Bull. Chem. Soc. Ethiop. **2025**, 39(3), 397-408.
DOI: https://dx.doi.org/10.4314/bcse.v39i3.1

ISSN 1011-3924
Printed in Ethiopia
Online ISSN 1726-801X

AN ENHANCED SPECTROPHOTOMETRIC METHOD FOR DETERMINATION OF HYDROGEN PEROXIDE DURING VACUUM ULTRAVIOLET PHOTOLYSIS OF WATER

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(Received April 19, 2024; Revised December 8, 2024; Accepted December 13, 2024)

ABSTRACT. This study re-evaluated the DPD/POD (N,N-diethyl-*p*-phenylenediamine/peroxidase from horseradish) spectrophotometric method for accurately detecting low-concentration hydrogen peroxide in water. It established that the absorption coefficient of the adduct product, DPD•+, at a wavelength of 320 nm was approximately two times higher than at 551 nm, indicating lower detection limits at 320 nm for H_2O_2 measurement. An optimal POD/DPD ratio of 1 was identified for effective H_2O_2 concentration determination. The effect of selected anions (chloride, sulfate, nitrate, and carbonate) on H_2O_2 determination was found to be negligible at concentrations below 1 g L^{-1}; however, at higher concentrations, these anions exhibited varying impacts on H_2O_2 measurement. The enhanced DPD/POD method is demonstrated as an effective tool for investigating the mechanism of vacuum ultraviolet (VUV) processes by accurately detecting low-concentration H_2O_2 formed in situ during the photolysis of water. The findings provide insights into the optimal conditions for H_2O_2 determination by this spectrophotometric method and highlight the minimal influence of inorganic anions under specific conditions. This study not only enhances the understanding of H_2O_2 measurement in VUV-induced reactions but also underscores the potential applications of the DPD/POD method in exploring the dynamics of VUV processes.

KEY WORDS: Spectrophotometric method, Hydrogen peroxide, Peroxidase from horseradish, Vacuum ultraviolet

INTRODUCTION

Hydrogen peroxide (H_2O_2) is a widely utilized chemical, finding applications across a range of industries including industrial bleaching, cleaning, disinfection, and chemical synthesis, among others [1]. In environmental engineering, H_2O_2 is heralded for its versatility and efficacy as an oxidizing agent, playing a pivotal role in various advanced oxidation processes (AOPs). H_2O_2 can be employed to degrade persistent organic pollutants, disinfect water supplies, and remove unwanted tastes and odors, offering a cleaner and safer water source for communities and ecosystems [2]. Its application in AOPs, such as the Fenton and vacuum ultraviolet (VUV) processes, leverages the production of hydroxyl radicals (HO•). These radicals possess a high oxidation potential, capable of breaking down complex pollutants into less harmful compounds or mineralizing them completely into carbon dioxide and water. Due to the importance of H_2O_2, the accurate and convenient measurement of H_2O_2 concentration seems crucial for its mechanism study [3].

Traditional methods for determining H_2O_2 concentration, such as direct titration with potassium permanganate, iodine, or cerium, often necessitate strong acid conditions to ensure precise detection. These methods can be time-consuming and labor-intensive [4]. In recent years, electrochemical methods have been intensively studied for H_2O_2 analysis due to their high sensitivity and convenience. These methods explore the relationships between the concentration of solution components and physical quantities such as electrode potential, charge, current, voltage, and conductivity during electrochemical reactions [5]. The primary goal of these

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electrochemical studies is the development of effective electronic sensors. For example, Parrilla *et al.* [6] developed a novel electrode coated with a Nafion layer to assess its potential response towards H_2O_2 concentration, revealing high sensitivity within the range of 10^{-5} to 10^{-3} mol L^{-1} of H_2O_2. Additionally, fluorescence/chemiluminescence methods have been extensively utilized for the measurement of H_2O_2 concentration in the micro molar range, finding widespread applications in analytical chemistry [7, 8]. These methods rely on the quantitative analysis of the relationship between the luminescence intensity of a test solution excited under specific conditions and the concentration of specific substances. In chemiluminescence-based analysis, H_2O_2 functions as an oxidant to oxidize luminescent reagents, generating detectable signals. Common luminescent reagents interacting with H_2O_2 include luminol, lucigenin, plant compounds, and sodium bisulfite [9, 10].

