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Enhancing Heterogeneous Catalytic Activity of Iron (II) Phthalocyanine by Ethanol and Its Application in 2,4-dichlorophenol Detection

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Abstract: A chemical system for facile and accurate detection of 2,4-dichlorophenol (DCP) via iron (II) phthalocyanine (Fe(II)Pc) catalyzed chromogenic reaction is reported for the first time. In this system, DCP could be oxidized by dioxygen with the catalysis of Fe(II)Pc and then coupled with 4-aminoantipyrine (4-AAP) to generate pink antipyrilquinoneimine dye. Control experiments showed that the addition of ethanol could obviously enhance the catalytic activity of heterogeneous Fe(II)Pc catalysts because of the partial dissolution of Fe(II)Pc nanocubes, which was confirmed by the SEM analysis. On the basis of the detection results of DCP in the range from 2×10^{-5} to 9×10^{-4} mol/L, we obtained a regression equation (A = 0.187 5 + 0.01 209C (R^2=0.995 6)) with the detection limit (3σ) of 3.26×10^{-6} mol/L, which could be successfully used in detecting the real samples.

Key words: iron (II) phthalocyanine; 2,4-dichlorophenol; catalysis; chromogenic reaction

1 Introduction

Chlorophenol is an important organic raw material widely used for the manufacture of fungicide, herbicide, pesticide and other industrial chemical products[1-6]. In the past decades, the abuse of chlorophenols and even direct discharge of them into natural environment had resulted in heavy contamination. Nowadays, chlorophenol has been listed as the top priority pollutant for its high toxicity, extreme persistence and bioaccumulation in aquatic ecosystems. Therefore, monitoring of chlorophenol pollutant has become an urgent task faced by the environmental protection departments of most countries[7-9].

Several standard analytical methods, such as high performance liquid chromatography (HPLC) and gas chromatography (GC) have been commonly used for measurement of chlorophenol compounds and their derivatives[8-12]. However, the application of these methods suffered from their disadvantages of high-cost, time-consuming, complicated pretreatment process, and poor reproducibility. Therefore, the development of a simple and convenient approach for chlorophenol detection is necessary and fascinating to the chemists. In recent years, enzyme-based spectrophotometric methods have been described in many literatures[13-16]. Although these methods have advantages of good accuracy and fast detection, the high cost and easy inactivation of natural enzymes generally limited their real application.

Metal phthalocyanine (MPc), as an available and low-cost biomimetic catalyst, could activate many types of chemical reaction under either mild or rigorous conditions[17,18], which made it more applicable than natural enzymes. Among them, MPc catalyzed chromogenic reactions were of great importance. In 2006, Rajendiran reported the research on metal tetrasulfophthalocyanines catalyzed co-oxidation of phenol through a spectroscopic approach[19]. Recently, our group presented that tetranitro iron (II) phthalocyanine (TNFe(II)Pc) could catalyze oxygen oxidation of phenol and chlorophenol substrates to the corresponding dyes in the presence of 4-AAP[20].

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Besides these two literatures, there were few reports upon the catalysis of MPc for chromogenic identification of chlorophenol pollutants.

In this study, we found that chromogenic reaction of 2,4-dichlorophenol (DCP) could proceed in aqueous solution with the catalysis of iron (II) phthalocyanine (Fe(II)Pc), whose preparation was much simpler than that of TNFe(II)Pc. The introduction of different organic solvent, such as ethanol, N,N-dimethylformamide, dimethyl sulfoxide or acetonitrile into the aqueous solution could obviously improve the catalytic activity of heterogeneous Fe(II)Pc and the sensitivity of chromogenic analytical method. Moreover, the UV-Vis spectroscopic method via ethanol enhanced Fe(II)Pc catalysis was established for DCP measurement and applied to the detection of real samples.

