A Study on Spectral Analysis of Trace H$_2$O$_2$ in Electrochemistry

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Abstract — **Electrochemistry is an efficient, fast and green method for the COD removal from sewage. The electrochemical treatment process of sewage containing polymer in an oilfield produces some reactive intermediates such as H$_2$O$_2$ which can remove COD by indirect oxidation. Ti and 5-Br-PADAP with H$_2$O$_2$ can form a stable colored ternary complex at pH = 1 ~ 1.5, and there is an obvious absorption peak of this ternary color system at about 561nm with UV spectrophotometer. The results are confirmed with the Beer-Lambert Law in the range of 0.2～10 μmol/L of H$_2$O$_2$, therefore a method of spectrophotometry can be established to determine traces of reactive intermediates about H$_2$O$_2$ in the process of electrochemical treatment of sewage. This method is simple, rapid, cheap, reproducible with high sensitivity, and can obtain satisfying results in practical applications.**

Keywords-polymer- containing wastewater, electrochemistry, reactive intermediates, spectrophotometry

I. INTRODUCTION

The degradation of organic pollutants in the process of electrochemical treatment of sewage divides direct and indirect oxidization. Indirect oxidization [1-5] refers to make use of active groups with strong oxidation in the anode reaction, such as H$_2$O$_2$, OH, O, O$_3$ etc. And the hypochlorous acid (HClO), hypochlorous acid (ClO$^-$) and other products[6,7] will also be produced in the case of the presence of Cl$^-$. These active substances which have the characteristics of short life and strong oxidation can effectively oxidize and decompose pollutants to achieve the purpose of removal of pollutants. In different sewage systems, these oxidizing active groups exist in a very small amount. The study on degradation mechanism of organic compounds in process of electrochemical treatment of oilfield sewage is based on H$_2$O$_2$. A method with high-sensitivity is needed to measure the amount of H$_2$O$_2$, because of the trace active intermediate H$_2$O$_2$, so as to guide the control process of electrochemical treatment. The detection method of H$_2$O$_2$ are chemi-luminescence, electrochemical method, spectrophotometry and so on[8,9], and adds enzyme into reaction system can improve detection in sensibility. It can form a stable ternary complex in the range of low pH by the Ti (IV)-5-Br-PADAP method to detect trace H$_2$O$_2$. The project establish a set of simple, rapid, reproducible, highly sensitive and low-cost method of detection to rapidly detect trace H$_2$O$_2$ through experimental research.

II. EXPERIMENTATION

A. *Experimental Instruments and Chemicals*

Ti standard solution (Macklin, 1000μg/mL), 5-Br-PADAP (A.R) Shanghai leafy biological reagents, H$_2$O$_2$ (A.R), anhydrous alcohol (A.R); double distilled water after treated with KMnO$_4$ oxidization .

UV-2450 UV-Vis spectrophotometer (Shimadzu), Thermo pH meter.

1000μg / mL Ti (Ⅳ) standard solution is diluted by anhydrous ethanol to a concentration of 6.32×10^{-4}mol / L as a stock solution.

5-Br-PADAP solution (described as B in following text) is formulated at a concentration of 2×10^{-3} mol / L with ethanol .

Preparation of Ti (Ⅳ) -5-Br-PADAP solution: Ti (Ⅳ) and B stock solution are mixed at equal molar ratio into a concentration of 4.8×10^{-4}mol / L.

Preparation of H$_2$O$_2$ stock solution: dilute 1 mL of concentrated H$_2$O$_2$ solution by double distilled water into 1000 mL, and use 2.18×10^{-2}mol/L KMnO$_4$ to calibrate standard solution H$_2$O$_2$, and calibrate regularly with new KMnO4 solution to prevent the decomposition of H$_2$O$_2$ and cause concentration errors ; Dilute H$_2$O$_2$ by double distilled water as needed when using.

The concentration of hydrochloric acid stock solution is 12mol / L , and it is diluted by the need to use.

Preparation of HCl- KCl buffer solution (pH = 1.5): add 50 mL 0.2 mol / L KCl solution into 41.5 mL 0.2mol/L hydrochloric acid, then it was diluted by double distilled water to 200ml.