In contrast to the methods descripted, spectrophotometry, known for its convenience and cost-effectiveness, is primarily used to measure the absorbance of a substance at a specified wavelength using a spectrophotometer [11]. Xiao *et al.* [12] achieved rapid detection and simultaneous measurements of various components using a UV-Vis spectrophotometer based on the rapid oxidation of excess potassium iodide by H_2O_2 in the presence of molybdic acid. Despite its rapid detection capability, the use of molybdenum may contribute to environmental pollution due to its toxicity. Bader *et al.* [13] proposed using a nontoxic coloring agent, N,N-diethyl-*p*-phenylenediamine (DPD), which reacts with H_2O_2 in the presence of horseradish peroxidase (POD), forming a pink product with a high absorption coefficient at 551 nm. This DPD/POD spectrophotometric method has become widely adopted in environmental processes for water and wastewater treatment due to its simplicity, precision, and low detection limit.

Despite the wide adoption of the DPD/POD method, developed over three decades ago, there has been limited progress in its refinement. Recognizing the potential for further improvement, this study aims to reassess the DPD/POD method, examining factors that may influence the accuracy and detection limits of the method. Additionally, the refined DPD/POD method will be applied to determine low-concentration H_2O_2 formed *in situ* during the vacuum ultraviolet (VUV) photolysis of water, providing a crucial tool for exploring VUV processes.

EXPERIMENTAL

Chemicals and reagent

N,N-Diethyl-*p*-phenylenediamine (DPD, >98%, AR) was purchased from Shanghai Yi En Chemical Technology Co., Ltd. (Shanghai, China). Peroxidase from horseradish (POD, AR) was obtained from VETEC Ventiltechnik GmbH (Berlin, Germany). Hydrogen peroxide (30% w/w, AR) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and its concentration was calibrated using potassium permanganate titration method. Potassium dihydrogen phosphate (>99%, AR) was supplied by Yongda Chemical Reagent Co., Ltd. (Tianjin, China). All other chemicals used were of analytical grade and utilized without further purification. Solutions were prepared with deionized water to ensure the absence of any contaminants that could affect the experimental results.

Instruments and apparatus

A conventional annular photoreactor with a reaction volume of 400 mL was used as the experimental setup, which was detailed in our previously study [2]. Vacuum ultraviolet (VUV) lamp (25 W) was purchased from Geili Co., Ltd. (Yancheng, Jiangsu Province, China). The spectrophotometer (DR6000) used was from Hach Co., Ltd. (Loveland, Colorado, USA).

Experimental procedure

The DPD solution was freshly prepared for each set of experiments by dissolving 0.10 g of DPD in 10 mL of 0.05 mol L^{-1} H_2SO_4 solution, ensuring a consistent reaction environment. Similarly, the POD solution was prepared by dissolving 10 mg of POD in 10 mL of ultrapure water. This standardization of solutions ensured that the concentrations of reactive species were kept consistent across all experiments. Photolysis experiments were conducted in a custom-built photoreactor equipped with a vacuum ultraviolet (VUV) lamp (25 W), emitting at a wavelength of 185 nm. The reaction chamber was filled with 400 mL of the sample solution, allowing for sufficient interaction between the VUV radiation and the solution. A sample of 2.7 mL was extracted at predetermined intervals of 10 seconds during the photolysis process, ensuring a comprehensive analysis of the reaction kinetics over time. For each sampling point, the mixture of 0.3 mL of a 0.5 mol L^{-1} phosphate buffer solution, 5 μL of DPD solution, and 5 μL of POD solution was added to the sample. The absorbance was measured at 320 nm using a Hach DR6000 spectrophotometer exactly 45 seconds after the addition of the reagents to allow for the color development. This timing was meticulously observed to ensure consistency in the measurement of H_2O_2 concentrations across all experiments.

