Determination of hydroxyl radicals in advanced oxidation processes with dimethyl sulfoxide trapping and liquid chromatography

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Abstract

In this paper, a simple and sensitive method for the determination of hydroxyl radicals generated in advanced oxidation processes is described. The proposed method employed the reaction between hydroxyl radicals and dimethyl sulfoxide (DMSO) to generate quantitatively formaldehyde, which then reacted with 2,4-dinitrophenylhydrazine (DNPH) to form the corresponding hydrazone (HCHO–DNPH) and analyzed by liquid chromatography–UV. Factors affecting the derivatization reaction of HCHO and trapping reaction of hydroxyl radicals, as well as the applicability of the method, were investigated. The detection limit for hydroxyl radicals was $0.54 \mu\text{mol L}^{-1}$. The method had been used to determine the yield of hydroxyl radicals in various advanced oxidation processes (AOPs) to compare their oxidation ability.

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1. Introduction

During the last two decades, advanced oxidation processes (AOPs) have attracted an increasing scientific and technique attention for water decontamination. In these processes, the hydroxyl radicals, generated from ozonation [1], UV/H₂O₂ [2], UV/Fe³⁺/H₂O₂ [3], UV/TiO₂ [4], Fenton reaction [5], Fenton-like reaction [6] and other systems [7], play an important role in degradation of organic substances in water. It is of continuous interest to find new efficient chemical or physical systems to generate hydroxyl radicals for water treatment. In most papers reported, the degradation efficiency is evaluated through the post-process determination of residuals or intermediates, which is time-consuming and inefficient. More important, the degradation efficiency of organic compound depends greatly on the character of the compound. Some systems show high efficiency for one kind of substances, but

low or no effect for another [6,8]. Therefore, quantitative determination of the generation rate and the concentrations of hydroxyl radicals in the advanced treatment processes is necessary for a better understanding of degradation efficiency of different systems and to what extent the hydroxyl radicals involving in the degradation of pollutants [9,10].

Current methods for the detecting hydroxyl radicals suffer from one or more problems. One of the methods is the electron spin resonance spectroscopy (ESR), which measures the electron paramagnetic resonance spectrum of a spin adduct derivative after trapping [11,12]. But this method is insensitive and cannot be employed readily to acquire quantitative estimate of •OH production because the •OH adduct is not stable. Besides, the expensive instruments make it unsuitable for routine analysis. Another method is aromatic hydroxylation, in which the hydroxylated products generating from the reaction of hydroxyl radicals with aromatic compounds, such as phenol, benzoic acid or salicylic acid, are separated by gas chromatography (GC) or liquid chromatography (LC) and detected with different detector [13–16]. Though this method is

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handy and sensitive, there are some problems associated with its use in the detection of hydroxyl radicals in AOPs. These include the following: (i) multiple reaction products; (ii) secondary generation of superoxide; (iii) limited solubility; and (iv) forming complex with iron (II, III), such as salicylic acid, to influence the determination of hydroxyl radicals in Fenton and Fenton-like reaction [17].

Dimethyl sulfoxide (DMSO) has great advantages as a molecular probe for the detection of the hydroxyl radicals in AOPs. First, DMSO is highly water soluble to trap most hydroxyl radicals generated in AOPs. Secondly, it cannot form complexes with iron or other metal ions to influence the detection of $\bullet\text{OH}$ in Fenton and Fenton-like reactions. Thirdly, it is nontoxic at relatively high concentrations, which makes it suitable to determine $\bullet\text{OH}$ in some AOPs involving microorganism [18,19]. Fourthly, it is highly reactive with the hydroxyl radicals ($k = 4.5 \sim 7.1 \times 10^9 \text{ mol L}^{-1} \text{ s}^{-1}$) forming methanesulfinic acid (MSA), methyl radicals and formaldehyde [20–23]:

In the past decades, methanesulfinic acid has been adopted for determination of hydroxyl radicals by spectrophotometric method [20,21] and HPLC [22,23]. However, recent study [24,25] indicates that methanesulfinic acid is only an intermediate product, which also reacted rapidly with hydroxyl radicals leading to methanesulfonic acid and sulfate formation ($k = 6.2 \sim 12 \times 10^9 \text{ mol L}^{-1} \text{ s}^{-1}$). Another highly sensitive method based on methyl radicals reacting with a fluorescamine-derivatized nitroxide forming a stable *o*-methylhydroxylamine, has been developed for the determination of hydroxyl radicals in biological systems [17,26]. Since it was found that the methane generated by the hydrogen extraction of methyl radicals (Reaction 2) was only 0.3–0.5% of the formaldehyde producing by the reaction of methyl radicals and oxygen (Reactions 3 and 4), formaldehyde, generated in the DMSO/ $\bullet\text{OH}$ system, was also used to detect hydroxyl radicals. Based on the Hantzsch reaction of formaldehyde, ammonia and acetylacetone, a fluorescence method was proposed for the determination of hydroxyl radicals by Klein et al. [27]. Though this method is simple and sensitive, it needed high temperature (60–90 °C) and long time for Hantzsch reaction (30–60 min).

This paper aims to develop a sensitive method available readily for the determination of hydroxyl radicals in AOPs. The proposed method is based on the reaction between hydroxyl radicals and DMSO to produce formaldehyde quantitatively, which then reacts with 2,4-dinitrophenylhydrazine (DNPH) to form the corresponding hydrazone (DNPhO) [28,29] and analyzed by LC-UV. The quantitative analysis

of hydroxyl radicals can be done through the determination of the concentration of formaldehyde. The method has been used to investigate the generation rate of hydroxyl radicals in different advanced treatment processes.

2. Experimental

2.1. Apparatus

The HPLC equipment used was an Agilent 1100 LC including a BinPump and a VWD detector. The VWD detector was set at 355 nm. The system has an injection value with a 20 μL loop. An Agilent Zorbax Eclipse XDB-C18 column (150 $\times$ 4.6 mm, particle size 5 μm) was used as analytical column. To perform the isocratic elution at a flow rate of 1.0 mL/min, a mixture of methanol and water (60:40, v/v) was used as mobile phase. Both solvents were previously filtered through a 0.45 μm PTFE filter and degassed ultrasonically.

2.2. Chemicals and reagents

Deionized water used in all experiments was purified with a Milli-Q water ion-exchange system. All chemicals were of ACS reagent grade. Formaldehyde standards were obtained from the National Research Center for Reference Material (Beijing, China). Working solutions (0.1 and 4 mmol L⁻¹) were prepared daily by appropriate dilution of the stock solutions with water. Analytical grade DNPH was obtained from Beijing Chemicals Corporation (Beijing, China) and was dissolved in acetonitrile to prepare a 6 mmol L⁻¹ solution. By dissolving 0.078 g (NH₄)₂Fe(SO₄)₂·6H₂O, 0.081 g Fe(NO₃)₃·9H₂O, and the according ligands (iron: ligand = 1:3, mol/mol) in 100 mL water, 2 mmol L⁻¹ ferrous, ferric and their complexes solutions were prepared. The ligands used are: ethylene diamine tetraacetate (EDTA) and bipyridine (bipy).

