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Quantification of photocatalytically-generated hydrogen peroxide in the presence of organic electron donors: Interference and reliability considerations

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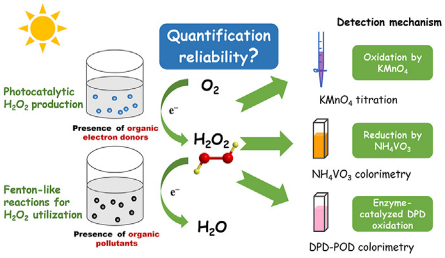
HIGHLIGHTS

- Organic electron donors interfere with photo-generated H_2O_2 quantification.
- $KMnO_4$ titration and NH_4VO_3 or DPD-POD colorimetry were compared for H_2O_2 detection.
- The accuracy of the $KMnO_4$ titration method is compromised by aromatic compounds.
- P-benzoquinone reacts with NH_4VO_3 and DPD and interferes with H_2O_2 quantification.
- A flowchart that helps to select a suitable H_2O_2 detection method is provided.

GRAPHICAL ABSTRACT



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ABSTRACT

Photocatalytic H_2O_2 production is an innovative on-site H_2O_2 synthesis method to treat organic pollutants through Fenton-like reactions, avoiding the need and potential liability of H_2O_2 storage and transportation. Accurate quantification of H_2O_2 is crucial to explore the mechanism of photocatalytic H_2O_2 production and optimize reaction parameters. In this work, three common H_2O_2 quantification methods (i.e., titration with potassium permanganate ($KMnO_4$), and colorimetry with ammonium metavanadate (NH_4VO_3) or N,N-diethylp-phenylenediamine-horseradish peroxidase (DPD-POD)) were compared and their susceptibility to interference by seven types of representative organics were considered. Interference mechanisms were explored based on the electron-donating (E_{gap}) and electron-accepting (E_{LUMO}) ability of the present organics. The accuracy of the $KMnO_4$ titration method is greatly compromised by aromatic compounds even at 0.1 mM due to the increased $KMnO_4$ consumption by direct oxidation. The presence of *p*-benzoquinone that directly reacts with NH_4VO_3 and DPD compromises these colorimetric methods, especially DPD-POD colorimetry at concentrations as low as 0.1 mM. The DPD-POD method should also be scrutinized in the presence of phenols due to significant disturbance by oxidation byproducts (e.g. hydroquinone inducing immediate color disappearance). A flowchart was generated to provide guidelines for selecting an appropriate H_2O_2 quantification method for different water matrices treated by Fenton-like reactions.

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1. Introduction

Hydrogen peroxide (H_2O_2) is a green oxidant that is commonly used in environmental remediation, especially advanced oxidation processes (AOPs) for water treatment since it can generate highly oxidizing hydroxyl radicals (•OH) and produce only water as a by-product (Miklos et al., 2018; Huang et al., 2020). Currently, commercial H_2O_2 is mainly produced by anthraquinone method, which is limited by high energy consumption and organic by-products generation (Campos-Martin et al., 2006; Gao et al., 2020). Moreover, the instability of the synthesized high-concentration H_2O_2 results in safety problems during storage and transportation. Therefore, the on-site production of H_2O_2 in practical concentrations has drawn significant interest (Perry et al., 2019; Pi et al., 2020).

Photocatalytic H_2O_2 production is a novel on-site H_2O_2 synthesis method that only needs water and oxygen as raw materials, and light as energy input (Fukuzumi et al., 2018; Hou et al., 2019; Sun et al., 2020). In the present studies, H_2O_2 production processes are achieved mainly by oxygen reduction reactions (ORR). Semiconductor photocatalysts, such as TiO_2 (Zheng et al., 2018; Wang et al., 2019), g-C_3N_4 (Shiraishi et al., 2014) and their modifications (Chu et al., 2020; Feng et al., 2020a; Lu et al., 2020), are excited by light to produce photo-generated electron-hole pairs, and the photo-generated electrons can react with oxygen through one-electron or two-electron pathways to generate H_2O_2. Organic electron donors, especially alcohols, are often added to accelerate separation of electron-hole pairs and promote H_2O_2 production (Zhang et al., 2020b). The concentration of photo-generated H_2O_2 is usually in the micromole to millimolar level, which can be utilized for in-situ degradation of refractory organic pollutants, such as aromatic compounds (Luo et al., 2010; Asghar et al., 2015; Xiong et al., 2019). Due to the significance of H_2O_2 to wastewater treatment, accurate quantification of H_2O_2 is of vital importance for optimizing in situ generation and reaction conditions.