Reproducibility and statistical analysis

Each experiment was performed in triplicate to ensure the reproducibility of the results. The average values and standard deviations were calculated for each set of measurements. Statistical analyses were conducted using SPSS 29.0 software, with a p-value < 0.05 considered statistically significant.

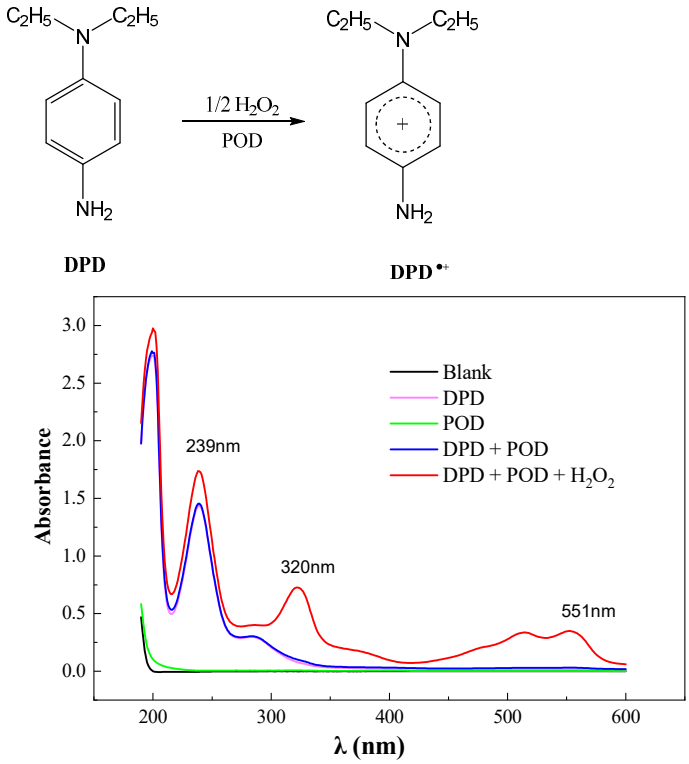
RESULTS AND DISCUSSION

Absorption spectra of $DPD^{\bullet+}$

The investigation into the oxidation of DPD by peroxidase (POD) in the presence of hydrogen peroxide (H_2O_2) revealed the formation of the $DPD^{\bullet+}$ radical cation (Eq. (1)), a process initiated by the oxidation of POD [14]. This reaction pathway led to the generation of a stable pink-colored radical cation, owing to resonance stabilization, that exhibited characteristic absorption peaks. Specifically, the absorption spectra analysis covered a range from 190 nm to 600 nm, identifying three prominent peaks at 239 nm, 320 nm, and 551 nm (Figure 1), corresponding to the absorbance of $DPD^{\bullet+}$. The peak at 239 nm showed the highest absorbance value of 1.74 but was deemed unsuitable for H_2O_2 determination due to significant background interference from DPD itself. Upon comparing the 320 nm and 551 nm wavelengths, previously utilized in standard practices, we discovered that the absorbance at 320 nm was markedly higher. This finding was substantiated by measuring the absorbance of standard H_2O_2 solutions at both wavelengths, demonstrating a stronger correlation between H_2O_2 concentration and absorbance at 320 nm ($r^2 > 0.999$) (Figure 2). The absorption coefficient at 320 nm was approximately twice that at 551 nm ($\varepsilon = 30200$ M^{-1} cm^{-1} *vs.* $\varepsilon = 15900$ M^{-1} cm^{-1}), indicating a significantly lower detection limit for H_2O_2 at 320 nm [9].

The enhanced absorption at 320 nm not only suggests an improved sensitivity in detecting low concentrations of H_2O_2 but also highlights the potential for refining analytical methods for environmental monitoring and analytical chemistry [12]. The reduced detection limit at this wavelength could lead to more accurate assessments of oxidative stress markers in environmental samples, where precise quantification of H_2O_2 is critical. Moreover, the determination of an optimal absorption wavelength is paramount for the development of more efficient and less resource-intensive analytical techniques. The shift from 551 nm to 320 nm represents a significant methodological advancement, offering a pathway to refine the DPD/POD spectrophotometric

method for broader applications. The enhanced detection sensitivity at 320 nm also allows for more precise monitoring of trace hydrogen peroxide concentrations, which is critical in environmental monitoring scenarios. Moreover, the method's lower detection limit supports the analysis of water quality in diverse ecosystems, including those with minimal pollutant levels, enhancing environmental protection and regulatory compliance efforts.



