Analytical Methods

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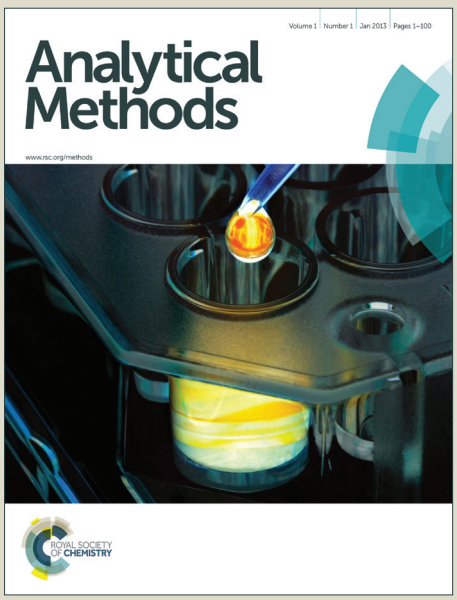

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ARTICLE

Determination of hydroxyl radical photochemically generated in surface waters under sunlight by high performance liquid chromatography with fluorescence detection

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Hydroxyl radical can be generated in various kinds of surface water under sunlight, which has great impacts on the transformation and degradation of pollutants in water due to its high reactivity. Here we report a sensitive and simple method for the determination of hydroxyl radical based on trapping hydroxyl radical with dimethyl sulfoxide to produce formaldehyde quantitatively, which then reacted with ammonium and acetylacetone. The product, 3,5-diacetyl-1,4-dihydro-2,6-lutidine, was analyzed by high performance liquid chromatography with fluorescence detector. Factors affecting the derivatization reaction of formaldehyde and trapping reaction of hydroxyl radical, as well as the applicability of the method in the determination of hydroxyl radical in the typical surface waters under sunlight, were investigated. Under the optimized conditions, the quantitative limit for hydroxyl radical was 0.067 μmol L^{-1}, with a quantitative range of 0.067~13.4 μmol L^{-1} and a correlation coefficient of 0.9978. By the proposed method, the generation of hydroxyl radical in lake water, sea water and wetland water under sunlight in presence and absence of nitrate and nitrite was measured.

1. Introduction

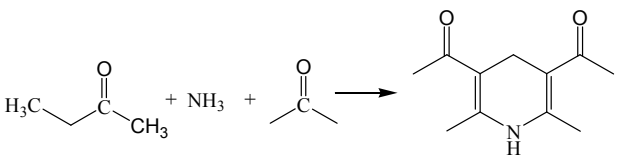
Hydroxyl radical is one of the most reactive oxygen free radical, which can react with most organic substances unselectively at near diffusion-controlled rate. In the natural surface water, the steady-state concentration of hydroxyl radical is commonly about 10^{-19}-10^{-16} mol L^{-1}, with a production rate ranging from 10^{-12}-10^{-10} mol L^{-1} s^{-1}, while in some special sites, the steady-state concentration of hydroxyl radical can reach about 10^{-12} mol L^{-1} with a production rate of about 10^{-8} mol L^{-1} s^{-1}.[1,2] At this concentration, taking the high reaction rate constant into consideration, hydroxyl radical maybe have great influence on the fate and transformation of many substrates in the aquatic environments. In the past decades, hydroxyl radical has drawn more and more attention in the processes that impact the fate and transformation of organic and inorganic contaminants in the environment.[3-6] In the natural water, hydroxyl radical can be produced through various pathways, mainly including photo-Fenton reaction,[7] photolysis of nitrate and nitrite,[8] and photolysis of dissolved organic matter (DOM).[9] The quinones redox induced by hydrogen peroxide is thought to be another possible hydroxyl radical source, which perhaps play an important role in the hydroxyl radical generating induced by DOM in the dark.[10] Though great efforts have been made in the past decades, the generation of hydroxyl radical in the natural water and its influence on the transformation of pollutants are still far away from being understood clearly. One of the important reasons is that the high reactive activity and short lifetime of hydroxyl radical add difficulties for its quantification in the natural water.