H_2O_2 quantification methods can be classified into methods based on the involvement of H_2O_2 into redox reaction or not. The usually employed methods are based on the H_2O_2 reactivity in redox reactions, such as colorimetric, fluorescence, and chemiluminescence approaches (Nosaka and Nosaka, 2017). However, there are very few methods can directly detect H_2O_2 without the occurrence of redox reactions but demanding advanced equipment (Song et al., 2017). In photocatalytic H_2O_2 production and Fenton-like reactions, the most widely used H_2O_2 quantification methods are titration with potassium permanganate ($KMnO_4$) (Hirakawa et al., 2016; Kofuji et al., 2018; Zhu et al., 2020), and colorimetry with ammonium metavanadate (NH_4VO_3) (Trovo et al., 2009; Mendez-Arriaga et al., 2010; Pan et al., 2018) or with N,N-diethylp-phenylenediamine-horseradish peroxidase (DPD-POD) (Zhao et al., 2014; Shi et al., 2018; Zhang et al., 2020c). These three methods are based on the oxidability, reducibility, and enzyme-catalyzed oxidation of the detection reagent, respectively (Huckaba and Keyes, 1948; Bader et al., 1988; Nogueira et al., 2005). They are easy to apply, and their quantification range matches the concentration of H_2O_2 involved in the reactions of generation and utilization (Table S1).

Although the accuracy of these methods has been established in simple systems, their reliability in the context of photocatalytic H_2O_2 production and Fenton-like reactions during treatment of common pollutants has barely been systematically compared. A recent research by Gill and Zheng (2020) suggests that some anions and aliphatic organics in the electrolytes may interfere with the quantification of electrochemically generated H_2O_2. Considering that organic compounds are susceptible to redox reactions during H_2O_2 detection, it is necessary to re-evaluate the accuracy of different H_2O_2 detection methods and clarify the underlying interference mechanisms by different compounds in photocatalytic H_2O_2 production systems and Fenton-like reactions

In this work, the $KMnO_4$ titration, NH_4VO_3 colorimetric and DPD-POD colorimetric H_2O_2 quantification methods are compared in photocatalytic systems, and interference effects and mechanisms by seven organic compounds are considered. To assess variability in photocatalytic H_2O_2 production yields, three H_2O_2 concentrations ranging from micromolar to millimolar levels are selected (i.e., low- (50 μM), medium- (200 μM) and high-concentrations (1000 μM)). This work therefore informs the selection of suitable H_2O_2 quantification methods for studies and optimization efforts involving photocatalytic and Fenton-like advanced oxidation processes.

2. Experimental section

2.1. Reagents

Hydrogen peroxide (30 wt%), potassium permanganate, ammonium metavanadate, sulfuric acid (H_2SO_4), absolute ethanol, acetaldehyde, acetic acid, acetone, phenol, *p*-benzoquinone and bisphenol A were analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. N,N-diethylp-phenylenediamine (DPD) and horseradish peroxidase (POD) were procured by Sigma Aldrich Co. Ltd. All reagents were used without further purification.

2.2. Analytic procedure

To evaluate the influence of coexisting organics on photo-generated H_2O_2 detection, some commonly used organic sacrificial agents and/or target pollutants and their oxidation intermediates were selected. They were four aliphatic organics: ethanol, acetaldehyde, acetic acid, acetone, and three aromatic organics: phenol, *p*-benzoquinone and bisphenol A. Different concentrations of organics (0.1, 1 mM, and 10 mM) were added to the H_2O_2 solutions at low (50 μM), medium (200 μM), and high (1000 μM) concentrations. H_2O_2 concentration was tested by $KMnO_4$ titration method, NH_4VO_3 colorimetric method, and DPD-POD colorimetric method. The influence of coexisting organics on H_2O_2 quantification was expressed by relative errors (Eq. (1)). All the experiments were conducted in triplicate, and results are presented as mean values and standard deviations.

$$\text{Relative error} = \frac{c_{measured} - c_{true}}{c_{true}} \times 100\% \tag{1}$$

The specific detection procedures for the three methods are as follows.

$KMnO_4$ titration method: The concentration of $KMnO_4$ solution (about 0.02 M) was standardized by sodium oxalate ($Na_2C_2O_4$) at 70 °C. Then 35 mL of H_2O_2 samples including 2.5 mL of 6 M H_2SO_4 were titrated dropwise by the calibrated $KMnO_4$ solution until a faint pink color persisted for 30 s (Huckaba and Keyes, 1948). The concentration of H_2O_2 was calculated based on the consumed volume of $KMnO_4$ solution.

NH_4VO_3 colorimetric method: 31 mmol NH_4VO_3 powder was dissolved in 10 mL of H_2SO_4 solution (9 M). After cooling to room temperature, the solution was adjusted to 500 mL with deionized water to obtain NH_4VO_3 solution. To detect H_2O_2 concentration, 1 mL of NH_4VO_3 solution and 1 mL of sample were added to a colorimetric tube and diluted to 10 mL with deionized water. After developing color for 10 min, the absorption of solution was detected by a UV−Vis spectrophotometer (TU-1810, Persee) at $\lambda = 450$ nm (Nogueira et al., 2005; Molamahmood et al., 2020).