B. *Principles for the determination*

It is reported in the literatures [8-10] that the detection of active intermediates H$_2$O$_2$ can use Ti (IV) -B , the basic principle of which is based on the high coordination number of Ti (IV) , and it can cooperate with B and H$_2$O$_2$ respectively. Moreover, the space volume of H$_2$O$_2$ is less

than B, so the ternary complexes spatial effect of Ti (IV) and H_2O_2 with B is good, and it can form a stable ternary complex in low pH, and there is an obvious absorption peak of this ternary color system at about 561nm whose absorption coefficient $\varepsilon_{561nm} = 7.3 \times 10^4$ L / mol / cm. Within the range of $0.2 \sim 10 \mu mol/L$ H_2O_2 the results confirm with the Beer-Lambert Law. However, the pH value stable range of this ternary complex is very narrow, and it has significant absorption peak in the range of pH = 1 ~ 1.5, and any slightest error in the experimental operation will lead to undetectable of H_2O_2.

III. RESULTS AND DISCUSSIONS

C. H_2O_2 Standard Curve

Series concentration gradient standard H_2O_2 solution within the range of $0.2 \sim 10 \mu mol/L$ were prepared, and then 2mL of various concentrations of these standards H_2O_2 solution, 3 mL of anhydrous alcohol, 1 mL of 0.32mol/L HCl, 2 mL of HCl- KCl buffer solution (pH = 1.5), 2 mL of Ti (IV) -B solution were transferred to a 10 mL volumetric flask. After diluting with 0.32mol/L HCL solution to the scheduled volume and well mixed, the solution was heated to 50 ℃ in water bath about 20min, then cool it to room temperature by water (about 10 min). In the end, a 1cm quartz colorimetric utensil with reagent blank was used as reference solution, and scanned at wavelength range of 200 ~ 700nm by the UV-2450 UV-Vis spectrophotometer (Shimadzu), and measure the absorbance at a maximum absorption wavelength of about 560nm the experimental results show that the Beer-Lambert Law is hold within the range of $0.2 \sim 10 \mu mol/L$ H_2O_2. the standard curve equation of H_2O_2 can be obtained: $A = 0.00646C + 0.00132$,the correlation coefficient $R^2 = 0.9728$ (A- absorbance, C- H_2O_2 concentration μmol / L). Fig.1.
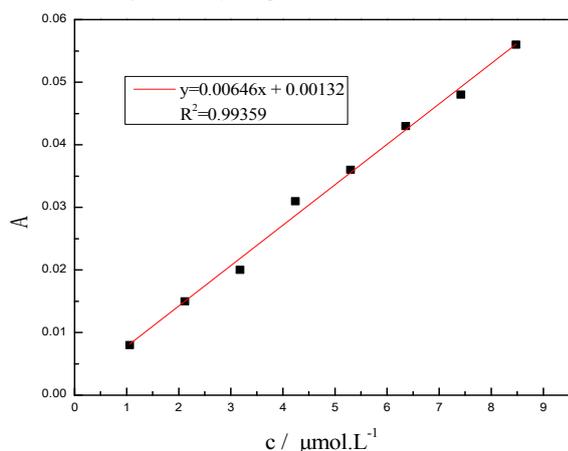

Figure 1. Absorbance standard curve of different concentrations of H2O2 within the range of low concentration