The high reactive activity makes it nearly impossible for the detecting hydroxyl radical directly. So almost all methods for the detecting hydroxyl radical is indirect, in which different probes are used to trapping hydroxyl radical to produce specific products, which can then be detected by various analytical methods, such as electron spin resonance spectroscopy (ESR),[11] high performance liquid chromatography (HPLC),[12-15] gas chromatography (GC)[16] and capillary electrophoresis.[17] ESR is not an appropriate method for the determination of hydroxyl radical photochemically generated in natural water, due to its poor sensitivity even after improvement by spin trapping method[18]. Hydroxylation of aromatic compounds, such as phenol,[13] benzoic acid[15] or salicylic acid,[12] and phthalhydrazide[18] are other approaches for the determination of hydroxyl radical with high sensitivity. Although a detection limit of 0.6~90 nmol L^{-1} for hydroxyl radical can be archived using hydroxylation of aromatic compounds, some drawbacks should be taken into consideration when these methods are applied into the determination of hydroxyl radical photochemically generated in natural water. One of the most important drawbacks is the competitive absorbing of light between the photoactive substances in the natural water and the probes itself or the hydroxylated products, such as phenol,[19] quinone,[20] and salicylic acid,[21] which have strong absorbing in UVA (320 nm-400 nm) or UVB (280 nm-320 nm) band. The second drawback is the further

photo-degradation of the hydroxylated product[22] or the reaction between the hydroxylated product and hydroxyl radical during long-term irradiation experiments,[23,24] which will underestimate the concentration of hydroxyl radical. The third drawback is the formation of complexes between the probes and transition metal ion,[25] which has an unnegligible influence on the hydroxyl radical generation through photo-Fenton or photo-Fenton-like reaction.

Dimethyl sulfoxide (DMSO) has many advantages as the probe for the detection of photochemically generated hydroxyl radical in natural water, due to its nonoptical activity under the light above 280 nm, high water solubility, weak complex ability and nontoxcity at relatively high concentration. DMSO can react with hydroxyl radical at a rate of 4.5~7.1 $\times 10^9$ mol L^{-1} s^{-1}, producing methanesufinic acid (MSA), methyl radicals and formaldehyde.[26-30] Basing on this reaction, MSA has been adopted to be the target compound for the determination of hydroxyl radical by HPLC.[26] However, it should be noted that MSA is only the intermediate product, which can also react with hydroxyl radical at very high reaction rate (k= 6.2~12$\times 10^9$ mol L^{-1} s^{-1}). [27] A very sensitive method has been reported for the determination of hydroxyl radical generation in the natural water under sunlight basing on the methyl radicals reacting with a fluorescamine-derivatized nitroxide reagent to form a stable *o*-methylhydroxylamine.[28] However, the preparation and purification of the direct quantitative compound (*o*-methylhydroxylamine) is difficult.[29] We have established a method basing on the reaction of formaldehyde and 2, 4-dinitrophenylhydrazine (DNPH) for the determination of hydroxyl radical generated in advanced oxidation processes (AOPs).[30] However, a detection limit of 0.54 μmol L^{-1} and quantitative lower limit of 1 μmol L^{-1} makes this method not suitable for the detection of hydroxyl radical in natural water, which generates at a relatively low rate compared to AOPs.

This paper aims to develop a sensitive and readily available method for the detection of hydroxyl radical photo-generated in natural water. Hydroxyl radicals photo-generated in natural water can react with DMSO to produce formaldehyde quantitatively, which then reacts with acetylacetone and ammonium salt, resulting 3,5-diacetyl-1,4-dihydro-2,6-lutidine (Scheme 1), which exhibits fluorescence at 505 nm under the excitation wavelength of 419 nm.[31] The product can then be separated and analyzed by HPLC with fluorescence detector (FLD). One mole of formaldehyde was generated from two mole of hydroxyl radicals reacting with DMSO,[30] so the quantitative analysis of hydroxyl radical can be realized through the determination of formaldehyde generated in the system. The method has been applied into the detection of hydroxyl radical photo-generated in lake water, sea water and wetland water under sunlight.



