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# A Fiber Optic Sensor for Determination of 2,4-dichlorophenol based on Iron(II) Phthalocyanine Catalysis

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**Abstract:** A new fiber optic sensor based on the oxidation of 2,4-dichlorophenol (DCP) catalyzed by iron(II) phthalocyanine (Fe(II)Pc) was developed for the determination of DCP. The optical oxygen sensing film containing fluorescence indicator $Ru(bpy)_3Cl_2$ was used to detect the consumption of oxygen in solution. Moreover, a lock-in amplifier was used to determine the lifetime of the sensor head by detecting its phase delay change. The results reveal that the sensor has a linear detection range of $1.0\times10^{-6}$ - $9.0\times10^{-5}$ mol/L and a response time of 5 min. The sensor also has high selectivity, good repeatability and stability. It can be used effectively to determine DCP concentration in real samples.

**Key words:** 2,4-dichlorophenol; iron(II) phthalocyanine; phase delay change; fiber optic sensor; stability

## 1 Introduction

Chlorinated phenols are common environmental pollutants due to their wide application in the production of herbicides, pesticides, preservatives and plant growth regulators[1-3]. 2,4-dichlorophenol (DCP) is of particular interest because it is a precursor for the synthesis of carcinogenic endocrine, 2,4-dichlorophenoxyacetic acid, which is the active ingredient of more than 1500 herbicides. It had been regarded as the toxic organic substance to be specially controlled[4]. Therefore, the detection of DCP concentration is very important to environmental protection and human health. Methods for the determination of 2,4-DCP have included the gas chromatography[5,6], flow injection analysis[7], HPLC[8], photocatalysis[9], electrode[10,11], and electrochemical sensor[12,13], but these methods suffer from the disadvantages such as time-consuming, high cost, complicated sample preparation and impossibility of on-line and real time detection. Fiber optic sensors have many advantages including fast response, high precision, strong ability to resist disturbance, and possibility of on-line and real time detection[14]. Fiber optic sensors based on enzyme catalysis provide an 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. Metallophthalocyanines (MPc) are the biomimetic enzymes 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 (II) phthalocyanine (Fe(II)Pc)[15]. The influences of organic solvents, Fe(II)Pc dosage, solution pH and temperature on the DCP oxidation were studied. In this work, we designed and fabricated a fiber optic DCP sensor based on the oxidation of DCP catalyzed by Fe(II)Pc. The sensor properties were studied. The sensor has a detection range of $1.0\times10^{-6}$-$9.0\times10^{-5}$ mol/L and a response time of 300 s. The detection results of real samples by using this sensor indicate a promising application prospect.



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# 2 Experimental

## 2.1 Reagents and apparatus

Fe(II)Pc was synthesized and purified according to the Ref.[16]. Fluorescence indicator ($Ru(bpy)_3Cl_2$) was purchased from Sigma-Aldrich. Cellulose acetate(CA) and DCP were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used in all the experiments. All the reagents were of analytical grade and used without further purification.

A lock-in amplifier (SR830, Standford Research Systems, USA) was used for measuring the phase delay of the sensor head.

## 2.2 Preparation of optical oxygen sensing film

The oxygen sensing membrane was prepared by using $Ru(bpy)_3Cl_2$ as the fluorescence indicator and CA as the matrix according to our previous work[17]. Briefly, 0.1g cellulose acetate was added into 3.0 mL acetone and stirred at room temperature for 2 h. A certain amount of $Ru(bpy)_3Cl_2$ water solution was added in the mixture and it was stirred at room temperature for 6 hours to form an uniform solution. The solution was dipped onto a glass culture dish with a diameter of 6 cm, making it well-distributed. The cellulose acetate membrane embedded with fluorescent indicator was obtained after the acetone and water were volatilized.