D. Absorption Curve of Ternary Complex Ti(IV) -B-H_2O_2

B is a very high sensitivity of pyridylazo dyestuff type chromogenic agent[10], whose maximum absorption peak is at 450nm. The coordination number of Ti (□) is high so Ti (□) and B can be formed chelate compound in a wide range of pH, then be formed ternary complexes after adding H_2O_2. The space volume of H_2O_2 is less than B, and the ternary complexes spatial effect of Ti (IV) and H_2O_2 with B is excellent, so they can form a stable ternary complex. Fig.2 shows the maximum absorption peak of B at 445nm. When Ti (□) and B are mixed at an equal molar ratio, the mixing proportion of Ti (□)-B chelate compound is 1: 2, so Ti (□) solution is excessive. But the absorption peak is appeared at 452nm, probably because Ti (□) and B did not cooperate fully, and it leaded to residual B. Moreover, the new absorption peak is appeared at 594nm obviously, it indicated Ti (□) and B were successfully formed chelate compound, and the absorption peak of B had a red shift due to the existence of Ti (□)-B chelate compound. When H_2O_2 solution was added, only one absorption peak was appeared at 560nm in the system. It indicated that H_2O_2 and Ti (□) -B chelate compound form a new ternary complexes of Ti (□) - B-H_2O_2, and the absorption peak of it was significant.
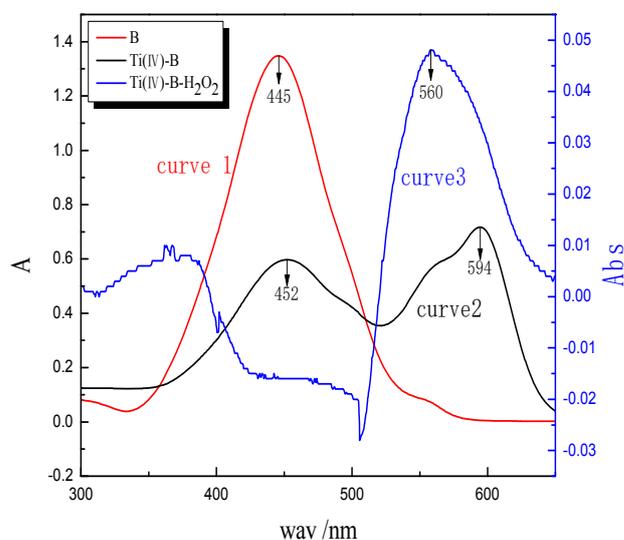

Figure 2 Absorption curve of the ternary system Ti (IV) -B-H2O2

E. Main Affecting Factors on Chromogenic Condition of Ti (IV) -B-H_2O_2

Order of adding reagents As the order of adding reagents mentioned[11,12] (2mL of various concentrations of these standards H_2O_2 solution, 2 mL of Ti (IV)-B solution, 3 mL of anhydrous alcohol, 2 mL of pH = 1.5 HCl- KCl buffer solution, and dilute with 0.32mol/L HCL solution to the mark line of 10 mL volumetric flask, and mix), the result is

shown in the curve 4 of Fig 3, and we can found that: the absorption peak of the system at 561nm is very unclear, but there is an obvious absorption peak at 594nm, indicating that the resulting ternary complexes of Ti (□)-B-H_2O_2 is very unstable. Change the order of adding reagents. 2ml of various concentrations of these standards H_2O_2 solution, 3ml of anhydrous alcohol, 1ml of 0.32mol/L HCL, 2ml of pH = 1.5 HCl- KCl buffer solution, 2ml of Ti (Ⅳ) -B solution to a 10ml volumetric flask, and dilute with 0.32mol/L HCL solution to the mark line of volume, and mix. The result is shown in the curve 5 of Fig.3, and we can found that: The system has only one absorption peak at 561nm and the absorption peak is very obvious, indicating that the resulting ternary complexes of Ti (□) -B- H_2O_2 is stable. The root cause may be as follows: Ti (□) -B and H_2O_2 cannot form a stable ternary complexes in the environment of system 1 without a suitable pH and suitable amount of anhydrous ethanol, the environment without a suitable pH will result in the decomposition of H_2O_2, and ultimately result in the little amount of the ternary complexes Ti (Ⅳ)-B-H_2O_2, so the characteristic absorption peak will disappear.
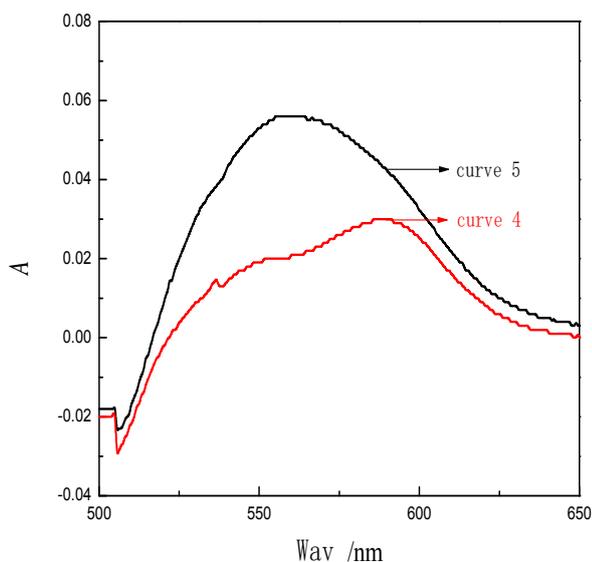

Figure 3. Absorption Curve of Adding Reagent   Different Order.