Scheme 1 The formaldehyde derivatization reaction

2. Experimental

2.1 Instruments

The HPLC system used was Agilent 1200 LC equipped with a quatpump and a FLD detector. An Agilent Zorbax SB-C18 (150 mm × 4.6 mm, particle size 5 μm) was used as analytical column. The injection volume was set as 50 μL. The FLD detector was set at 419 nm for excitation wavelength and 515 nm for emission wavelength. Mobile phase used was a mixture of acetonitrile and pure water (20:80, v/v) with a flow rate of 1.0 mL min^{-1}. Both solvents were previously filtered through 0.45 μm PTFE filter and degassed ultrasonically. The chromatographic column temperature was set as 20 ˚C. 0.5 L FEP (fluorinated ethylene-propylene) bottles, purchased from Nalgene (USA), which are almost transparent to UV-Vis radiation (66% for UVB, 83% for UVA and 98% for visible region),[32,33] were used as reaction vessel for the natural water under sunlight.

2.2 Chemicals and water samples

All chemicals were at least analytical reagent grade and used as received. Solutions were prepared using deionized water, which was purified with a Milli-Q water treatment system. Acetonitrile was from Tedia Company (USA). Formaldehyde standards were obtained from the National Research Center for Reference Material (Beijing, China). Working solutions were prepared daily by appropriate dilution of the stock solutions with water. Dimethyl sulfoxide (DMSO) and acetylacetone were purchased from Sinopharm (Beijing) and diluted to 20 mmol L^{-1} and 0.2% (v/v), respectively. Ammonium solutions, nitrate solutions and nitrite solutions were prepared by dissolved the appropriate amount of NH_4Cl, KNO_3 and $NaNO_2$ in deionized water. The pH of derivitization solution was adjusted by using 0.2 mol L^{-1} phosphate buffer.

Sea water was collected at Qingdao, Shandong province (36°3'41.7522" N, 120° 19'12.8886" E). The lake water was collected at Jiaozuo, Henan province (35°11'15.9684" N, 113°16'4.1802" E). The wetland water was collected at Baiyangdian, Hebei province (38°51'55.35" N, 116°3'47.3322" E). The samples were collected in June 2013 and stored in the dark at 4 °C before use.

2.3 Trapping and determination of photo-generated hydroxyl radical

The photochemical experiments were carried out under sunlight on the roof in Henan Polytechnic University in July, 2013. Two hundred mL surface water contained 20 mmol L^{-1} DMSO was transferred into 500 mL FEP bottle, and then a certain amount of NO_3^- or NO_2^- was added. Then FEP bottles were placed under sunlight to generate hydroxyl radical. At regular times, three duplicate samples (0.2-2 mL for different water sample and different illumination time) were taken from the bottles. Then, 2 mL 0.2 mol L^{-1} NaH_2PO_4 -Na_2HPO_4 buffer solution, 0.4 mL of acetylacetone (20 mmol L^{-1}), and 0.4 mL of ammonium chloride (5 mol L^{-1}) were added to the water samples and diluted to 10 mL with de-ionized water. The mixture was incubated at 50 ˚C for 20 min in water bath and then cooled to room temperature. Fifty μL of the mixture was injected into HPLC for separation and detection with FLD.

3. Results and discussion

3.1 HPLC analysis

Under the optimized experimental conditions, formaldehyde derivatives and other components in the system are well separated within 7 min by using an Agilent Zorbax SB-C18 column. With the mobile phase of acetonitrile-water (20: 80, v/v), at a flow rate of 1 mL min^{-1}, the retention time of formaldehyde derivative was about 5.9 min. Fig. 1 shows the typical liquid chromatograms of formaldehyde derivative solutions, obtained for blank, formaldehyde standard solution and formaldehyde produced from the oxidation of DMSO by photo-generated hydroxyl radical in surface water. No interference from the components in surface water was observed on the determination of formaldehyde derivatives under the selected experimental conditions.

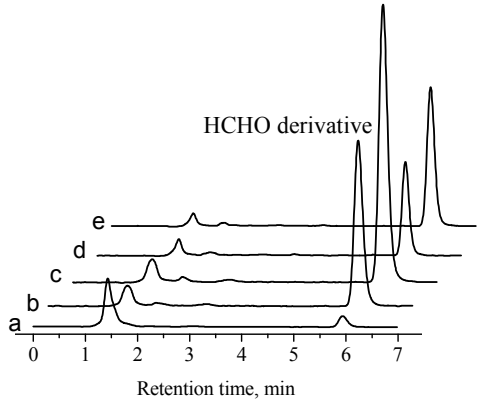


Fig. 1 Chromatograms of the formaldehyde derivatization product obtained for blank (a) , formaldehyde standard solution (b, 0.33 μmol L^{-1}; c, 0.66 μmol L^{-1}), formaldehyde produced from the oxidation of DMSO by hydroxyl radical generated in lake water (d) and in lake water with 0.8 mmol L^{-1} NO_3^- under sunlight for 8 hour(e).