DPD-POD colorimetric method: 3 mL of phosphate buffer

(0.5 M, pH = 6), 1 mL of sample, 50 μL of DPD solution (10 mg mL^{-1}) and 50 μL of POD solution (1 mg mL^{-1}) were successively added to a colorimetric tube and diluted to 10 mL using deionized water. After developing color for 30 s, the absorbance was analyzed at 551 nm on a UV–Vis spectrophotometer (Bader et al., 1988; Wei et al., 2019).

2.3. Computational assessments

To clarify the redox properties, energy of the highest occupied molecular orbital (E_{HOMO}, eV) and the lowest unoccupied molecular orbital (E_{LUMO}, eV) of organic compounds were calculated by the Gaussian 09 W software. M06-2X coupled with 6–311++G(d, p) basis set using the universal solvation model based on solute electron density was used to calculate the optimized geometry and vibrational frequencies (Su et al., 2020). The gap of E_{LUMO} and E_{HOMO} (E_{gap}, eV) was calculated as $E_{gap} = E_{LUMO}$ - E_{HOMO}.

3. Results and discussion

3.1. Reliability of $KMnO_4$ titration method

$KMnO_4$ titration method is based on the reaction described by Eq. (2), where the highly oxidizing MnO_4^- (purple-red in color) can be reduced by H_2O_2 to generate colorless Mn^{2+} under acidic conditions (Klassen et al., 1994). According to the $KMnO_4$ concentration (c_{KMnO_4}) and its consumed volume (V_{KMnO_4}) during the titration, the H_2O_2 concentration ($c_{H_2O_2}$) can be calculated by Eq. (3). The detection limit of this method was 0.3 μM (Klassen et al., 1994; Song et al., 2017).

$$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O \tag{2}$$

$$c_{H_2O_2} = \frac{5}{2} \times \frac{c_{KMnO_4} \times V_{KMnO_4}}{V_{H2O2}} \tag{3}$$

The effect of aliphatic and aromatic organics on H_2O_2 quantification by the $KMnO_4$ titration method is shown in Fig. 1. Alcohols are frequently used as the electron donors for photocatalytic H_2O_2 production, and aldehydes, ketones and carboxylic acids are common byproducts that may accumulate in the solution (Tsukamoto et al., 2012; Zhang et al., 2020a). For aliphatic organics (Fig. 1a–1c), the presence of ethanol or acetaldehyde leads to a significant overestimation of H_2O_2 concentration. The relative error increases with the increase of ethanol or acetaldehyde concentration (from 36% to 64% for ethanol and from 33% to 49% for acetaldehyde when H_2O_2 concentration is 50 μM). In contrast, the presence of acetic acid or acetone exhibits much less influence on H_2O_2 quantification. These differences in extent of interference can be explained by differences in the electron donating ability of chemicals, which was assessed by the HOMO-LUMO gap (E_{gap}). Since the low E_{gap} facilitates electron transfer and donation, compared with ethanol (9.73 eV) and acetaldehyde (9.57 eV), acetic acid (10.22 eV) exhibits the lowest reactivity with $KMnO_4$ (Table 1) (Karelson et al., 1996; Shao et al., 2020). Although acetone shows a low theoretical E_{gap} value (9.24 eV), it performs negligible disturbance on the measured results of $KMnO_4$ titration method. This may be ascribed to its higher half-wave potential, leading to less potential to be oxidized by $KMnO_4$ than aldehydes with similar structure ($E(acetone)_{1/2} = -1.52$ V vs. saturated calomel electrode (SCE) and $E(acetaldehyde)_{1/2} = -1.89$ V vs. SCE) (Speight, 2005; Zhou et al., 2020).

The presence of the three tested aromatic organics can induce enormous errors in H_2O_2 quantification by this titration method (Fig. 1d–f). Among them, phenol is a common pollutant in Fenton-like reactions, *p*-benzoquinone is a possible oxidation intermediate, and bisphenol A is a refractory emerging contaminant. For a H_2O_2 sample with a known concentration of 50 μM, *p*-benzoquinone induces the largest relative error (873% for 0.1 mM or 10.8 mg L^{-1}), followed by phenol (496% for 0.1 mM or 9.4 mg L^{-1}) and bisphenol A (241% for 0.1 mM or 22.8 mg L^{-1}). These differences in the extent of interference can be ascribed to their E_{gap} values as well. The E_{gap} for phenol, *p*-benzoquinone, and bisphenol A are 7.93 eV, 6.87 eV and 7.33 eV, respectively (Table 1). Among them, *p*-benzoquinone is highly susceptible to be oxidized by $KMnO_4$, which increases the consumption of $KMnO_4$, thus increasing the measured H_2O_2 concentration. Since 1.0 mM of aromatic organics can bring a thousand-fold relative error to the measurement of 50 μM H_2O_2, the effect of 10 mM of organics was not further explored in this method.