2 Experimental

2.1 Instrumental

UV-Vis spectrometer (Shimadzu UV-2450) was used to record the absorbance of dyes formed in the Fe(II)Pc catalyzed chromogenic reaction. IR spectroscopic data were recorded on a Thermo Nicolet Nexus FT-IR spectrometer with standard KBr pellet method. Elemental analysis was carried out on an Elementar Vario EL III Elemental Analyzer. Field emission scanning electron microscope (FESEM) analysis was performed on Zeiss ULTRA PLUS instrument.

2.2 Materials and reagents

Phthalic anhydride, urea, ammonium molybdate (VI) tetrahydrate, $FeSO_4{\bullet}7H_2O$, 4-aminoantipyrine (4-AAP), DCP were analytically pure and purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used in all the experiments.

2.3 Preparation and characterization of Fe(II)Pc

The synthesis of Fe(II)Pc was similar to the reported method[21], but with some modification. 7.4 g phthalic anhydride, 12 g urea, 100 mg ammonium molybdate, and 3.48 g $FeSO_4{\bullet}7H_2O$ were added into a 100 mL two-necked flask filled with nitrogen. The mixture was heated slowly until all the organic solid was dissolved completely and then the reaction temperature was maintained at 200 ℃ for 5 h. After cooling to room temperature, the dark blue product was ground and added into 500 mL of 1 mol/L NaOH solution, boiled for 1 h and then filtered, washed with deionized water. Next, the crude product was added into 500 mL of 1 mol/L HCl solution with similar after-treatment. Finally, Fe(II)Pc solid was dried at 100 ℃ overnight in vacuum.

2.4 Typical chromogenic reaction of DCP

A 35 mL of 0.1 mol/L PBS solution, 5 mL of 4-AAP stock solution (1.0×10^{-3} mol/L), 5 mL of DCP stock solution (1.0×10^{-3} mol/L), and 5 mL absolute ethanol were added into a 50 mL glass beaker. The chromogenic reaction was initiated by the addition of 19.9 mg Fe(II)Pc powder into the reaction solution followed by ultrasonic treatment for 2 min and continuous magnetic stirring at room temperature. The reaction solution was collected and filtered by a syringe with a membrane (0.22 μm) to remove Fe(II)Pc particles at regular intervals. The absorbance spectra of filtrates from 200 to 800 nm were recorded by a UV-Vis spectrophotometer, and the deionized water blank was used as the reference solution. For the optimization experiments, the variables, such as the dosage of Fe(II)Pc catalyst, pH, and temperature were adjusted according to the experimental parameters of typical chromogenic reaction.

3 Results and discussion

3.1 Enhancing catalytic activity of Fe(II)Pc by organic solvent

Since chlorophenol pollutant was soluble in water, we first performed the liquid-phase catalytic oxidation of DCP with Fe(II)Pc powder dispersed with ultrasound in aqueous solution. Fig.1(a) shows the time-dependent UV-Vis absorbance spectra of oxidation of DCP in the presence of 4-AAP and Fe(II)Pc catalyst in pH7.0 PBS solution at room temperature. In this catalytic system, DCP could be oxidized by dissolved oxygen in the presence of Fe(II)Pc, and then rapidly combined with 4-aminoantipyrine to generate pink dyes. The gradually increased absorbance intensities of peaks at 510 nm indicated the increasing amount of formed dyes[19,20]. However, when the reaction was carried out with continuous nitrogen-bubbling to eliminate the dissolved O_2 in solution, it was found that the dye formation rate was greatly prohibited compared to the system with dissolved O_2 in it, demonstrating that dissolved O_2 was the oxidant for DCP oxidation.