(1)

Figure 1. Absorption spectra of different reaction solutions ([H_2O_2] = 10 μM; DPD = 5 μL; POD = 5 μL).

Dosages of DPD and POD

Exploration into the optimal dosage of DPD revealed that absorbance at 320 nm increased linearly with DPD concentration until reaching a plateau (Figure 3), suggesting a saturation point beyond which additional DPD does not contribute to increased detection sensitivity for H_2O_2. This phenomenon is attributed to the stoichiometric balance required for effective H_2O_2 decomposition, where an excess of DPD ensures complete reaction without contributing to background noise. The determined optimal DPD/H_2O_2 molar ratio was established at 2.67, slightly above the theoretical stoichiometry of 2, aligning with findings by Zhang *et al.* [15] and supporting the need for excess reagent to ensure complete reaction completion.

Conversely, the influence of POD dosage on the system's sensitivity to H_2O_2 detection was markedly different. Minimal background absorption was observed with varying POD levels, highlighting its role as a catalyst rather than a reactant in the formation of $DPD^{\bullet+}$. The absorbance increased with the POD/DPD ratio up to a certain threshold (0.8), beyond which no significant

improvement in detection sensitivity was noted (Figure 4). This suggests that a balanced POD/DPD ratio is critical for maximizing the efficiency of the spectrophotometric detection of H_2O_2. Following the guidelines by Bader *et al.* [13], a POD/DPD ratio of 1 is recommended as optimal for achieving accurate H_2O_2 concentration determinations.

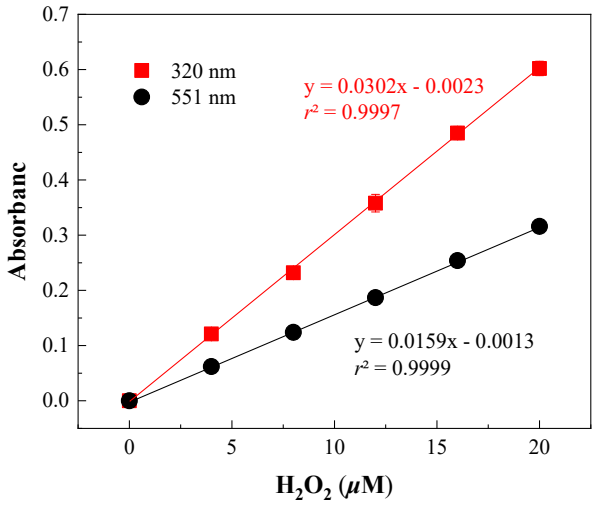


Figure 2. Standard curves of absorbance *vs.* H_2O_2 concentration at different absorbance wavelengths (DPD = 5 μL; POD = 5 μL).

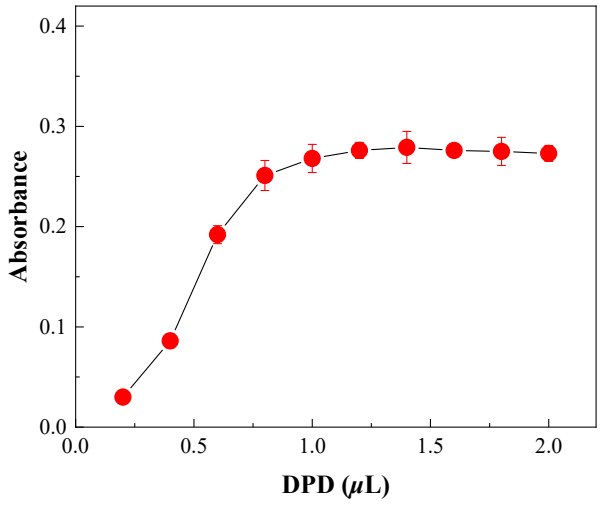


Figure 3. Effect of DPD dosage on the absorbance of the reaction solution at 320 nm ([H_2O_2] = 10 μM; POD = 5 μL).