The accuracy of this method is more susceptible to interference by organics when the H_2O_2 concentration is low. For example, with the presence of ethanol or acetaldehyde, the measured results for low- (50 μM) and medium-concentration (200 μM) H_2O_2 samples exhibit significant relative errors. But the relative errors decrease to a low level when the actual H_2O_2 concentration is 1000 μM. Accordingly, when aliphatic organics are present in photocatalytic reactions, the $KMnO_4$ titration method is only suitable for quantifying high-concentration H_2O_2 (above 1000 μM). Aromatic organics can result in tremendous relative errors even for 1000 μM H_2O_2 (>50% when organic concentration is 0.1 mM and >500% when organic concentration is 1.0 mM). Thus, the $KMnO_4$ titration method is not advisable for H_2O_2 quantification with the presence of aromatic organics.

3.2. Reliability of NH_4VO_3 colorimetric method

In the NH_4VO_3 colorimetric method, ammonium metavanadate serves as a reductant to react with H_2O_2 in acidic medium. The generated peroxovanadium cations display red-orange color and absorb strongly at 450 nm (Eq. (4)) (Nogueira et al., 2005). Accordingly, the concentration of H_2O_2 can be calculated from the measured absorbance by the standard curve, which is shown in Fig. S1. The absorbance is linearly related to H_2O_2 concentration in the range of 0–40,000 μM (R^2 = 0.9999). The limit of detection is 65.8 μM according to 3σ/k, where σ represents the standard deviation of the y-intercept and k is the slope of the curve. Therefore, NH_4VO_3 colorimetric method is suitable for the quantification of H_2O_2 at medium and high concentrations.

$$VO_3^- + 4H^+ + H_2O_2 \rightarrow VO_2^{3+} + 3H_2O \tag{4}$$

Fig. 2 displays the effect of various organic compounds on the quantification of H_2O_2 by NH_4VO_3 colorimetric method. The relative errors caused by the presence of organics in this method are much smaller than those in $KMnO_4$ titration method. The measured H_2O_2 concentration is relatively more accurate in the presence of only aliphatic organics, and the maximum relative error is 11%, which occurs for the case of the coexisting of 10 mM acetic acid (i.e. 600 mg L^{-1}) and 1000 μM H_2O_2 (Fig. 2a and b). This can be attributed to the strongest electron accepting ability of acetic acid in the four aliphatic organics, since it has the minimum E_{LUMO} (0.14 eV, Table 1) (Karelson et al., 1996; Avigdori et al., 2020). Therefore, acetic acid is likely to be reduced by NH_4VO_3 or react with NH_4VO_3 intermediates, and accordingly disturb the measured H_2O_2 concentrations.

As for aromatic organic compounds, both phenol and bisphenol A caused minor interference on the measured results, with relative errors less than 5% and 3%, respectively (Fig. 2c and d). After subtracting the background absorbance of *p*-benzoquinone solution,

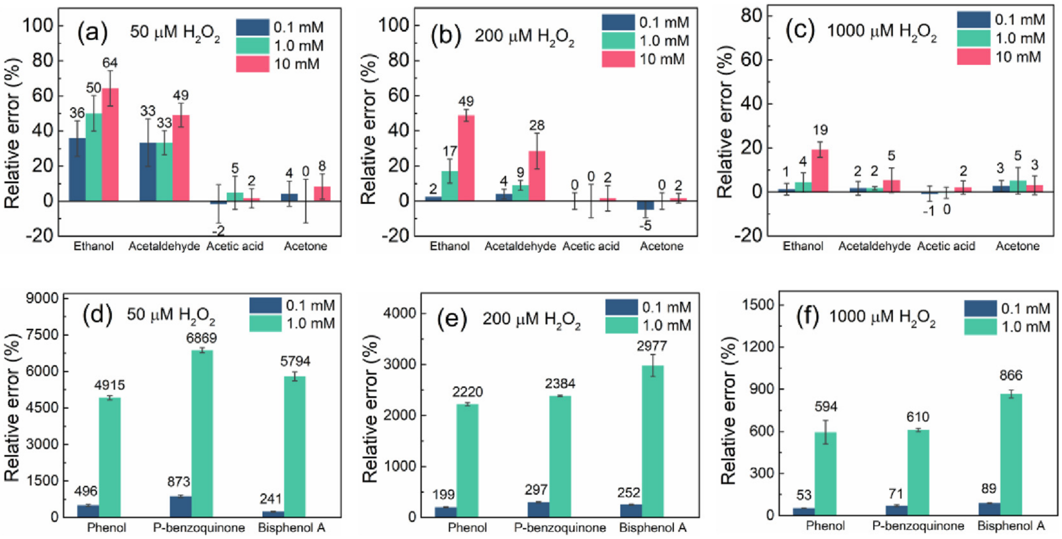

Fig. 1. The effect of aliphatic (**a, b** and **c**) and aromatic (**d, e** and **f**) organics on the quantification of H_2O_2 in $KMnO_4$ titration method.