## 2.3 Preparation and principle of fiber optic sensor

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

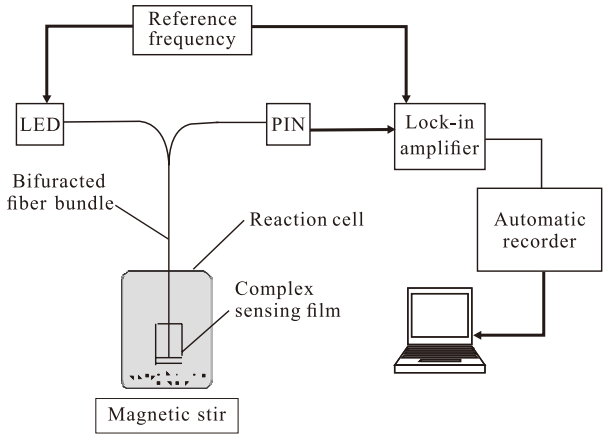


Fig.1 Schematic diagram of the detecting system

This sensor was based on the fluorescence quenching and consumption of oxygen[17]. The oxygen concentration change was detected by detecting the fluorescence of $Ru(bpy)_3Cl_2$ quenched by oxygen. Since a novel lock-in amplifier was used, the quenching could be described as

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

where, $\varphi_0$ and $\varphi$ are the phase delay of the sensor in the absence and presence of oxygen, respectively, and $K_{sv}$ is the Stern-Volmer constant. [Q] is the oxygen concentration. By detecting the data of phase delay $\varphi$ the quantification of DCP is achieved

## 2.4 Measurements

For detecting the DCP concentration, measurements were performed with the setup shown schematically in Fig.1. The sensor head was placed into a tiny reaction cell which contained DCP buffer solution and a certain amount of Fe(II)Pc. An entire airtight reaction cell was introduced to eliminate the interference of oxygen from the open air. All the measurements were carried out at 20 ℃ with continuous and constant stirring. The fluorescence signal was collected by PIN and guided to the lock-in amplifier through the output bundle, and then transferred to phase-delay which was collected by the computer. The following measurement could be performed after a simple washing of the sensor head and Fe(II)Pc with buffer solution. All the measurements were performed in triplicate.

# 3. Results and discussion

## 3.1 Preparation and characterization of optical oxygen sensing film

The oxidation of DCP in solution catalyzed by Fe(II)Pc was a oxygen-consuming process and the consumption of oxygen was detected by the optical oxygen sensing film on the sensor head. Therefore, the properties of optical oxygen sensing film influence the sensor properties greatly. For the preparation of sensing film, we studied the influence of temperature, raw materials ratio and indicator concentration on the properties of sensing film. The results showed that the uniform sensing film with good repeatability and stability could be obtained when 3.5 mL acetone and 0.100g CA were used at 25 ℃ (indicator concentration was 0.8 mg/mL). The SEM of this sensing film is shown in Fig.2(b). Compared with the blank film in Fig.2(a)(CA film without indicator), the sensing film

was more uniform because some pores disappeared after the filling of indicator into the pores.

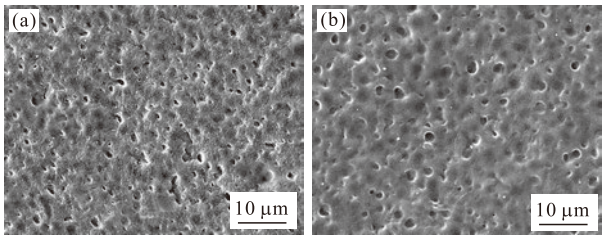


Fig.2 SEM images of CA film (a) and optical oxygen sensing film (b)

### 3.2 Dynamic range of the sensor

This sensor was based on the fluorescence quenching and consumption of oxygen. The DCP concentration detection could be achieved by detecting the change of phase delay of the sensor head. In our previous work[15], we obtained the optimal conditions for the oxidation of DCP catalyzed by Fe(II)Pc: the solution pH was 7.0, the Fe(II)Pc amount was 19.9 mg, reaction temperature was 20 ℃, and ethanol amount was 5 mL (the total volume of system was 50 mL ). In this study we used these optimal conditions for the fiber optic DCP sensor based on Fe(II)Pc catalysis. Ethanol was not added in the system because it could cause serious negative effect on the optical oxygen sensing film.