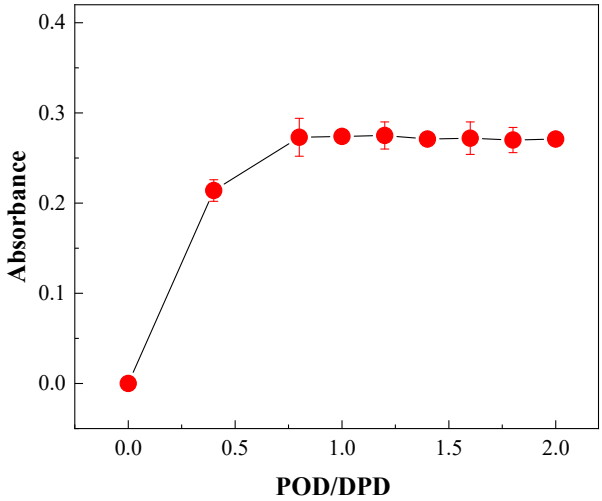


Figure 4. Effect of POD/DPD ratio on the absorbance of the reaction solution at 320 nm ([H_2O_2] = 10 μM; DPD =2 μL).

Effect of solution pH

The influence of solution pH on the spectrophotometric measurement of H_2O_2 using the DPD/POD method was meticulously analyzed, revealing a pronounced effect on the assay's sensitivity. The results demonstrated a clear trend where the absorbance at 320 nm decreased as the solution pH increased from 4.5 to 9.5 (Figure 5). This trend is indicative of the pH-dependent stability of the $DPD^{\bullet+}$ radical cation, with optimal stability and thus maximal absorbance observed at lower pH levels. The theoretical underpinning of the observed pH effect relates to the proton-coupled electron transfer mechanisms involved in the oxidation of DPD by H_2O_2. At lower pH values, the increased proton availability facilitates the formation of the $DPD^{\bullet+}$ radical cation, enhancing the method's sensitivity. Practically, this insight allows for the refinement of the DPD/POD method, making it more adaptable to a wider range of environmental conditions and sample matrices where pH can vary widely [16]. In comparison, the historical selection of a slightly acidic pH at 6.0 [13] for the determination of H_2O_2 was found to be suboptimal based on our experiments. A pH of 4.5 not only improved the sensitivity of the detection but also minimized potential interferences from the matrix or other reactive species present in environmental samples. This adjustment signifies a pivotal enhancement in the method's analytical performance, as corroborated by Zhang *et al.* [15], who emphasized the importance of pH in optimizing the spectrophotometric detection of various analytes.

Effect of inorganic anions

The impact of selected inorganic anions (chloride, sulfate, nitrate, and bicarbonate) on the spectrophotometric detection of H_2O_2 was also systematically explored (Figure 6). This investigation is critical for environmental applications where these anions are prevalent and could potentially interfere with analytical measurements. To isolate the influence of anions from cations, sodium salts of the selected anions were utilized, ensuring consistency in the cationic background across all experiments. Contrary to initial assumptions that anions might broadly impact the

assay's sensitivity, the results revealed a nuanced interaction between anions and the detection of H_2O_2. Chloride, the most common anion in natural waters, showed no significant effect on the assay's sensitivity, even at concentrations up to 20 g L^{-1}, due to its negligible absorbance at 320 nm (Figure 7) [1]. This indicates the robustness of the DPD/POD method in chloride-rich environments. A slight decrement in absorbance was observed with sulfate concentrations increasing beyond 1 g L^{-1}, suggesting a potential quenching effect on the $DPD^{\bullet+}$ radical cation's absorbance at elevated sulfate levels. This observation necessitates consideration in sulfate-predominant water bodies [11]. Interestingly, nitrate ions enhanced the assay's sensitivity at concentrations above 1 g L^{-1}, possibly due to the nitrates' own absorbance properties at 320 nm (Figure 7), which could amplify the perceived H_2O_2 concentrations [16]. This effect underscores the need for caution when interpreting results from nitrate-rich samples. The influence of bicarbonate on the method's performance was negligible at concentrations below 1 g L^{-1}, with a slight positive impact observed at higher concentrations. This might reflect bicarbonate's role in buffering the solution pH, potentially affecting the stability of the $DPD^{\bullet+}$ radical cation.