To improve the catalytic activity of Fe(II)Pc, we tried to introduce the suitable organic solvent into the aqueous solution for the activation of Fe(II)Pc catalyst. Fig.1(b) presents the comparison of absorbance of dyes formed in different organic solvent-water solutions. It is

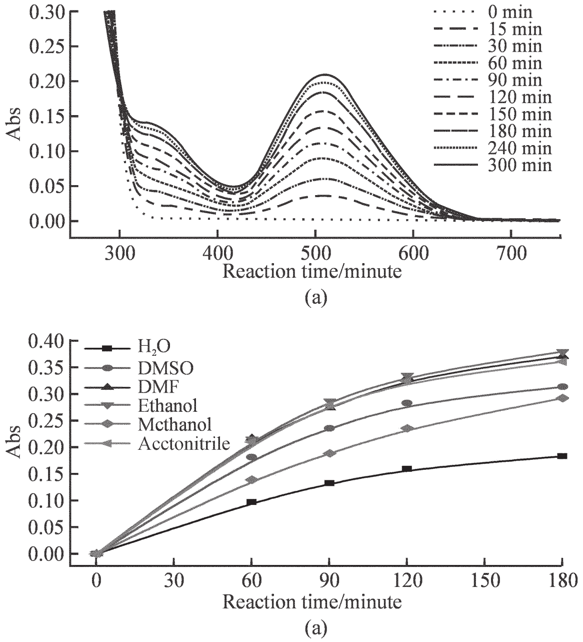

Fig.1 (a) Stacked UV-Vis absorption spectra of Fe(II)Pc catalyzed oxidation of DCP in the presence of 4-AAP; (b) The comparison of absorbance of dyes formed in Fe(II)Pc catalyzed chromogenic reaction with the addition of different solvent

obvious that about two-fold output of dyes formed with the addition of 5 mL ethanol or N,N-dimethylformamide (DMF) or acetonitrile compared with those generated in pure aqueous system (curve a, b and c *versus* curve f). Also, the introduction of other organic solvent such as dimethyl sulphoxide (DMSO) or methanol was beneficial for increasing dye production (curve d and e *versus* curve f). It is thought that the addition of organic solvents facilitated the dissolution of more Fe(II)Pc complexes than the pure aqueous solution, and thus improved the catalytic activity of Fe(II)Pc because the amount of exposed active sites were increased.

3.2 SEM morphology analysis of Fe(II)Pc catalyst

We performed scanning electron microscopic (SEM) analysis for as-prepared Fe(II)Pc catalyst. Fig.2(a) shows that a large amount of irregular microaggregates with the size of 2-10 μm were found in the products. From the detailed observations in Fig.2(b), we found that each microaggregate was composed of a large quantity of crystalline nanocubes with side length of about 100 nm. The formation of mesoporous structures was considered to be closely related to the aggregation of these nanocubes, which should improve the catalytic efficiency by increasing the surface reaction sites. Since the addition of ethanol could accelerate the dissolution of Fe(II)Pc, the morphology of catalysts should be changed after the catalytic reaction. Fig.2(c) shows that the recycled Fe(II)Pc nanocubes become much smaller and more irregular along with the appearance of smooth surface, suggesting the partial dissolution of Fe(II)Pc nanocubes into ethanol solution during the catalytic reaction. Therefore, some individual Fe(II)Pc molecules should diffuse into the reaction solution, which was beneficial to accelerate the chromogenic reaction between DCP and 4-AAP.

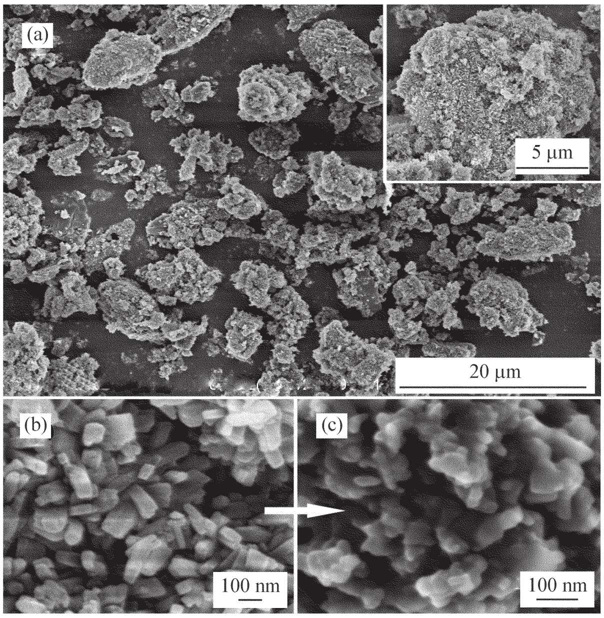

Fig.2 (a) SEM images of Fe(II)Pc microaggregates and the magnified image of a microaggregate (Inset); (b) SEM image of Fe(II) Pc before catalytic reaction; (c) SEM image of Fe(II)Pc after one-recycling catalytic experiment