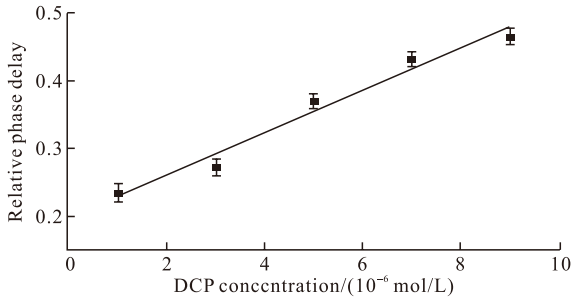


Fig.3 Calibration curve of fiber optic DCP sensor in the DCP concentration range of $1.0\times10^{-6}$-$9.0\times10^{-6}$ mol/L. $T$ = 20 ℃, Fe(II)Pc dosage=19.9 mg (the total volume of system is 50 mL), pH=7.0)

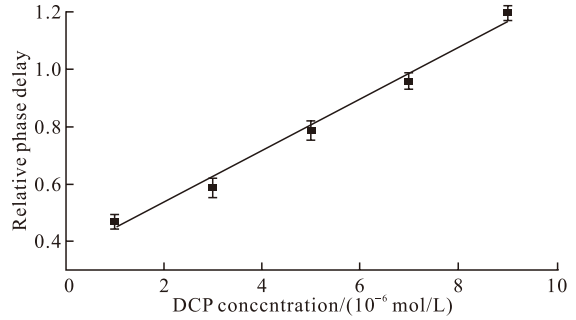


Fig.4 Calibration curve of fiber optic DCP sensor in the DCP concentration range of $1.0\times10^{-5}$-$9.0\times10^{-5}$ mol/L. $T$ = 20 ℃, Fe(II)Pc dosage=19.9 mg (the total volume of system is 50 mL), pH=7.0)

Fig.3 shows the relationship between the change of phase delay φ and DCP concentration in the range of $1.0\times10^{-6}$ mol/L - $9.0\times10^{-6}$ mol/L (The Integrated Waste Water Discharge Standard of China for DCP is $3.68\times10^{-6}$ mol/L). There was a good linear relationship between $\varphi$ and DCP concentration, which was defined by the equation of $y$=0.188 6+0.067$x$ and $R^2$ = 0.996 4, where $\varphi$ was the difference between the phase delay of sensor head with certain DCP concentration and with no DCP in the solution. The detection limit was $7.4\times10^{-7}$ mol/L (S/N=3). The response time of the sensor was 5 min because most of the DCP was oxidized in this time. There was also a good linear relationship between φ and DCP concentration in the range of $1.0\times10^{-5}$ mol/L - $9.0\times10^{-5}$ mol/L (Fig.4), which was defined by the equation of $y$=0.353 0+0.090$x$ and $R^2$=0.9950.

### 3.3 Reversibility and long-term stability of the sensor

Reversibility is an important characteristic of the sensor, which was assessed by exposing the sensor to five cycles of buffer, $5.0\times10^{-5}$ mol/L DCP solution, respectively. The results are shown in Fig.5. It has a highly reproducible and reversible response to DCP solution with RSD=4.1%, indicating the good reversibility of the sensor.

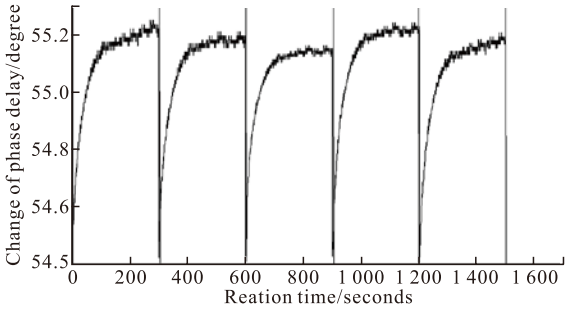


Fig.5 Reversibility of the fiber optical DCP sensor (DCP= $5.0\times10^{-5}$ mol/L, pH=7.0, $T$ = 20 ℃), Fe(II)Pc dosage =19.9 mg

The long-term stability of the sensor was studied, which included the stability of biomimetic enzyme and optical oxygen sensing film. Fe(II)Pc has very good stability and could be kept at room temperature for 12 months with no change of catalysis property. With the catalysis of Fe(II)Pc, the oxygen sensing film was used to detect the DCP solution with a DCP concentration of $5.0\times10^{-5}$ mol/L.

