A Fiber Optic Sensor for Determination of 2,4-Dichlorophenol based on Iron(III) Tetrasulfophthalocyanine Catalysis

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Abstract

A fiber optical sensor was developed for the determination of 2, 4-dichlorophenol (DCP). The sensor was based on DCP oxidation by oxygen with the catalysis of iron(III) tetrasulfophthalocyanine (Fe(III)PcTs). A lock-in amplifier was used for detecting the lifetime of the oxygen sensing film by measuring the phase delay of the sensor head. The linear detection range and response time of the biosensor were 1.0×10-5-9.0×10-5 mol/L and 250 s, respectively. The sensor displayed good performance comparised with HPLC and electrochemical sensor.

Keywords

Fiber optic sensor; Phase delay; 2,4-dichlorophenol; Iron(III) tetrasulfophthalocyanine.

1. Introduction

Chlorinated phenols are common environmental pollutants due to their wide application in the production of herbicides, pesticides, preservatives, plant growth regulators[1-4]. 2,4-dichlorophenol (DCP) is of perticular interest since it is a precursor for the synthesis of carcinogenic endocrine, 2, 4-dichlorophenoxyacetic acid, which is the active ingredient of more than 1500 herbicides3-5. Therefore, the detection of DCP concentration is of crucial importance to environmental protection and human health. Methords for the determination of DCP have included the gas chromatography6,7, flow injection analysis[5], HPLC[6], photocatalysis[7], electrode[8, 9], electrochemical sensor[2,10,11].

Fiber optic sensor has many advantages such as high precision, fast response, strong ability to resist disturbance, possibility of on-line and real time detection[12]. Fiber optic sensors based on enzyme catalysis provide the effective way for DCP detection. However, the natural enzymes have the drawbacks such as poor stability, very limited source, and difficult extraction and purification, which limit their applications. Therefore, the biomimetic enzymes have been studied and developed as an effective alternative to the nature ones. Iron(III) tetrasulfophthalocy-anine (Fe(III)PcTs) are the biomimetic enzyme which are stable and cost effective, and could be an effective replacement for the nature enzymes.

In our previous work, we studied the oxidation of DCP catalyzed by iron(III) tetrasulfophthalocyanine (Fe(III)PcTs). The influence of organic solvents, iron(III) tetrasulfophth-alocyanine (Fe(III)PcTs) dosage, solution pH and temperature to the DCP oxidation were studied. In this work, a fiber optic sensor based on the DCP oxidation by oxygen with the catalysis of Fe(III)PcTs as a biomimetic enzyme has been designed, and the performance of the sensor was investigated. The sensor has the detection ranges of 1.0×10^{-5}~9.0×10^{-5} mol/L and the response time of 250s. The proposed sensor has good performance comparised with HPLC and electrochemical sensor.

2. Experimental

2.1 Reagents and apparatus

Fe (III)PcTs was synthesized and purified according to the literature[13]. The oxygen sensitive membrane was prepared by using Ru $(bpy)_3Cl_2 \cdot 6H_2O$ as the fluorescence indicator and cellulose acetate as the matrix according to our previously work[14]. All the reagents were of analytical grade and used without further purification.

The absorption spectra were determined using a UV-2450 spectrophotometer (Shimadzu, Japan). A lock-in amplifier (SR830, Standford Research Systems, U. S. A) was used for measuring the phase delay of the sensor head.

2.2 Preparation and principle of fiber optic sensor

The detecting system consists of a lock-in amplifier, a LED with the excitation wavelength of 416 nm as the light source, a sensor head with a oxygen sensing membrane and a computer for data processing (see Fig. 1).

The principle of the sensor is based on the fluorescence quenching and consumption of oxygen [15]. The change of oxygen concentration was detected by measuring fluorescence of Ru $(bpy)_3Cl_2$ quenched by oxygen. Since a lock-in amplifier is used, the quchening could be described as

$$\frac{\tan\phi_0}{\tan\phi} = 1 + K_{sv}[Q] \tag{1}$$

Where φ0 and φ are the phase delay change of the sensor in the absence and presence of the oxygen quencher, respectively, and Ksv is the Stern-Volmer constant. [Q] is oxygen concentration. Since φ is very small (i.e. $< 5^o$) in the experiment, tanφ≈φ. By collecting the data of phase delay φ the quantification of DCP is achieved.