2.3. Generation and trapping of $\bullet\text{OH}$

Different systems as reported are used as the source of hydroxyl radicals. They are (1) Fe²⁺/H₂O₂ [5]; (2) Fe³⁺/H₂O₂ [6]; (3) Fe²⁺-EDTA/H₂O₂; (4) Fe³⁺-EDTA/H₂O₂ [30]; (5) Fe²⁺-bipy/H₂O₂; (6) Fe³⁺-bipy/H₂O₂ [31]; (7) UV-H₂O₂; and (8) UV-Fe²⁺/H₂O₂ [3]. The reaction mixture contained 250 mmol L⁻¹ DMSO, 0.2 mmol L⁻¹ Fe²⁺, Fe³⁺ or their complexes, and 8 mmol L⁻¹ H₂O₂. The generation of hydroxyl radicals by UV-H₂O₂ and UV-Fe²⁺/H₂O₂ were carried out under a 40 W ultraviolet lamp with an irradiation area of 0.79 cm². The mixture (final volume 2 mL, pH 7.0) was maintained at 25 °C for a certain time, then 2.5 mL pH 4.0 H₃PO₄-NaH₂PO₄ and 0.2 mL 6 mmol L⁻¹ DNPH was added and diluted to 5 mL. The mixture was maintained at room temperature for 30 min and analyzed by LC-UV.

Fig. 1. Chromatograms of the HCHO–DNPH solutions obtained for blank (A), standard solution (B, $4 \mu\text{mol L}^{-1}$), standard solution (C, $40 \mu\text{mol L}^{-1}$), Fenton reaction (D), Fe^{3+} -bipy/ H_2O_2 system (E) and UV- H_2O_2 system (F).

3. Results and discussion

3.1. HPLC analysis

Under the selected experimental conditions, DNPH and HCHO–DNPH are well separated within 7 min using an Agilent Zorbax Eclipse XDB-C18 column. With the mobile phase of methanol–water (60: 40, v/v), and a flow-rate of 1 mL/min the retention times were about 2.7 and 5.4 min for DNPH and HCHO–DNPH derivatives, respectively. Fig. 1 shows the typical liquid chromatograms of HCHO–DNPH solutions, obtained for blank, standard solution and produced from the oxidation of DMSO by different AOPs system in 60 min.

3.2. Derivatization procedure of HCHO

3.2.1. Effect of DNPH concentration

The optimization of derivatizing reagent concentration was conducted in 5 mL of pH 4.0 H_3PO_4 – NaH_2PO_4 buffer solution spiked with formaldehyde and DNPH, and with a derivatization time of 30 min. Experiments revealed that

when $80 \mu\text{mol L}^{-1}$ of formaldehyde was reacted, the peak area increased with DNPH concentration in the range of 0 – $160 \mu\text{mol L}^{-1}$, and kept constant when the concentration of DNPH was above $160 \mu\text{mol L}^{-1}$. Therefore, $240 \mu\text{mol L}^{-1}$ of DNPH was adopted in the following studies.

3.2.2. Effect of pH

Phosphonic acid (sulfuric acid) and sodium hydroxide were chosen to adjust the pH in the range of 1–7. Fig. 2 shows the effect of the pH on the peak area of HCHO–DNPH. The peak area increased drastically with pH from 1 to 2, kept almost constant from 2 to 6, and dropped sharply above 6. The optimal pH for the reaction of formaldehyde and DNPH was 2 to 6. In the following studies, pH 4.0 H_3PO_4 – NaH_2PO_4 buffer solution was selected.

3.2.3. Effect of derivatization temperature and time

The temperature usually proposed in the literature is 40°C [28]. Experiments performed at this temperature gave similar results compared to those obtained at room temperature. Therefore, room temperature was selected to make the experimental procedure easier. The effect of reaction time on the yield of HCHO–DNPH derivative at room temperature was thus investigated. The peak area of HCHO–DNPH increased drastically with reaction time from 0 to 15 min, and kept almost constant after 20 min reaction (Fig. 3), and 30 min was selected in the following studies.

3.3. Linearity, detection limit and precision

The calibration curve was plotted taking peak area of the HCHO–DNPH derivative. The solutions containing formaldehyde range from 5 to 800 nmol in 5 mL were analyzed. The regression equation is $Y = 19.4 + 2.02X$, where X is amount of formaldehyde (nmol) and Y is the peak area, with a correlation coefficient of $\gamma = 0.9993$. The detection limit calculated based on three times of the standard deviation divided by the slope of the calibration curve was $0.27 \mu\text{mol L}^{-1}$. The detection limit for hydroxyl radicals can be calculated according the Eqs. (1), (3) and (4), which indicate 1 mol of formaldehyde is generated from 2 mol of hydroxyl radicals reacting with DMSO, with a result of $0.54 \mu\text{mol L}^{-1}$. Five measurements of $\bullet\text{OH}$ producing from Fe^{3+} -bipy/ H_2O_2 system in 60 min gave an RSD of 3.8%.