3.2 Derivatization of formaldehyde

3.2.1 Effect of solution acidity. The solution acidity was found to have great influence on the derivatization of formaldehyde. With other experimental conditions fixed, the pH of solution was adjusted in the range of 3 to 10.5 using 0.2 mol L^{-1} phosphate buffer. The influence of solution acidity on the peak area of formaldehyde derivative was shown in Fig. 2. It can be seen that the peak area increased dramatically with the pH from 3 to 4, changed very little from 4 to 6, and then dropped sharply from 6 to 10.5. The optimal pH for the derivatization of formaldehyde was 4 to 6. In the following studies, a pH of 5.4 phosphate buffer was selected.

3.2.2 Effect of derivatization temperature and time. The influences of derivatization temperature and time were also investigated with other experimental conditions fixed, and the results were shown in Fig. 3 and Fig. 4. It can be seen that the peak area of formaldehyde derivative increased with the temperature from 30 to 40 ˚C, kept almost constant from 40 to 70 ˚C, and dropped sharply above 70 ˚C. So a derivatization temperature of 50 ˚C was selected in the following studies. At the temperature of 50 ˚C, a derivatization time of 20 min was enough for the formaldehyde derivatization reaction (Fig. 4).

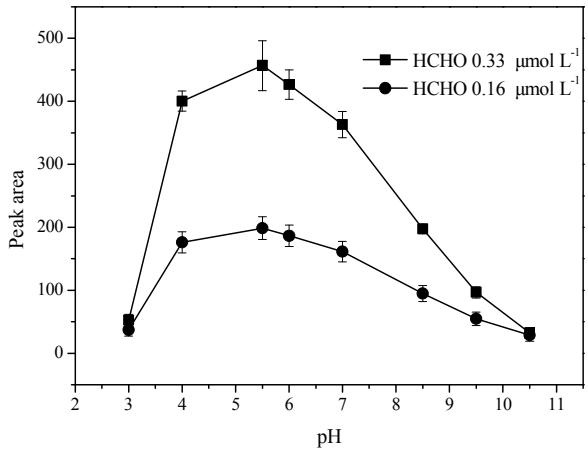


Fig. 2 Effect of solution acidity on the derivatization of formaldehyde. Derivatization temperature: 50 ℃ for 20 min; acetylacetone: 0.8 mmol L^{-1}; ammonium chloride: 0.2 mol L^{-1}, formaldehyde: 0.33 μmol L^{-1}..

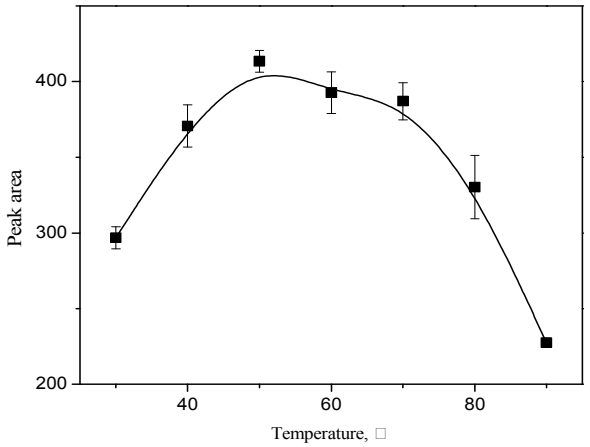


Fig. 3 Effect of temperature on the derivatization of formaldehyde. pH: 5.4; derivatization time: 20 min; acetylacetone: 0.8 mmol L-1; ammonium chloride: 0.2 mol L^{-1}; formaldehyde: 0.33 μmol L^{-1}.