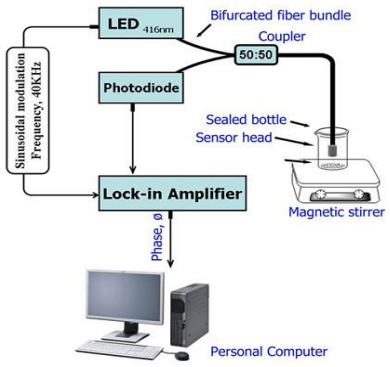

Fig. 1 Schematic diagram of the detecting system

2.3 Measurements

For the detection of DCP concentration, measurements were performed with the set up shown schematically in Fig. 1. The reaction of DCP assisted with 4-AAP using Fe(III)PcTs as catalyst was performed as follows: A 40 mL of deionized water, 5 mL of 4-AAP aqueous solution (1.0×10^{-3} mol/L) and different concentration of DCP (1.0×10^{-3} mol/L stock solution) were added into a 80 mL glass beaker with magnetic continuous stirring. The catalytic reaction was initiated by addition of 31.0 mg of Fe(III)PcTs powder followed by the ultrasonic treatment for 1 min to make it dissolved in the mixture. The following measurement could be performed after a simple washing of the sensor head with buffer solution.

3. Results and Discussion

It has been reported that phenolic compounds could be oxidized with the catalysis of phthalocyanine metal complex [16-17]. Herein the catalytic activity of Fe (III)PcTs was investigated using DCP as the substrate. Fig. 2 shows the UV-Vis absorption spectra for chromogenic reaction of DCP with 4-AAP in the presence of Fe (III)PcTs at regular intervals. The absorbance at 510 nm increased during the catalytic oxidation due to the formation of chloro-substituted antipyrilquinoneimine dye [18]. It can be seen that the intensity of characteristic peak of dye at 510 nm gradually increased within 180 min, indicating the continuous transformation of DCP with 4-AAP to dye in the presence of Fe (III)PcTs. However, contrast experiment showed that the auto-oxidation reaction without Fe (III)PcTs was negligible (data not shown). The UV-Vis spectra of this system showed no obvious change after 180 min, demonstrating the completion of catalytic reaction.

Since the solution was exposed to air and there were no other oxidants in it, dissolved O_2 was considered to be the possible oxidant for DCP oxidation. To confirm this, 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 (Fig. 3), demonstrating that dissolved O_2 was the oxidant for DCP oxidation. We compared the catalytic oxidation of DCP in dark environment with that in the environment with light. No notable differences between them were observed, indicating that light is not necessary to this oxidation of DCP in the presence of Fe(III) PcTs (Fig. 3).

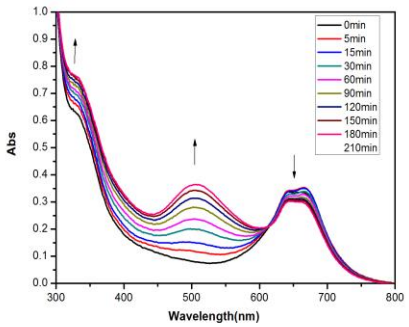

Fig.2 Stacked UV-Vis absorption of catalytic oxidation of DCP with 4-AAP at regular intervals. Conditions: T = 25 ^{o}C, pH =6.0, [DCP] =1.0×10^{-4}M, [4-AAP]=1.0×10^{-4}mol/L, [Fe(III)PcTs] = 0.62 mg/mL.