Effect of pH   The acidity has a great effect on the absorbance of the system. While pH= 1.0 ∼ 1.5, the absorbance at a wavelength of 561 nm was high, while 2 <pH <1, the absorbance at a wavelength of 561nm decreased. Measure the absorbance value in different systems of pH = 0.5,1.00,1.50,2.00 and 5.00 by HCl- KCl buffer solution and adjusting the concentration and amount of HCL solution to control the pH of the system in this study. The result is shown in Fig.4. we can found that: When pH = 1.0 ∼ 1.5 the absorbance is higher, and the resulting ternary complexes is more stable. The cause may be as follows: the stronger the alkaline of the system is, the more stably the ternary complexes Ti (□) -B-H_2O_2 forms, however, if the system is so alkaline that it will accelerate the decomposition of H_2O_2 and the system cannot form a

ternary complexes of Ti (□) -B-H_2O_2. Therefore, pH of the system cannot be too high or too low, the optimum condition is pH = 1.0 ∼ 1.5, This study adopts pH = 1.5.
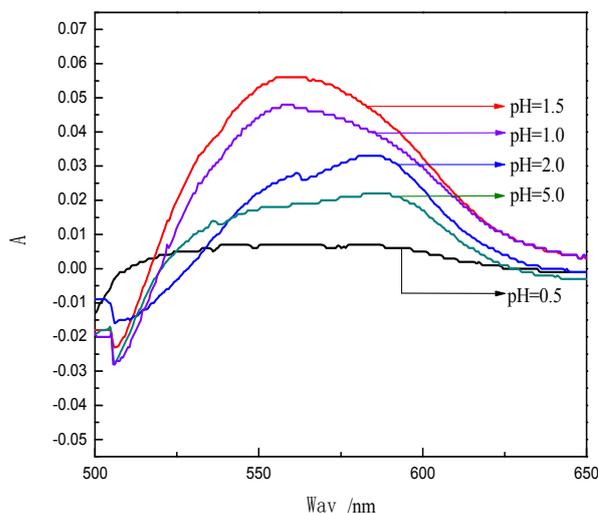

Figure 4 Absorption Curve of Different pH.

Effect of the amount of anhydrous ethanol   The ternary complexes of Ti (□) -B-H_2O_2 can be more stable in ethanol, so the influence of the amount of ethanol on the ternary complexes is studied in this paper. The concentration of ethanol is controlled as 10% 30%, 50% and 60% respectively in the four kinds of systems by adjusting concentration of ethanol in Ti (□) stock solution and the amount of ethanol in paragraph *Ⅱ (B)* step to control the concentration of ethanol in the system, the results are shown in Fig.5. indicating that the chromogenic sensitivity increases with the concentration of ethanol increasing in the system, when the concentration of the alcohol is more than 50% of total volume, the absorbance increases little. Over 50% of the total volume of ethanol is added in the study.

Effect of heating temperature and time   Heating can facilitate the formation of Ti (□) -B-H_2O_2 ternary complexes to improve its stability, However, if the heating temperature is too high, it will accelerate the volatilization of ethanol to reduce the absorbance, therefore the sensitivity is finally reduced. The result of the experimental study shows the absorbance of the system heated at 50 □ is higher. It is heated about 20min at 50 □ water bath, then it is cooled to room temperature in the study.