Then the oxygen sensing film was immersed in water for 2 days and the same detection was performed. It was found that $\varphi$ was reduced by 3.4% after the immersion. When the oxygen sensing film was immersed in water for 7 days, $\varphi$ was reduced by 8.9%. The indicator leakage would be the reason for

the decrease of $\varphi$. Since the response time of the sensor was 5 min, the sensing film would be immersed in water for a short time for one detection. Therefore, this sensor has good long-term stability.

### 3.4 Sensor selectivity against interference

The selectivity of this sensor was evaluated by the interference rates:

$$\text{Interference rate (\%)} = (\text{interference value}/\text{actual concentration of DCP}) \times 100\% \quad (2)$$

$$\text{Interference value} = \text{detecting concentration of sample with interferents-actual DCP concentration} \quad (3)$$

The actual DCP concentration was $5.0\times10^{-5}$ mol/L and the concentration of interferents was $5.0\times10^{-3}$ mol/L. The results are summarized in Table 1. We can see that all the interferents did not cause significant interference on the response of this sensor, showing a good selectivity for this sensor.

**Table 1 Effect of interfering ions on the phase delay measured on the DCP solution**

| Interferents | Interference rate/% |
|---|---|
| NaCl | 1.6 |
| $CaCl_2$ | −2.1 |
| $FeCl_3$ | −3.9 |
| KCl | 5.4 |
| NaBr | −2.9 |
| $MgSO_4$ | −3.8 |
| $Na_2CO_3$ | 2.9 |
| $Na_2SO_4$ | 3.4 |
| $Na_3PO_4$ | −5.6 |

### 3.5 Practical application

**Table 2 Detection of practical samples using fiber optic DCP sensor based on Fe(II)Pc catalysis**

| Sample | DCP added /($10^{-5}$ mol/L) | DCP found /($10^{-5}$ mol/L) ($n$=3) | Recovery /% |
|---|---|---|---|
| Water in Yangtse River | 5.00 | 4.87 ± 0.18 | 97.4 |
| Water in East Lake | 5.00 | 4.93 ± 0.21 | 98.6 |

The fiber optic DCP sensor based on Fe(II)Pc catalysis was used to determine the DCP concentration in samples from water of Yangtse River and East Lake in Wuhan, China. The results are shown in Table 2. It can be seen that the recovery was satisfactory, indicating a promising application prospect for this sensor.

## 4 Conclusions

A fiber optic DCP sensor based on DCP oxidation catalyzed by Fe(II)Pc was successfully developed for the detection of DCP concentration. This sensor has a detection range of $1.0\times10^{-6}$ - $9.0\times10^{-5}$ mol/L and a response time of 5 min. Since the Integrated Waste Water Discharge Standard of China for DCP is $3.68\times10^{-6}$ mol/L, the proposed sensor can meet the need of practical application. This sensor is easily prepared and has a long lifetime. It also has short response time, good repeatability, selectivity and stability. The detection results of DCP concentration in practical samples demonstrate a promising application prospect.