In summary, the selected anions had no discernible influence on the determination of H_2O_2 when their concentration was below 1 g L^{-1}. However, their effects varied when the concentration surpassed 1 g L^{-1}. This diverse effects of inorganic anions on H_2O_2 determination highlight the importance of matrix consideration in environmental water analysis. When employing the DPD/POD method, understanding the specific water chemistry, especially the predominant anionic species and their concentrations, is vital.

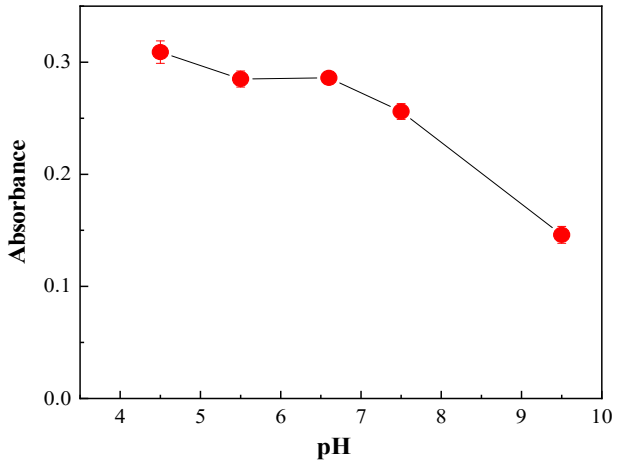


Figure 5. Effect of solution pH on the absorbance of the reaction solution at 320 nm ([H_2O_2] = 10 μM; DPD = 5 μL; POD = 5 μL).

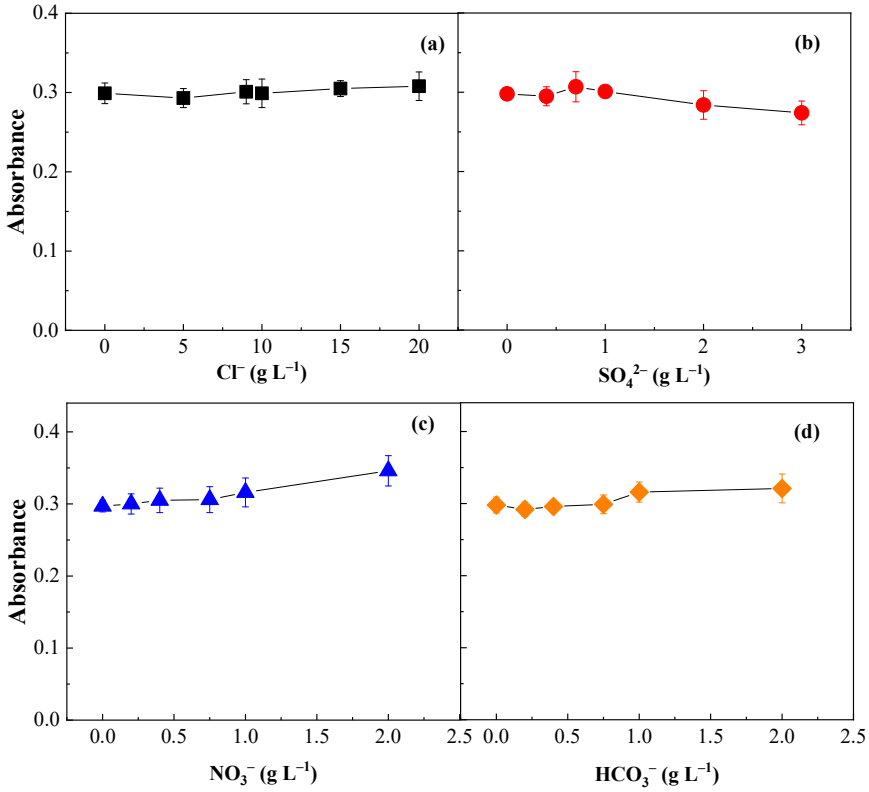


Figure 6. Effects of (a) chloride, (b) sulfate, (c) nitrate and (d) bicarbonate on the absorbance of the reaction solution at 320 nm ([H_2O_2] = 10 μM; DPD = 5 μL; POD = 5 μL).