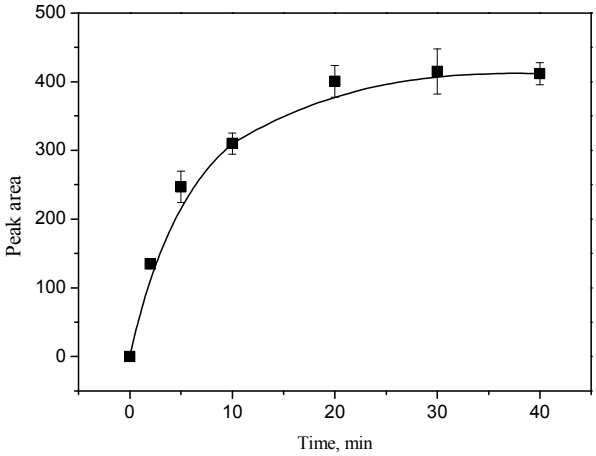


Fig. 4 Effect of reaction time on the derivatization of formaldehyde. pH: 5.4; derivatization temperature: 50 ℃; acetylacetone: 0.8 mmol L^{-1}; ammonium chloride: 0.2 mol L^{-1}; formaldehyde: 0.33 μmol L^{-1}.

3.2.3 Effect of acetylacetone and ammonium chloride concentration. The optimizations of derivatizing reagents concentration, including acetylacetone and ammonium chloride were conducted in pH 5.4 phosphate buffer solution spiked with formaldehyde, with a derivatization time of 20 min at 50 ˚C. The results were shown in Fig. 5 and Fig. 6. It can be seen that in 10 mL of the reaction solution containing 0.33 μmol L^{-1} formaldehyde, 0.8 mmol L^{-1} acetylacetone and 0.2 mol L^{-1} ammonium chloride were enough for the formaldehyde derivatization reaction at 50 ˚C with a derivatization time of 20 min.

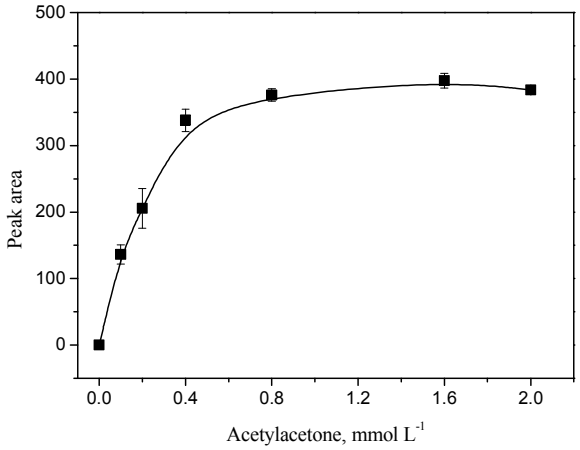


Fig. 5 Effect of acetylacetone concentration on the derivatization of formaldehyde. pH: 5.4; derivatization temperature: 50 ℃; ammonium chloride: 0.2 mol L^{-1}; formaldehyde: 0.33 μmol L^{-1}.

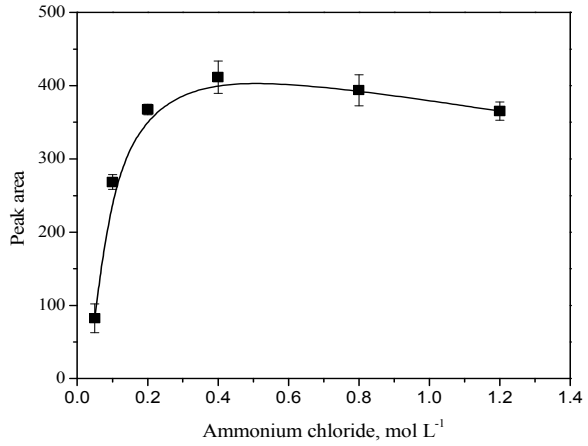


Fig. 6 Effect of ammonium chloride concentration on the derivatization of formaldehyde. pH: 5.4; derivatization temperature: 50 ℃; acetylacetone: 0.8 mmol L^{-1}; formaldehyde: 0.33 μmol L^{-1}.

