μmol/L hemin-CTAB micelles, 100 μmol/L TCP, 5:1 $H_2O_2$/TCP ratio.

**Table 1** Hydrogen peroxide oxidation of TCP catalyzed by hemin-CTAB micelles

| Run | Catalyst | C/S (mol%) | pH | Conversion (%) |
|---|---|---|---|---|
| 1 | Hemin | 3 | 4 | 100 |
| 2 | Hemin | 4 | 4 | 98.9 |
| 3 | Hemin | 6 | 4 | 98.8 |
| 4 | Hemin | 8 | 4 | 98.0 |
| 5 | Hemin | 14 | 4 | 97.0 |

a) Reaction conditions: 30 μmol/L hemin in the CTAB micelles, and the ratio of $H_2O_2$:TCP is 5:1.

### 3.2.4 Effect of imidazole bases

The distal histidine (His-42) of HRP can promote the formation of Compound I and plays an important role in peroxidase catalysis [64–66]. Basically, it is the imidazole group in histidine that is generally considered to be as the essential functional group in the catalytic oxidation process of HRP [44–51]. We therefore investigated the effects of different imidazole bases on the activity of hemin-CTAB micelles (Figure S2). The activity for hemin-CTAB micelles without the addition of imidazole base was defined as 100%. At pH 4, the reaction was enhanced by the presence of imidazole bases at the low ratio of imidazole bases/hemin (1:1). For the most effective imidazole base 2-MeIm, the relative activity could increase to 150%. Similar results have appeared in the literature. Newmyer *et al.* [51] compared the effectiveness of different imidazoles in stimulating catalysis of an H42A mutant of HRP. They concluded that 2-substituted imidazoles such as 2-MeIm were the most effective imidazoles because the 2-substituted imidazoles did not coordinate to the iron. Im and 1-MeIm, which both coordinated to the heme iron atom, were found to be less effective. Therefore, in the literature, 2-substituted imidazoles are generally considered to be the sterically hindered imidazole bases [67]. Similarly, Uno *et al*. [68] have discovered that at acidic pH, the bis-coordination of the imidazole base to the iron atom of hemin is enhanced, and that the unhindered bases are less effective activators. Sterically hindered 2-MeIm, which could effectively lower the formation of bis-ligating hemin, resulted in higher activity. Therefore, due to the stereo-hindrance effect, 2-MeIm can effectively inhibit the bis-ligating hemin and has the best effect on the degradation of TCP.

We changed the ratio of 2-MeIm/hemin to find the optimum ratio for the degradation of TCP (Figure 5). At the low ratio of 2-MeIm/hemin (1:1), the relative activity could increase to 150%. However, as more 2-MeIm was used (2-MeIm/hemin ratios of 2:1, 3:1, and 4:1), the relative activity decreased to about 110%. This result was probably because that part of the excessive imidazole bases coordinated with iron atoms to form bis-ligating hemin, even in the sterically hindered imidazole bases "2-MeIm". As a result, both the fifth and sixth sites were occupied by 2-MeIm, and there was no blank site for $H_2O_2$ to oxidize the

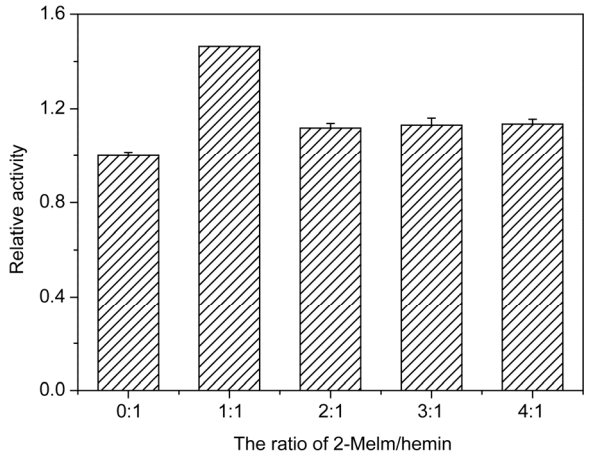



**Figure 5** The ratio of 2-MeIm/hemin for degradation of TCP by hemin-CTAB micelles (comparing the degradation percentage of TCP in the first 30 min). Reaction conditions: 30 μmol/L hemin-CTAB micelles, 230 μmol/L TCP, 5:1 $H_2O_2$/TCP ratio.

ferric hemin(III) to form Compound I to degrade the TCP. Therefore, in the following experiment, we set the ratio of 2-MeIm/hemin to 1:1.

### 3.2.5 Effect of temperature

The effect of temperature on the degradation rate of TCP was studied at 25, 40 and 60 °C (Figure 6). With the increase of temperature, the degradation percentage of the TCP increased. The activity for hemin-CTAB micelles at 25 °C was defined as 100%. The relative activity was respectively enhanced to 160% at 40 °C and 300% at 60 °C. Because high temperature results in high-energy collisions among the substrate, catalyst, and $H_2O_2$, and also increases the substrate degradation. We could increase the removal rate of TCP by elevating the reaction temperature. However, the enzyme-catalyzed reaction rate initially rises as the temperature increases. The rate is then negatively affected at the higher temperatures; most of the enzymes will be deactivated at 40 °C. In addition, the enzyme will be stored at 4 °C or lower. These, harsh conditions for the storage and usage of the enzyme as well as the high price of the enzyme have greatly limited its use in practical application. However, the newly formed hemin-CTAB micelles show better thermostability at high temperatures. Moreover, hemin-CTAB micelles show extremely better activity (three fold) for the degradation of TCP at high temperatures than at room temperature. For all of these reasons, the easily obtained hemin-CTAB-micelles catalyst is promising for the treatment of waste water containing TCP, instead of using HRP and other enzymes.