3.4. Effect of DMSO concentration on trapping of $\bullet\text{OH}$ and the recovery of HCHO

It is necessary to use a concentration of DMSO high enough to trap most hydroxyl radicals and prevent the side-reaction of hydroxyl radicals with other species in the system. The formation rate of HCHO on DMSO concentration in different systems was investigated. The results are shown in Fig. 4. In the absence of DMSO, HCHO–DNPH was not

Fig. 2. Effect of pH on derivatization of formaldehyde. HCHO: $80 \mu\text{mol L}^{-1}$, DNPH: $240 \mu\text{mol L}^{-1}$, derivatization time: 30 min.

detected, whereas with increasing DMSO concentrations, the signal of HCHO–DNPH increased in a hyperbolic fashion. Above 2 mmol L^{-1} DMSO, the signal was independent of DMSO concentration, which indicated the concentration of DMSO was enough to trap the $\bullet\text{OH}$ generated by systems studied in at least 60 min.

Since formaldehyde is a compound easy to be oxidized, 200 nmol HCHO were added to Fe^{3+} -bipy/ H_2O_2 system contained DMSO of different concentration to investigate the recovery of HCHO to make sure that HCHO was not further oxidized by $\bullet\text{OH}$. The results were listed in Table 1. It can be seen that HCHO is not oxidized by $\bullet\text{OH}$ even in the

Fig. 3. Effect of derivatization time on the peak area of HCHO–DNPH. HCHO: $80 \mu\text{mol L}^{-1}$, DNPH: $240 \mu\text{mol L}^{-1}$, pH: 4.0.

Fig. 4. Effect of DMSO concentration on the trapping of hydroxyl radicals. (□) Fe^{3+} -bipy/ H_2O_2 system; (○) Fenton reaction. Fe^{2+} or Fe^{3+} -bipy: 0.2 mmol L^{-1} , H_2O_2 : 8 mmol L^{-1} , reaction time: 60 min.

Table 1
Recovery of HCHO at different DMSO concentration

Concentration of DMSO (mmol L^{-1})	HCHO generated	HCHO added	HCHO founded	Recovery (%)
25	193	200	398	103
2.5	188	200	383	97.5
0.25	121	200	309	94
0	0	200	208	104

absence of DMSO. 1000 nmol methanol were also added to the Fe^{3+} -bipy/ H_2O_2 system to investigate the possible interference of methanol, which was also a product of the reaction between DMSO and hydroxyl radicals. The results (Table 2) show that without DMSO or with DMSO of low concentration (0.25 mmol L^{-1}), methanol will be oxidized to formaldehyde, to interfere the determination of formaldehyde. But with the DMSO concentration higher than 2.5 mmol L^{-1} , methanol cannot be oxidized, since most hydroxyl radicals are trapped by DMSO. From the results above, it can be safely concluded that: (i) HCHO is a stable product under our experimental conditions; (ii) methanol, another product

of the reaction between DMSO and hydroxyl radicals, cannot be oxidized to formaldehyde with a concentration of DMSO high enough. In all our studies, 250 mmol L^{-1} of the DMSO concentration was used to trap most hydroxyl radicals.