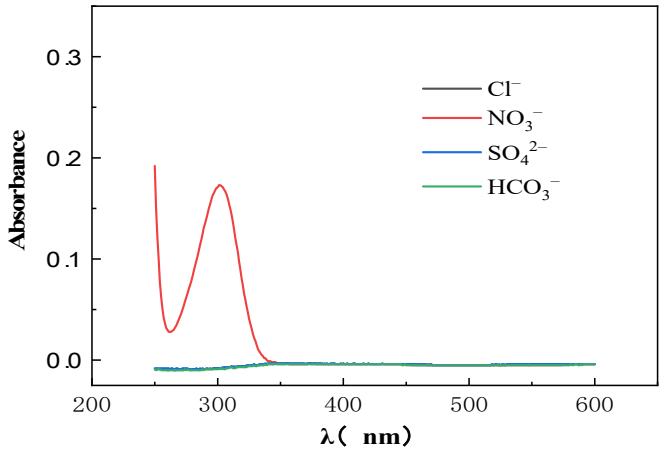


Figure 7. Absorption spectra of different anions with a concentration of 2 g L^{-1} for each.

Determination of H_2O_2 during the vacuum ultraviolet photolysis of water

As an AOP, the vacuum ultraviolet (VUV) process finds widespread application in various areas ranging from water treatment to the transformation of organic materials [17]. With a bond dissociation enthalpy of 498 kJ mol^{-1}, water's threshold wavelength is determined to be 240 nm. Upon exposure to 185 nm VUV radiation, water undergoes rapid photolysis, resulting in the formation of $HO^{\bullet}$ and $H^{\bullet}$ radicals (Eq. (2)). Two hydroxyl radicals can combine and form one H_2O_2 molecule (Eq. (3)). Since these radicals are highly unstable with a lifetime of less than one microsecond, detecting and quantifying them directly using common procedures is challenging. Therefore, the enhanced DPD/POD method for determining the stable H_2O_2 formed *in situ* during the VUV photolysis of water offers a crucial tool for exploring the VUV process. As Figure 8 shows, the concentration of H_2O_2 steadily increased with prolonged reaction time and reached a maximum value after 6 minutes of exposure. Subsequently, the H_2O_2 concentration stabilized at a quasi-stationary level of 13 μM. This quasi-stationary state occurs when the rate of H_2O_2 production (Eq. (3)) equals to the rate of H_2O_2 consumption (Eq. (4)).

The production of H_2O_2 exhibited pseudo-zero-order reaction kinetics during the initial 60 seconds of exposure, as shown in Figure 9. In this time region, the H_2O_2 production rate was determined to be 0.13 μM s^{-1}, showing a strong correlation coefficient of $r^2 = 0.997$. During a 60-second exposure to VUV irradiation, the concentration of H_2O_2 produced in water was found to be very low, measuring less than 8.0 μM. As a result of this low concentration and small rate constant of Eq. (4), compared to Eq. (2), the consumption of H_2O_2 by Eq. (4) was also insignificant. Hence, the primary factor influencing H_2O_2 production in the presence of generated $HO^{\bullet}$ was Eq. (1), which acted as the rate-determining step. Due to the considerably high concentration of water (55.6 mol L^{-1}), the VUV photolysis of water followed pseudo-zero-order reaction kinetics. Consequently, the H_2O_2 production also exhibited pseudo-zero-order reaction kinetics, mirroring that of water VUV photolysis at the initial stage of VUV exposure. This observation implies that the H_2O_2 production rate, as pseudo-zero-order reaction kinetics, was directly proportional to the absorbed VUV photon intensity, rendering it a good VUV actinometer [18, 19].