Above all, the degradation experiments indicate that pH, temperature, the addition of 2-MeIm and the amount of hydrogen peroxide influence the degradation process. We carried out two reactions at the optimum ratio of $H_2O_2$/TCP (5:1) in an acetate buffer (pH 4), but only one was successful (with the addition of 2-MeIm and at a high temperature of 60 °C). The degradation kinetic results of TCP are shown in Figure 7. Without 2-MeIm at room temperature, the degradation curve was nearly linear over a total degradation time of 12 h (Figure 7(a)). However, with the addition of 2-MeIm at 60 °C, 90% of the TCP was degraded in 2 h (Figure 7(b)). We can thus optimize conditions and obtain a high degradation rate for TCP, which may have applications in waste-water treatment. Today, the degradation of polychlorinated phenols is carried out by photocatalytic method and electrochemical method. Compared to the Fenton reaction, these two methods have higher mineralization ratios and faster degradation rates [69,70]. However, the Fenton reaction is comparably simple and does not require either without the visible-light irradiation or the preparation of electrodes.

## 3.3 Test of reusability

In the successive TCP oxidations with hemin-CTAB

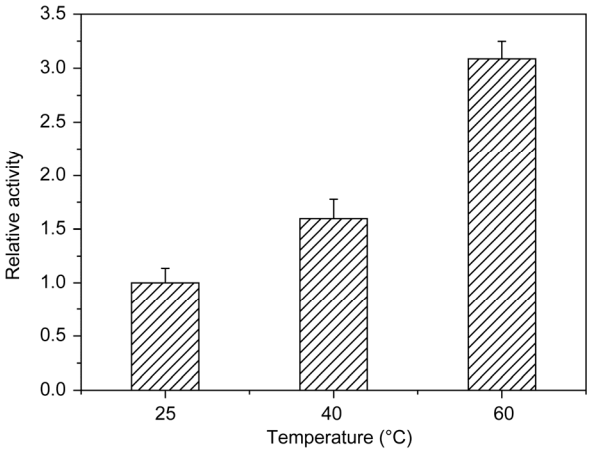



**Figure 6** Effects of temperature on the relative activity of hemin-CTAB micelles as indicated by the removal of TCP (comparing the degradation percentage of TCP in the first 30 min). Reaction conditions: 30 μmol/L hemin-CTAB micelles, 250 μmol/L TCP, 5:1 $H_2O_2$/TCP ratio.

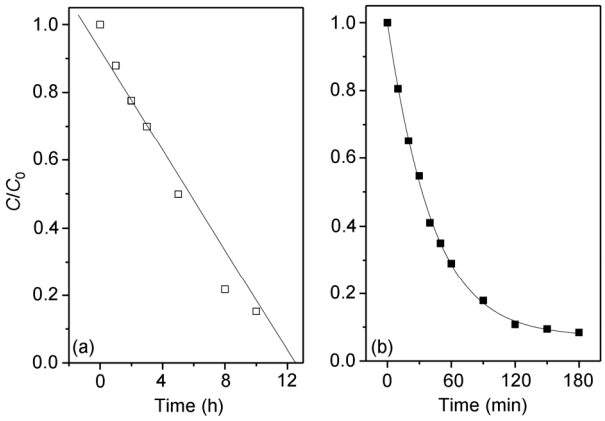



**Figure 7** The degradation kinetic of TCP. Reaction conditions: (a) 30 μmol/L hemin-CTAB micelles, 5:1 $H_2O_2$/TCP ratio, temperature 25 °C; (b) 30 μmol/L hemin-CTAB micelles, 5:1 $H_2O_2$/TCP ratio, 30 μmol/L 2-MeIm, temperature 60 °C.

micelles as the catalyst, the catalytic activity in the second cycle was 93% (100% for the first run), which confirmed that CTAB micelles can protect hemin from destruction by $H_2O_2$. In this system, the hemin molecule is buried in the center of the spheres of CTAB micelles, which protect them from rapid destruction by $H_2O_2$. Due to the adsorption of the product within the CTAB micelles, a low percentage of TCP was degraded in the third run. However, the hemin-CTAB micelles could be reused twice during the catalytic oxidation of TCP.

## 4 Conclusions

We found that hemin-CTAB micelles could act as an efficient catalyst for the oxidation of TCP. An acid condition (pH 4) and a high temperature (60 °C) favored the degradation. By avoiding the formation of bis-ligating hemin, 2-substituted imidazoles (e.g. 2-MeIm) were the most effective bases among the imidazole bases at the low concentration (2-MeIm/hemin, 1:1) at pH 4. At the above optimum conditions (e.g. pH, temperature, and the addition of 2-MeIm), 90% of the TCP could be degraded in 2 h at a 5:1 $H_2O_2$/catalyst ratio. The reusability test revealed that this catalyst could be reused. Based on its exceptional properties, hemin-CTAB micelles have great potential for environmental remediation.

### Supporting information

The supporting information is available online at chem.scichina.com and link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

*This work was financially supported by the National Natural Science Foundation of China (21222704, 21237002), the National Key Basic Research Program of China (2014CB441102), and the Collaborative Innovation Center for Regional Environmental Quality. We thank the Analytical Center and High Performance Computing Center of Nanjing University for the characterization of the samples and for computational study.*

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