Table 1
The E_{HOMO}, E_{LUMO} and E_{gap} of organic compounds.

Organics	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)
Ethanol	−9.56	0.17	9.73
Acetaldehyde	−9.28	0.29	9.57
Acetic acid	−10.08	0.14	10.22
Acetone	−9.10	0.15	9.24
Phenol	−7.78	0.15	7.93
P-benzoquinone	−9.51	−2.64	6.87
Bisphenol A	−7.32	0.01	7.33

0.1 mM *p*-benzoquinone exhibits negligible effect (relative errors < 1%) on the detected results. The effect of 1.0 mM *p*-benzoquinone is also small, and the relative errors are 13% and 1% for the medium- and high-concentration H_2O_2. However, 10 mM *p*-benzoquinone leads to a 75% exaggerated estimation of the medium-concentration of H_2O_2, while the relative error decreases to 12% when the H_2O_2 concentration increases to 1000 μM. The interference of *p*-benzoquinone on H_2O_2 determination in NH_4VO_3 colorimetric method can also be explained by its unique reactivity. The E_{LUMO} of *p*-benzoquinone (−2.64 eV) is much lower than that of phenol (0.15 eV) and bisphenol A (0.01 eV), so *p*-benzoquinone is more electron-withdrawing and easier to be reduced by ammonium metavanadate or the intermediates (Gao et al., 2021).

These results infer that when the H_2O_2 concentration in the reaction systems is relatively high (above 1000 μM), the detection results of NH_4VO_3 colorimetric method are relatively reliable, and the disturbance by the presence of organics is negligible. For reaction systems with the medium-concentration (200 μM) of H_2O_2, the tested results are also relatively accurate in the presence of aliphatic organics or low-concentration aromatic organics (below 1.0 mM). However, the presence of high concentration of *p*-benzoquinone (above 10 mM) can induce a sizable relative error for the medium-concentration of H_2O_2. Considering that benzoquinones are the intermediates of phenol oxidation in the photocatalytic processes (Liu et al., 2008), even though phenol shows little effect on the accuracy of tested results, the NH_4VO_3 colorimetric method should be scrutinized when high-concentrations (above 1.0 mM) of phenols and/or benzoquinones are present.

3.3. Reliability of DPD-POD colorimetric method

DPD-POD colorimetric method was developed in 1988 by H. Bader et al. and has been broadly used in photocatalytic systems for H_2O_2 quantification (Table S1) (Bader et al., 1988). This method relies on the POD-catalyzed DPD oxidation (Fig. 3a). H_2O_2 can oxidize POD into a higher valent state intermediate, which subsequently oxidizes DPD molecules to radical cations with imine group (DPD^+). H_2O_2 concentration can be determined by measuring the absorbance of the pink colored DPD^+ at 551 nm. Fig. S2 displays the standard curve of the DPD-POD colorimetric method. In the concentration range of 0–400 μM, the absorbance presents a highly linear response with H_2O_2 concentration ($R^2 = 0.9992$). The detection limit of this method is calculated to be 7.1 μM according to 3σ/k. Consequently, the DPD-POD colorimetric method can be directly used to quantify the low- (50 μM) and medium-concentration (200 μM) H_2O_2 samples, while the high-concentration (1000 μM) H_2O_2 samples are diluted for 10 times before detection.

The DPD-POD colorimetric method failed to reliably quantify H_2O_2 concentration in the presence of *p*-benzoquinone even at a low concentration (0.1 mM). As shown in Fig. S3, in the absence of H_2O_2, a pink color appears after adding DPD to a *p*-benzoquinone solution. The generated product also exhibits absorption at 551 nm, and the absorbance induced by 0.1, 1.0 mM and 10 mM *p*-benzoquinone equals to 55, 116 μM and 213 μM H_2O_2, respectively. The formation of the pink product is due to the direct reaction between *p*-benzoquinone and DPD, which generates quinone imine (pink in color), a similar oxidation product of DPD in DPD-POD colorimetric method (Fig. 3b) (Bontschev, 1962; Maleki and Nematollahi, 2011).