3.3 Optimization of experimental conditions

Due to the obvious advantages of ethanol, such as non-toxicity, low-cost and easy recycling than that of acetonitrile and DMF, ethanol was used in the optimization investigation of chromogenic reaction. Fig.3(a) shows the comparison of absorbance of formed dye with the addition of ethanol of 3, 5 and 10 mL, respectively. It is clear that the maximum absorbance of dyes formed within 180 min corresponded to the addition of 5 mL ethanol. However, more ethanol up to 10 mL could not contribute to more production of dyes. The detailed reason for this phenomenon was still unclear, the optimal amount of ethanol could be determined as 5 mL under our selected conditions.

Catalyst dosage is an important parameter for chromogenic reactions. A range of Fe(II)Pc dosage, from 8.53 to 28.42 mg was testified for observing the maximum absorbance from the beginning of reaction to 300 min. (Fig.3(b)) The results showed that more Fe(II)Pc catalyst would be contributed to more dyes generated. However, excess Fe(II)Pc catalysts of

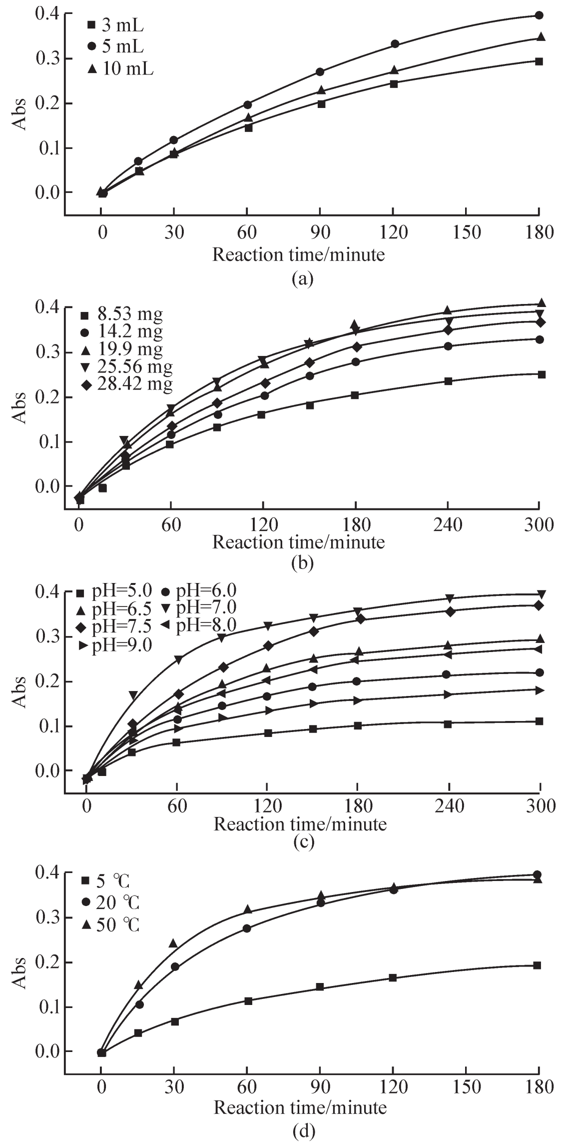

Fig.3 Effect of ethanol amount (a), Fe(II)Pc dosage (b), pH (c) and temperature (d) on absorbance of formed dyes

28.42 mg did not show the best catalytic efficiency probably for the adsorption of formed dyes on catalytic sites of Fe(II)Pc. Therefore, 19.9 mg of Fe(II)Pc was adopted as the optimal dosage under the experimental conditions.