3.3 Linearity, precision and detection limit

Under the optimized conditions, formaldehyde was analyzed with concentration ranged from 0.033 to 6.7 μmol L^{-1}. The calibration curve was plotted taking peak area of the formaldehyde derivative. The regression equation is $Y = 1180.95X - 30.22$, where X is amount of formaldehyde (μmol L^{-1}) and Y is the peak area (after deducting the blank area), with a correlation coefficient of $\gamma = 0.9977$. The detection limit calculated based on three times of the standard deviation of five determination results of blank divided by the slope of the calibration curve was 0.021 μmol L^{-1}. The detection limit for hydroxyl radicals can be calculated according the reaction between DMSO and hydroxyl radicals, which indicates 1 mol of formaldehyde is generated from 2 mol of hydroxyl radicals reacting with DMSO,[30] resulting a detection limit of 0.042 μmol L^{-1} and a quantitative lower limit of 0.067 μmol L^{-1}. Three measurements of hydroxyl radicals generated from the lake water, sea water and wetland water spiked with 0.2 mmol L^{-1} NO_2^- under sunlight for 8 hour gave a RSD of 6.0%, 2.8% and 2.1%, respectively.

3.4 Effect of DMSO concentration on the trapping of hydroxyl radical and recovery of formaldehyde

To determine the concentration of DMSO needed for quantitative trapping of the hydroxyl radicals, the dependence of the formaldehyde formation on the DMSO concentration was examined. Lake water samples contained different concentration of DMSO from 0 to 20 mmol L^{-1} were irradiated under sunlight for 8 hour. The formaldehyde formed was determined under the optimized condition, and the results were shown in Fig. 7. It can be seen that in absence of DMSO, no apparent formaldehyde derivative was detected, whereas with increasing DMSO concentrations, the signal of formaldehyde derivative increased in a hyperbolic fashion. Quantitative trapping of hydroxyl radicals were achieved at DMSO concentrations above 0.5 mmol L^{-1} for lake water alone, 1 mmol L^{-1} for lake water spiked with 0.4 mmol L^{-1} nitrate, and 2 mmol L^{-1} for lake water spiked with 0.4 mmol L^{-1} nitrite.

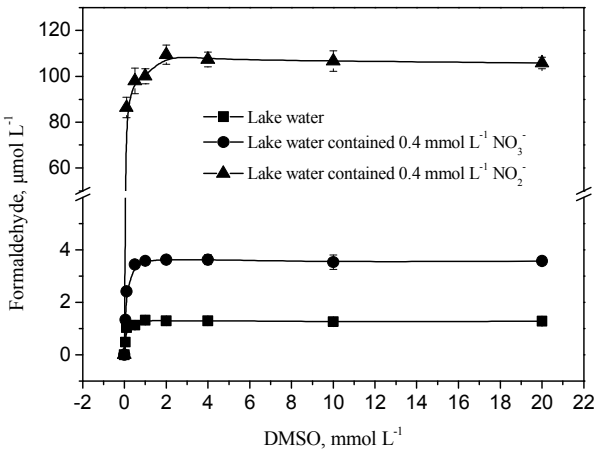


Fig. 7 Effect of DMSO concentration on the trapping of hydroxyl radical. The derivatization condition: pH 5.4; temperature: 50 ℃ for 20 min; acetylacetone: 0.8 mmol L^{-1}; ammonium chloride: 0.2 mol L^{-1}.

It is possible for formaldehyde to be further oxidized into carbon dioxide by hydroxyl radical to affect the measurement of hydroxyl radical. The recovery of formaldehyde under sunlight in lake water in absence and presence of DMSO of various concentrations was also investigated. Lake water contained 0.4 mmol L^{-1} nitrite and DMSO of different concentration was spiked with 66.66 μmol L^{-1} formaldehyde, and placed under sunlight for 8 hour. The formaldehyde generated and added was analyzed, and the results were listed in Table 1. It can be seen that formaldehyde was stable under sunlight under our experimental conditions. Methanol, another product of the reaction between hydroxyl radical and DMSO, can also be further oxidized into

formaldehyde to interfere the determination of hydroxyl radical. The transformation of methanol to formaldehyde in the lake water under sunlight was also investigated, and the results were listed in Table 2. It can be seen that in the absence of DMSO or with DMSO at low concentration (0.05 mmol L^{-1}), methanol can be transformed into formaldehyde. However, with a DMSO concentration higher than 0.5 mmol L^{-1}, no transformation of methanol can be observed, since most hydroxyl radical were trapped by DMSO. Taken together the results above, a DMSO concentration of 20 mmol L^{-1} was selected in the following study in order to ensure the quantitative detection of hydroxyl radicals generated with higher concentration of nitrate or nitrite under sunlight.