The effect of the other organics except *p*-benzoquinone on the quantification of H_2O_2 is shown in Fig. 4. Regardless of the H_2O_2 concentration, relative errors caused by the co-occurring organics are negligible (<8%). This result demonstrates the robust anti-interference ability of the DPD-POD colorimetric method, which can be attributed to the high selectivity of peroxidase. However, although the relative error caused by phenol is negligible, the DPD-POD colorimetric method is also not satisfactory for H_2O_2 quantification in the presence of phenolic substances due to the

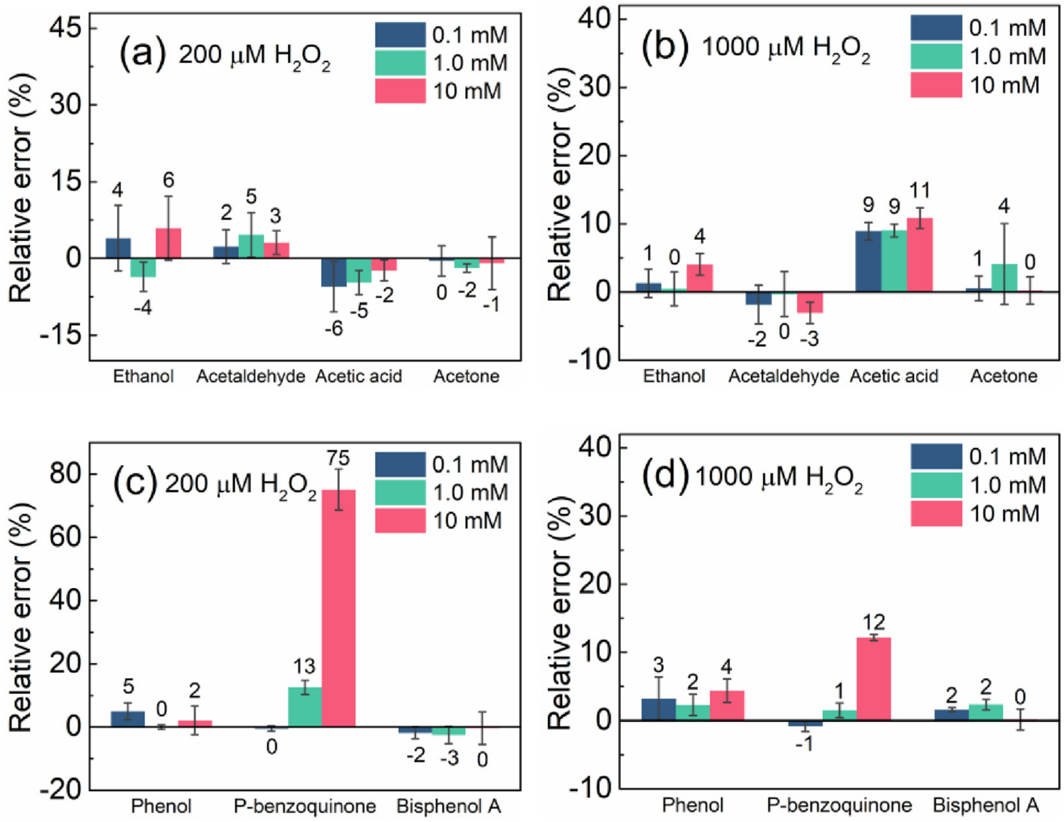

Fig. 2. The effect of aliphatic (**a** and **b**) and aromatic (**c** and **d**) organics on the quantification of H_2O_2 in NH_4VO_3 colorimetric method.

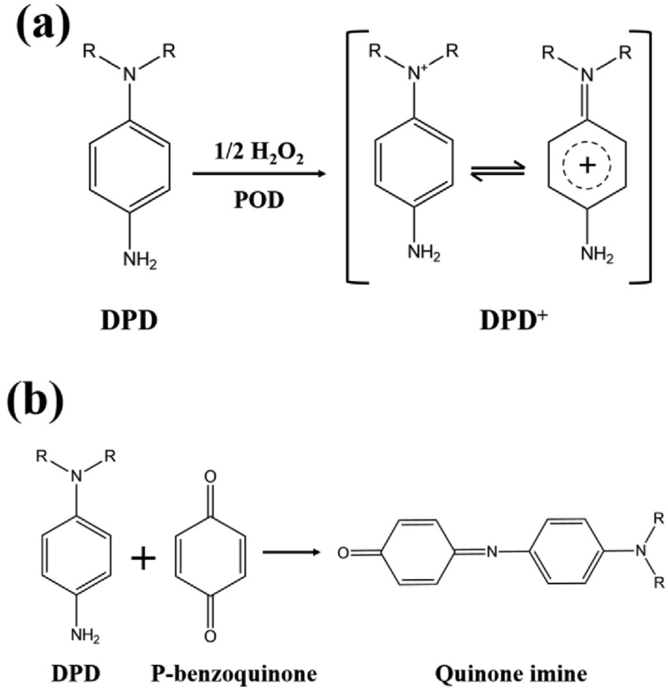

Fig. 3. (**a**) The formation of imine in DPD-POD colorimetric method (Bader et al., 1988) and (**b**) the formation of quinone imine in the reaction between DPD and *p*-benzoquinone (Bontschev, 1962; Maleki and Nematollahi, 2011).