The pH of reaction solution played an important role in chromogenic reaction of DCP[22]. We prepared PBS solution with different pH from 5.0 to 9.0 and observed the dye formation process. Fig.3(c) illustrates that the dye absorbance profile at pH7.0 exceeded those at other pH within 300 min and molecular chlorophenols were beneficial to the transformation of DCP to dyes (pK_a=7.85, DCP). Therefore, pH7.0 was chosen as the optimal experimental parameter.

The influence of temperature on chromogenic reaction was studied (Fig.3(d)). Similar to the catalytic process of TNFe(II)Pc[20], the results showed that more dyes formed in initial stages at higher temperature of 50 ℃, however, the final product of dyes was less than that at 20 ℃. Moreover, less dyes formed at low temperature of 5 ℃, which should be caused by the low activity of Fe(II)Pc catalyst and reaction rate of radicals. Consequently, 20 ℃ is a proper temperature for Fe(II)Pc catalyzed chromogenic reaction.

3.4 Analytical performance

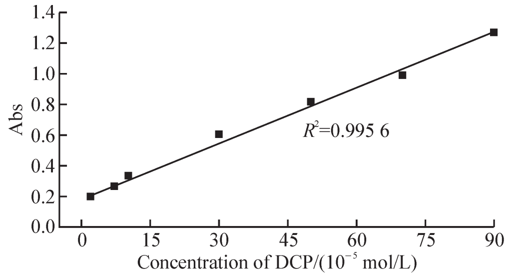

Fig.4 Calibration plot of DCP concentration dependence of the absorbance of formed dyes(Error bars in the figure show standard deviations calculated with three data points taken from different measurements)

According to the above optimal experimental results, the calibration plot of DCP detection could be determined. As shown in Fig.4, the absorbance of formed dyes during 120 min at 510 nm was proportional to the concentration of DCP in the range from 2.0×10^{-5} to 9.0×10^{-4} mol/L with a regression equation of A=0.187 5+0.012 09C and the square of the correlation coefficient (R^2) was 0.995 6. Herein, A and C referred to absorbance of dyes and DCP concentration, respectively. The detection limit was 3.26×10^{-6} mol/L (S/N=3). The proposed method revealed good repeatability, with a relative standard deviation (RSD) of 3.61% (n=6)

3.5 Applications

Table 1 Analytical results of the prepared sample and real samples

Samples	Amount in sample /(10^{-5} mol/L)	Amount found /(10^{-5} mol/L)	This method average recovery (n=5) /%	R.S.D. /%	HPLC method /(10^{-5} mol/L)
Prepared sample	20.0	19.87		2.4	19.95
Wuhan East Lake water	5.0	4.90	98.0	1.2	4.96
Running water	5.0	4.93	98.6	1.9	5.03

To measure the chlorophenol pollutants collected from the aquatic environments by our proposed method, lake water and running water was selected. Due to no chlorophenol compound in these water samples detected by HPLC method, standard addition method was applied by spiking DCP solution to standard solution. As can be seen in Table 1, the results are very close to those detected by HPLC method. The average recovery was in good agreement with the results from HPLC method and the relative standard deviation (R.S.D.) was satisfactory. Hence, our proposed method is suitable for the accurate detection of DCP pollutants.

4 Conclusions

In this study, we presented that catalytic activity of heterogeneous Fe(II)Pc for DCP oxidation reaction in aqueous solution could be obviously enhanced by the introduction of ethanol. SEM analysis of Fe(II)Pc nanocubes confirmed the partial dissolution of catalyst. The experimental parameters of Fe(II)Pc catalyzed chromogenic reaction were optimized to establish an improved analytical method for DCP measurement. This low-cost catalytic system consists of easily accessible Fe(II)Pc catalyst, 4-AAP chromogenic agent, nontoxic ethanol and green oxidant of oxygen from air and should provide an economical and facile route for accurate detection of DCP pollutant. The successful detection of real samples by the proposed method indicated a promising application prospect.

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