The ability to closely monitor and quantify H_2O_2 formation during VUV photolysis has profound implications. It provides a reliable measure of the process's effectiveness in generating oxidative radicals for pollutant degradation. The optimized DPD/POD method, capable of detecting H_2O_2, enhances our understanding of VUV-induced AOPs and their application in treating water and wastewater, ensuring the production of water that meets the purity standards.

$$H_2O \xrightarrow{VUV} HO^{\bullet} + H^{\bullet} \qquad \Phi_{185\,nm} = 0.33 \text{ [20]} \tag{2}$$

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \qquad k_2 = 4 \times 10^9 \text{ M}^{-1}\text{ s}^{-1} \text{ [20]} \tag{3}$$

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \qquad k_6 = 3.3 \times 10^7 \text{ M}^{-1}\text{ s}^{-1} \text{ [20]} \tag{4}$$

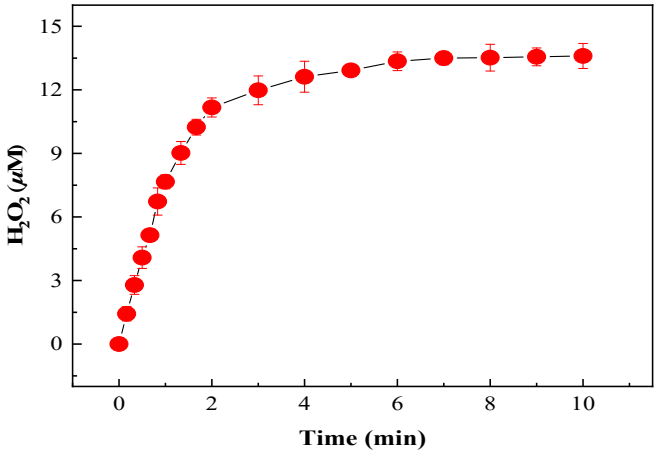


Figure 8. Production of H_2O_2 *vs*. reaction time during the VUV photolysis of water.

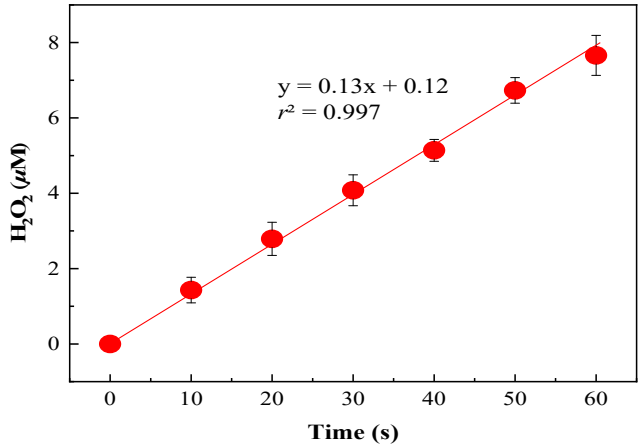


Figure 9. Linear regression between production of H_2O_2 and reaction time within 60 s during the VUV photolysis of water.

CONCLUSION

This research has refined the DPD/POD method for detecting low-concentration H_2O_2 in water, critical for assessing vacuum ultraviolet (VUV) photolysis in water treatment. It established 320 nm as the optimal wavelength for increased detection sensitivity and accuracy, optimized reagent ratios for DPD and POD, and explored how solution pH and anions affect H_2O_2 quantification. Future applications of the refined DPD/POD method could extend to broader environmental monitoring tasks, such as the detection of low-concentration reactive oxygen species in natural water systems. Additionally, integrating this enhanced method with other advanced oxidation processes could facilitate a more comprehensive understanding of pollutant degradation

dynamics. This work may also inspire the development of improved analytical tools for environmental and biochemical studies, leveraging the method's high sensitivity and adaptability.

ACKNOWLEDGMENTS

This paper was financially supported by the Shaoyang University Graduate Innovation Project (CX2024SY026), Natural Science Foundation of Hunan Province (2022JJ50227), and Aid Program for Science and Technology Innovative Research Team in Higher Educational Institutions of Hunan Province (Xiangjiaotong [2023] NO. 233).

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