interference of their oxidation intermediates. The direct reactions between the benzoquinone intermediates of phenols and DPD lead to the formation of interfering imines, which eventually result in erroneous measured H_2O_2 concentration. The production of hydroquinone, another intermediate with high reduction potential ($E_{gap} = 5.30$ eV) in phenol oxidation, induces significant errors in H_2O_2 detection due to immediate decolorization of DPD^+ (Fig. S4). The appearance of hydroquinone results in a drastically underestimated H_2O_2 concentration since the reduction of DPD^+ by hydroquinone is fast (Fukushima and Tatsumi, 1998). Overall, the DPD-POD colorimetric method can accurately measure the H_2O_2 concentration regardless the interference of aliphatic organics due to the selectivity of peroxidase, but this colorimetric method also should be scrutinized in the presence of phenols and benzoquinones.

3.4. Recommendations for method selection

No clear rule was discerned between the concentration of different co-occurring organic compounds and the resulting relative errors (Fig. S5). Furthermore, the concentrations of sacrificial agents and/or contaminants change during H_2O_2 quantification, which makes it is difficult to assign a specific relative error for each of the three methods under consideration. Therefore, we produced a flowchart to guide selection of the most suitable H_2O_2 quantification method for different case-specific conditions (Fig. 5).

The first consideration should be which organic sacrificial agents and/or contaminants are present in the photocatalytic reaction. If no organic is present in the reaction system, the choice of H_2O_2 detection method depends on their detection ranges. The $KMnO_4$ titration method is applicable for a wide range of H_2O_2 concentrations. The NH_4VO_3 colorimetric method is not appropriate for low concentrations of H_2O_2 below its detection limit

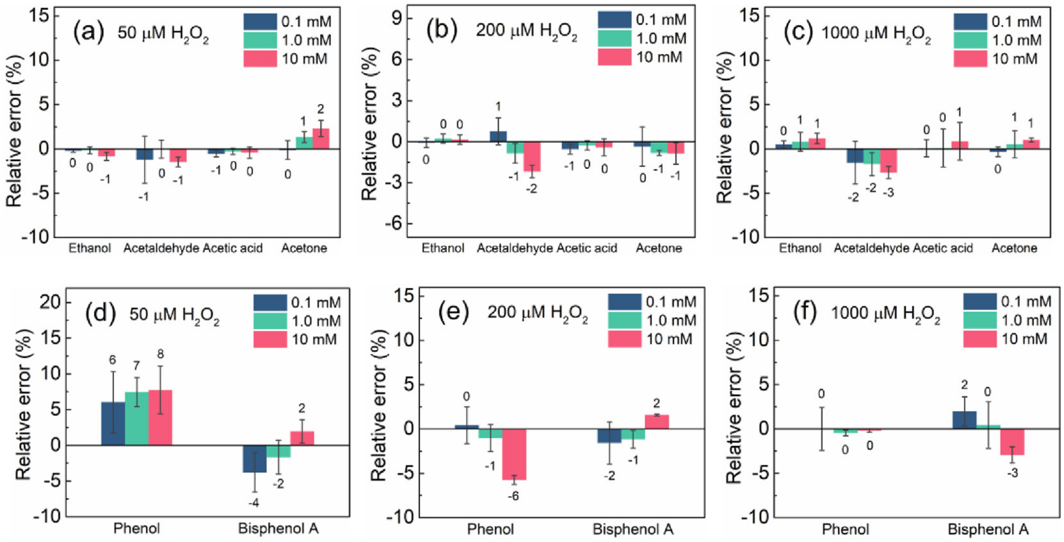

Fig. 4. The effect of aliphatic (**a, b** and **c**) and aromatic (**d, e** and **f**) organics on the quantification of H_2O_2 in DPD-POD colorimetric method.

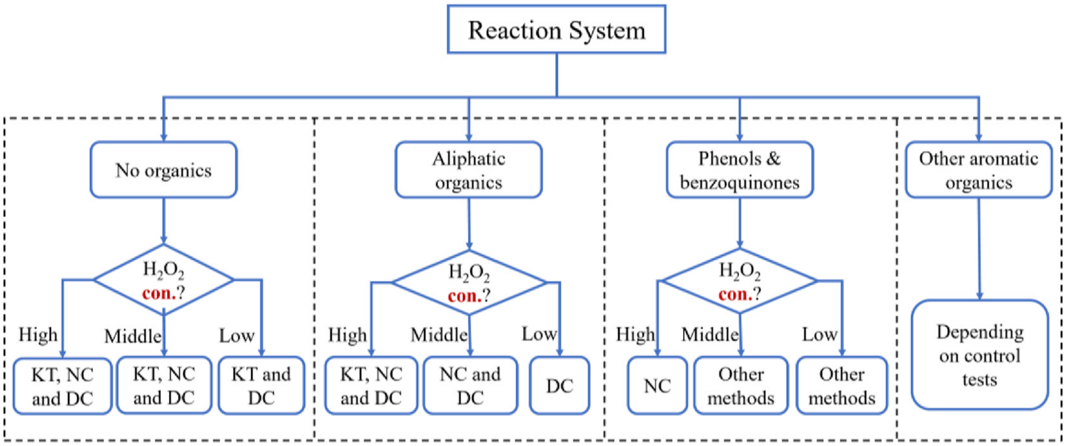

Fig. 5. Flowchart for selecting a suitable H_2O_2 detection method (con. = concentration, KT = $KMnO_4$ titration method, NC = NH_4VO_3 colorimetric method, DC = DPD-POD colorimetric method).