### References


[1] Jantra J, Zilouei H, Liu J, *et al*. Microbial Biosensor for the Analysis of 2,4-Dichlorophenol[J]. *Anal. Lett*., 2005, 38: 1 071-1 083

[2] Mckinley R, Plant JA, Bell JNB, *et al.* Endocrine Disrupting Pesticides: Implications for Risk Assessment[J]. *Environment International*, 2008, 34: 168-183

[3] Mehmood Z, Kelly DE, Kelley SL. Cytochrome P450 3A4 Mediated Metabolism of 2,4-dichlorophenol[J]. *Chemosphere*, 1997, 34 (11): 2 281-2 291

[4] Peng JF, Liu JF, Hu XL. Direct Determination of Chlorophenols in Environmental Water Samples by Hollow Fiber Supported Ionic Liquid Membrane Extraction Coupled with High-performance Liquid Chromatography[J]. *J. Chromatogr. A*, 2007, 1139: 165-170

[5] Donald F, Gurka SP, Richard T. Environmental Applications of Gas Chromatography/Atomic Emission Detection[J]. *Anal. Chem*., 1997, 69: 2 411-2 417

[6] Natalia C, Nerea A, Pilar VIL, *et al*. Capillary Gas Chromatography with Atomic Emission Detection for Determining Chlorophenols in Water and Soil Samples[J]. *Anal. Chim. Acta*, 2005, 552: 182-189

[7] Rosanam MA, Regina S, Wilson FJ, *et al*. Selective Trace Level Analysis of Phenolic Compounds in Water by Flow Injection Analysis-Membrane Introduction Mass Spectrometry[J]. *Environ. Sci. Technol*., 2001, 35: 2 084-2 088

[8] Mahugo CS, Padron MET, Ferrera ZS, *et al.* Development of a Solid-phase Microextraction Method with Micellar Desorption for the Determination of Chlorophenols in Water Samples Comparison with Conventional Solid-phase Microextraction Method[J]. *J. Chromatogr. A*, 2007, 1140: 13-20

[9] Huang YP, Li J, Ma WH, *et al*. Efficient $H_2O_2$ Oxidation of Organic Pollutants Catalyzed by Supported Iron Sulfophenylporphyrin under Visible Light Irradiation[J]. *J. Phys. Chem. B*, 2004, 108: 7 263-7 270

[10] Wang J, Chen G, Chatrathi MP, *et al*. Capillary Electrophoresis Microchip with a Carbon Nanotube-Modified Electrochemical Detector[J]. *Anal. Chem*., 2004, 76: 298-302

[11] Grace WM, Veronika QM, and Greg MS. Chlorinated Phenol Analysis Using off-Line Solid-Phase Extraction and Capillary Electrophoresis Coupled with Amperometric Detection and a Boron-Doped Diamond Microelectrode[J]. *Anal. Chem*., 2005, 77: 6 542-6 548

[12] Dilsat O, Kagan K, Burcu M, *et al*. Heterostructured Fluorohectorite Clay as an Electrochemical Sensor for the Detection of 2,4-Dichlorophenol and the Herbicide 2,4-D[J]. *Chem. Mater*., 2002, 14: 1 755-1 761

[13] Nicolette RH, Tesfaye TW, Omotayo A, *et al.* Microsomal Cytochrome P450-3A4 (CYP3A4) Nanobiosensor for the Determination of 2,4-dichlorophenol-An Endocrine Disruptor Compound[J]. *Electrochim. Acta*, 2009, 54: 1 925-1 931

[14] Doong RA, Tsai HC. Immobilization and Characterization of Sol-gel-encapsulated Acetylcholinesterase Fiber-optic Biosensor[J]. *Anal. Chim. Acta*, 2001, 434: 239-246

[15] Tong YL, Li DP, Huang J, *et al*. Enhancing Heterogeneous Catalytic Activity of Iron (II) Phthalocyanine by Ethanol and Its Application in 2,4-Dichlorophenol Detection[J]. *J. Wuhan Univ. Tech*., 2014, 29(3): 567-571

[16] Kasuga K, Tsutsui M. Some New Developments in the Chemistry of Metallophthalocyanines[J]. *Coord. Chem. Rev*., 1980, 32: 67-95

[17] Huang J, Fang H, Liu C, *et al.* A Novel Fiber Optic Biosensor for the Determination of Adrenaline Based on Immobilized Laccase Catalysis[J]. *Anal. Lett.*, 2008, 41: 1 430-1 442