Effect of the ratio and amount of Ti (□) –B The effects of different ratio of Ti (□) / B mixed solution on the absorbance is studied. When Ti (□) / B = 2 ∼ 0.2, it almost has no effects on the absorbance. When the amount of Ti (□) -B solution is over 2ml, the absorbance does not increase substantially, thus 2ml of Ti (□) -B solution is used in the study.
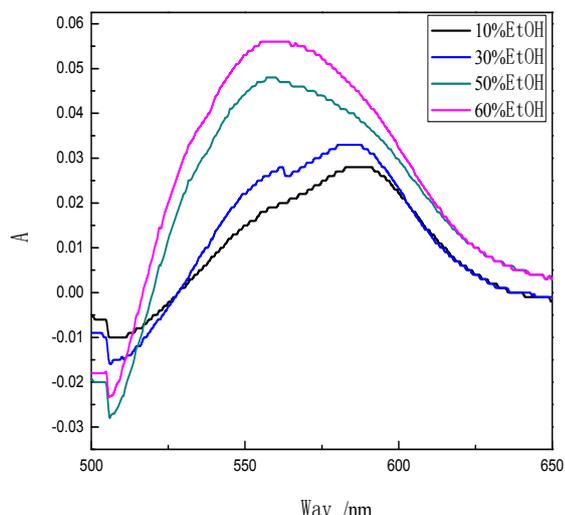
Figure 5 Absorption curve of different amount of anhydrous ethanol.

Linear range and the detection limit The Beer-Lambert Law is hold within the range of 0.2～10μmol/L H_2O_2 in the spectrometric detection of ternary complexes of Ti (Ⅳ) -B-H_2O_2. Here is the regression equation: A = 0.00646C + 0.00132 (wherein, A is absorbance, C is the concentration of H_2O_2, the unit of C is μ mol / L), R^2 = 0.99359. The detection limit is 0.1μg.

IV. DETECTION OF TRACE H_2O_2 IN ELECTROCHEMICAL PROCESS

Three-dimensional electrode reaction in electrochemical study was used to treat 5L water samples. The conditions are as follows: inert plate F, plate spacing d = 6cm, stable output current I = 6A .
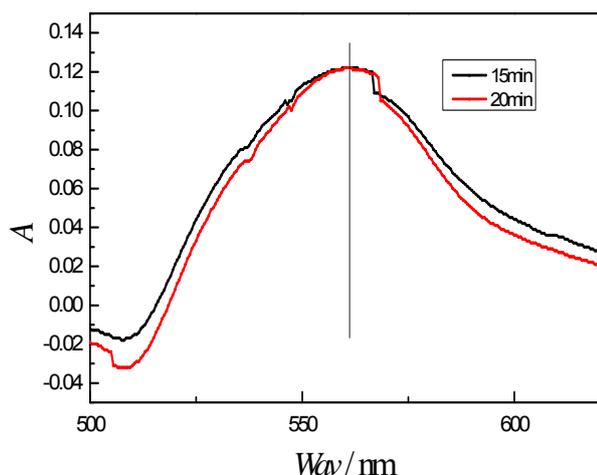

Figure 6 Absorption curve of H_2O_2 in sewage after electrochemical treatment about 15~20 min.

Take out 2mL water samples immediately after electrolysis process treatment about 15～20min into a 10 mL volumetric flask, then do like the steps(4)(5)(6) in a order. Measure the absorbance at a maximum absorption wavelength of about 561nm, and we get absorbance A=0.122 in the end. According to H_2O_2 quantitative curve equation: A = 0.00646C + 0.00132, the concentration of H_2O_2 is C = 18.68μmol / L, while handling a 15~20 min the H_2O_2 of water kind creation was basic to invariant. UV-Vis absorbs spectrum was shown in Fig 6.

V. CONCLUSIONS

A: Here are the conditions of detecting accurately a small amount of H_2O_2: pH = 1.0 ~ 1.5, 50% of ethanol, heated in water bath at 50□ about 20min, Ti (Ⅳ) and B solution mixed at the equal molar ratio, The order of adding reagents: 2ml of various concentrations of these standards H_2O_2 solution, 3ml of anhydrous alcohol, 1ml of 0.32mol/L HCL, 2ml of pH = 1.5 HCl- KCl buffer solution, 2ml of Ti (Ⅳ) -B solution to a 10ml volumetric flask, and dilute with 0.32mol/L HCL solution to the mark line of volume, and mix.

B: The standard working curve of trace H_2O_2 accurate detection within the range of 0.2 ～ 10μmol/L is A = 0.00646C + 0.00132, R^2 = 0.99359, and the Beer-Lambert Law is hold, and the detection limit is 0.1μg.

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