3.5. The quantitative relationship between hydroxyl radicals and formaldehyde

Hydroxyl radicals were generated quantitatively by the Fenton reaction by, adding a small known amount of H_2O_2 slowly into a well-stirred solution of 250 mmol L^{-1} DMSO containing excess Fe^{2+} (10 mmol L^{-1}). It was expected that the slow addition of H_2O_2 into excess Fe^{2+} would minimize the reaction of $\bullet\text{OH}$ with H_2O_2 to yield 1 mol of $\bullet\text{OH}$ for each mole of H_2O_2 [32,33]. The relationship between the formaldehyde detected and the hydroxyl radicals generated was shown in Fig. 5. These results indicated that there was good quantitative relationship between hydroxyl radicals and formaldehyde. One mole of formaldehyde was generated from 2.17 mol of hydroxyl radicals reacting with DMSO, which was consistent with the calculated generation of formaldehyde according Eqs. (1), (3) and (4).

Table 2
Influence of CH_3OH on the detection of HCHO at different DMSO concentration

Concentration of DMSO (mmol L^{-1})	HCHO generated (nmol)	CH_3OH added (nmol)	HCHO founded (nmol)
25	203	1000	213
2.5	205	1000	198
0.25	113	1000	138
0	0	1000	66.9

Fig. 5. The quantitative relationship between hydroxyl radicals and formaldehyde.

3.6. Studying on the generation of hydroxyl radicals by AOPs systems

Fig. 6 demonstrates the time course of $\bullet\text{OH}$ formation in various systems. In systems of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, the average generation rate of $\bullet\text{OH}$ in 120 min were 1.39 and 0.38 nmol min^{-1} , respectively. EDTA prevents the generation of $\bullet\text{OH}$ [30,34], the average generation rate of $\bullet\text{OH}$ in 120 min were only 0.26 and 0.06 nmol min^{-1} for Fe^{2+} -EDTA/ H_2O_2 and Fe^{3+} -EDTA/ H_2O_2 , respectively. Fe^{3+} -bipy/ H_2O_2 was the best system for the generation of $\bullet\text{OH}$, in which the average generation rate in 120 min was up to 6.57 nmol min^{-1} .

In all the systems studied, a rapid generation of $\bullet\text{OH}$ was observed in the first 5 min and then following by a slower rate. The initial rate and the followed slower rate were calculated and listed in Table 3. The generation rate

of $\bullet\text{OH}$ in $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ was up to 17.6 nmol min^{-1} , but dropped sharply in the following reaction with a rate of only 0.48 nmol min^{-1} . It was because Fe^{2+} was oxidized to Fe^{3+} quickly, and the later was reduced to Fe^{2+} by H_2O_2 slowly to form the chain reactions:

UV/ H_2O_2 and UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ systems showed high generation rate of $\bullet\text{OH}$, because the ultraviolet irradiation can

Table 3
The generation rate of hydroxyl radicals of various systems

Systems	Average generation rate in the first 5 min, nmol min^{-1}	Average generation rate from 10 to 120 min, nmol min^{-1}	Average generation rate in total 120 min, nmol min^{-1}
$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	17.6	0.48	1.39
$\text{Fe}^{3+}/\text{H}_2\text{O}_2$	1.56	0.32	0.38
Fe^{2+} -bipy/ H_2O_2	9.3	2.06	2.34
Fe^{3+} -bipy/ H_2O_2	22.4	4.49	6.57
Fe^{2+} -EDTA/ H_2O_2	3.68	0	0.26
Fe^{3+} -EDTA/ H_2O_2	1.32	0	0.06
UV- H_2O_2	6.72	2.40	2.76
UV- $\text{Fe}^{2+}/\text{H}_2\text{O}_2$	17.9	4.19	4.58

Fig. 6. Generation of hydroxyl radicals by different systems. (○) Fe²⁺/H₂O₂; (●) Fe³⁺/H₂O₂; (□) Fe²⁺-bipy/H₂O₂; (■) Fe³⁺-bipy/H₂O₂; (△) Fe²⁺-EDTA/H₂O₂; (▲) Fe³⁺-EDTA/H₂O₂; (◇) UV/H₂O₂; (◆) UV/Fe²⁺/H₂O₂. DMSO: 250 mmol L⁻¹, Fe²⁺, Fe³⁺ and their complexes: 0.2 mmol L⁻¹, H₂O₂: 8 mmol L⁻¹, the generation of hydroxyl radicals by UV-H₂O₂ and UV-Fe²⁺/H₂O₂ were carried out under a 40 W ultraviolet lamp with an irradiation area of 0.79 cm².