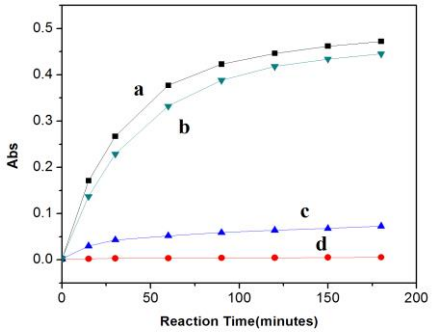

Fig.3 Oxidation process of DCP catalyzed by Fe(III)PcTs at different conditions (λ_{abs} = 510 nm). (a,■)Typical catalysis;(b, ▼) In dark; (c,▲) N_2 bubbled ; (d,●)WithoutFe(III)PcTs.([Fe(III)PcTs]= 0.62 mg/mL， pH =6.0, [DCP] =1.0×10^{-4}mol/L， T=25℃)

Because of Fe (III) PcTs and Fe (II) the Pc have the same conjugate ring structure, the mechanism of catalytic oxidation of DCP are similar. Fe (III) PcTs catalytic DCP oxidation process can be divided into three steps: (1) the DCP can be oxidized to $\bullet O_2^-$, and oxidation products of DCP are phenoxy free

radicals and quinoid free radicals; (2) 4-AAP can be oxidized to antipyrine amino radicals by $\bullet O_2^-$; (3) quinoid free radicals and antipyrine amino radicals can be coupling to the oxidation products antipyrine dyes.

The detection of DCP concentration is based on the fluorescence quenching and consumption of oxygen. By detecting the change of phase delay of the sensor head we can detect the DCP concentration. Fig.4 depicts the relationship between the change of phase delay φ and DCP concentration in the concentration range from 1.0 ×10-5 mol/L to 9.0 ×10^{-5}mol/L .There is a good linear relationship between φ and DCP concentration. The linear graph was defined by the equation of y=0.6704+0.0530x (R^2=0.9743). φ is defined as the difference between the phase delay of the sensor head with certain DCP concentration and with no DCP in the solution. Each experiment measured three times, the relative standard deviation R.S.D is 4.6%.The response time of the sensor was 250s because most of the DCP was oxidized in this time.

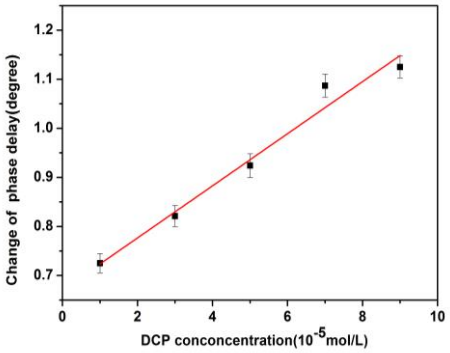

Fig.4 Typical calibration curve of the fiber optic DCP sensor at various concentration of DCP.Conditions: T = 25 °C, [Fe(III)PcTs] = 0.62 mg/mL， pH =6.0, Error bars in the figure show standard deviations calculated with three data points taken from different measurements.

On account of HPLC method is used to determination determine concentration, and electrochemical sensor is also atesting method of widely attention and research, we compared the proposed sensor with HPLC and electrochemical sensor (Table 1). Table 1 indicates that the detection lower limit of HPLC is very low, but the sample preparation process is very complicated, measurement time is very long, cost is very high, and HPLC is unable to realize real-time on-line detection. In addition, the detection lower limit of proposed sensor is two orders of magnitude lower than electrochemical sensor, and the response time is much faster than electrochemical sensor.

TABLE 1. Comparison of the proposed sensor with HPLC and Electrochemical sensor

Detection Method	Linear Detection Range	Lower Detection Limit	Response Time
HPLC[10]	0.05-20.0 (mg/L)	0.76(μg/L)	14min
Electrochemical sensor[1]	1.63-48.9 (mg/L)	3.26 (mg/L)	4.17min
Proposed sensor	0.16-1.47 (mg/L)	0.037(mg/L)	

Acknowledgements

This study is supported by Universities Excellent Young and Middle-aged Scientific and Innovation Team Project of Hubei Province (No T201630) and Hubei Provincal Department of Education Scientific Research Guidance Project (No B2016328).

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