(65.8 μM). The DPD-POD colorimetric method can be directly used for samples with H_2O_2 concentrations below 400 μM based on the measured calibrate curve, and samples with higher H_2O_2 concentrations than this value should be diluted before quantification.

When organics are present, interference by aliphatic compounds is generally less than that of aromatic organic compounds. The presence of aliphatic organic compounds (above 0.1 mM) will induce significant relative errors for the $KMnO_4$ titration method when H_2O_2 concentration is less than 200 μM, while the NH_4VO_3 and DPD-POD colorimetric methods are less susceptible to this interference. Accordingly, quantification of 50 μM H_2O_2 concentration with the DPD-POD colorimetric method in the presence of aliphatic compounds should be reliable. Both NH_4VO_3 and DPD-POD colorimetric methods are suitable for the determination of medium-concentration (200–1000 μM) H_2O_2 samples. As for samples with high H_2O_2 concentration (>1000 μM), all the three methods can be employed.

Aromatic organic compounds may cause large relative errors to all the three ranges of H_2O_2 concentrations measured by the $KMnO_4$ titration method even if the organic concentrations are only 0.1 mM. The accuracy of NH_4VO_3 colorimetric method can be seriously interfered by *p*-benzoquinone when its concentration is above 1.0 mM and H_2O_2 concentrations is below 1000 μM. The DPD-POD colorimetric method fails to quantify H_2O_2 in the presence of *p*-benzoquinone due to its controversial imine-generation reaction with DPD. Therefore, among the three methods, NH_4VO_3 colorimetric method is relatively reliable in the presence of benzoquinones with concentrations below 1.0 mM. When benzoquinones are present with high concentrations (above 1.0 mM), none of the three methods are recommended. Considering that *p*-benzoquinone and hydroquinone are possible oxidation intermediates of phenolic compounds (Yang et al., 2010; Liu et al., 2018), H_2O_2 quantification when such organics are present should be scrutinized. Other H_2O_2 detection methods, such as ion chromatography with UV detector, whose mechanism is not based on redox reactions should be considered (Song et al., 2017). Note that the degradation pathways of most aromatic compounds are to be oxidized to phenols, then open the ring and be mineralized (Wu et al., 2019; Feng et al., 2020b). Thus, in the presence of other aromatic compounds, it is important to carry out not only control experiments to assess interference by organics, but also consider interference by the oxidation intermediates. Other blank and control tests, to correct for the influence of background color on absorbance measurement, should be conducted in advanced to enhance reliable H_2O_2 quantification. It is also recommended to use more than one method for H_2O_2 quantification when appropriate.

4. Conclusions

Aliphatic and aromatic compounds are often present as sacrificial agents and/or target contaminants in photocatalytic in-situ H_2O_2 production and Fenton reactions. To determine the impact of these organics on H_2O_2 quantification, three common H_2O_2 methods were compared (titration with $KMnO_4$, and colorimetry with NH_4VO_3 or DPD-POD). Interferences by different organics were systematically compared through relative errors, and the interfering mechanisms were analyzed.

The accuracy of $KMnO_4$ titration method is greatly compromised by the presence of aromatic compounds at concentrations as low as 0.1 mM. The DPD-POD colorimetric method is unreliable when benzoquinones are present due to the direct reaction with DPD, while the NH_4VO_3 colorimetric method is relatively accurate in the presence of benzoquinones with concentrations below 1.0 mM (i.e. 108 mg L^{-1}). Based on the presented data, a flowchart was developed to guide the selection of a H_2O_2 detection method in different scenarios. We hope that this contribution will foster reliable quantification of H_2O_2 in photocatalytic systems and Fenton-like reactions to enhance system-specific optimization efforts.

Credit author contribution statement

Yan Wei: Conceptualization, Methodology, Investigation, Data curation, Writing – original draft preparation. **Jingzhen Zhang**: Methodology, Investigation, Validation. **Qian Zheng**: Resources, Investigation. **Jie Miao**: Resources, Investigation. **Pedro J J Alvarez**: Validation, Writing – review & editing. **Mingce Long**: Supervision, Validation, Conceptualization, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.130556.

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