induce the homolytic cleavage of hydrogen peroxide to generate hydroxyl radicals [35,36]. Compared to Fe²⁺/H₂O₂ system, Fe²⁺-bipy/H₂O₂ had a lower generation rate of hydroxyl radicals in the first 5 min, but a higher rate in the following process. Fe³⁺-bipy/H₂O₂ systems were found to have much higher generation rate of •OH than that Fe³⁺/H₂O₂. The changes of the UV-vis spectrogram during the reaction between Fe³⁺-bipy/H₂O₂ were studied. The results (data not shown) showed upon the addition of H₂O₂ to Fe³⁺-bipy solution, the absorption at 520 nm, which was the characteristic absorption of Fe²⁺-bipy, increased and reached max in about forty min. This phenomenon indicated that the reduction of Fe³⁺-bipy to Fe²⁺-bipy by H₂O₂ was much easier than the reduction of Fe³⁺ to Fe²⁺ by H₂O₂, resulting the high yield

of hydroxyl radicals by the blow reactions:

It was surprising that Fe³⁺-bipy/H₂O₂ had a higher generation rate than that of Fe²⁺-bipy/H₂O₂. It should be noted that the absorption at 520 nm of Fe³⁺-bipy after the addition of H₂O₂ was only 80% of the absorption of equivalent mol Fe²⁺-bipy. This indicated that there were probably other generation pathway of •OH besides Reactions (7) and (8). According to the statements of Gozzo [9] and Meunier [37], a possible mechanism was proposed, in which high-valency

Table 4
Comparison of different methods for the determination of hydroxyl radicals

Trapping reagent	Quantitative product	Separation	Detector	Detection limit	Ref.
Salicylic acid	2,3-dHBA ^a , 2,5-dHBA, catechol	HPLC, 23 min	UV	5–50 $\mu\text{g L}^{-1}$	[14]
Salicylic acid	2,3-dHBA, 2,4-dHBA, 2,5-dHBA, 2,6-dHBA, catechol	GC, 20 min	MS	0.05–1 $\mu\text{mol L}^{-1}$	[15]
DMSO	<i>o</i> -Methylhydroxylamine	HPLC, 11 min	Fluorescence	3.5 nmol L ⁻¹	[16]
DMSO	MSA ^b	HPLC 6 min	UV	8 $\mu\text{g L}^{-1}$	[21]
DMSO	HCHO	HPLC 7 min	UV	9.8 $\mu\text{g L}^{-1}$ (0.54 $\mu\text{mol L}^{-1}$)	This work

^a 2,3-Dihydroxybenzoic acid.

^b Methane sulfinic acid.

species of iron were involved:

4. Conclusions

The proposed method for the detection of hydroxyl radicals in AOPs is simple, sensitive and easy to be operated. A summary of the comparison of different methods for the determination of hydroxyl radicals is given in Table 4. For the current method, only one quantitative product is produced in the detection system, which makes the separation and quantification much easier. Because DMSO is highly water soluble, nontoxic at relatively high concentrations and has an appreciable rate of interaction with hydroxyl radical, it has been proved to be an ideal trap for hydroxyl radical. Formaldehyde and DNPH are available readily, which makes it convenient for the detection of hydroxyl radicals generated in AOPs. The proposed method has been used to determination of the yield of hydroxyl radicals in various AOPs to compare their oxidation ability. However, it should be noted that this method is not suitable for the determination of hydroxyl radicals when there are a large number of other organic substrates, which may have a major effect on the chemistry of methyl radicals.

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