Table 1 Recovery of formaldehyde under sunlight in presence of various concentration of DMSO

Concentration of DMSO, mmol L^{-1}	HCHO generated, μmol L^{-1}	HCHO added, μmol L^{-1}	HCHO founded, μmol L^{-1}	Recovery ,%
0	0	66.67	65.46	98.2
0.05	39.41	66.67	118.08	118.0
0.5	86.42	66.67	149.49	94.6
2	101.98	66.67	177.98	114.0
20	108.10	66.67	167.64	89.3

Table 2 Transformation of methanol into formaldehyde under sunlight in presence of various concentration of DMSO

Concentration of DMSO, mmol L^{-1}	HCHO generated, μmol L^{-1}	CH_3OH added, μmol L^{-1}	HCHO founded, μmol L^{-1}	CH_3OH transformation, %
0	0	50.00	13.76	27.52
0.05	35.44	50.00	41.31	11.7
0.5	89.53	50.00	88.54	-
2	104.76	50.00	98.32	-
20	112.31	50.00	115.44	-

With sufficiently elevated trapping agent concentration (DMSO, 20 mmol L^{-1} in this study), most of the photo-formed hydroxyl radical could be scavenged by trapping agent. Under such conditions, it is possible to directly get the generation rate of hydroxyl radical ($R_{\bullet OH}$) from the initial formation rate of product ($R_{product}$) of the reaction between trapping agent and hydroxyl radical[14]. In this study, 1 mol of formaldehyde is generated from 2 mol of hydroxyl radicals reacting with DMSO[30], which gives $R_{\bullet OH} = 2R_{HCHO}$.

3.5 Hydroxyl radical production in natural water under sunlight

The method established was preliminarily applied into the determination of hydroxyl radical production in different surface water under sunlight. Figure 8 shows the hydroxyl radical generation time curve in various surface waters (Fig. 8a) and surface waters appended with nitrate (Fig. 8b) and nitrite (Fig. 8c). The generation rates of hydroxyl radical in different surface water under sunlight were given in Table 3.

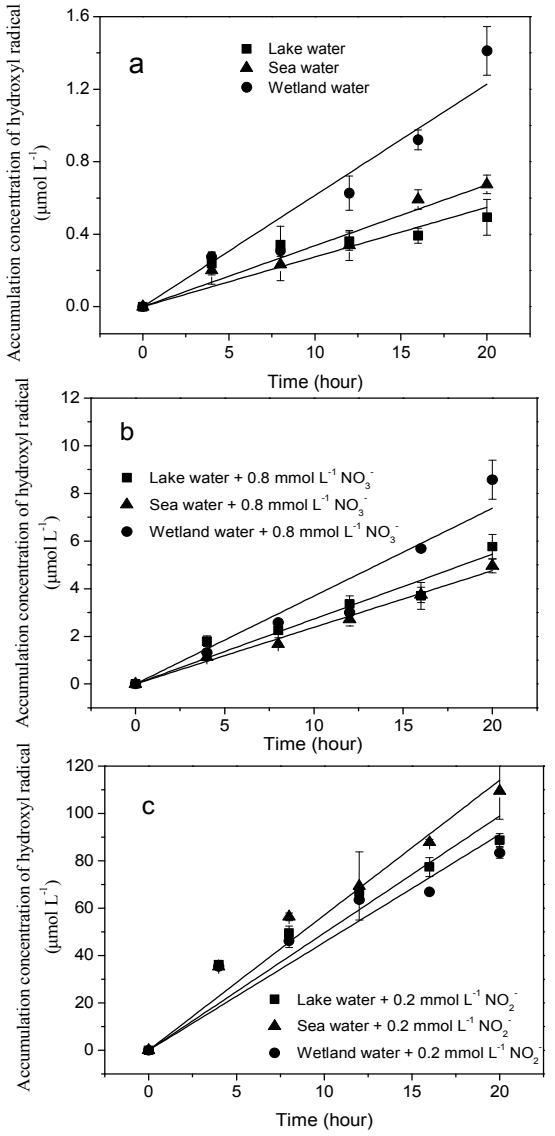


Fig. 8 Generation of hydroxyl radical in different water. a: surface water; b: surface water spiked with 0.8 mmol L^{-1} NO_3^-; c: surface water spiked with 0.2 mmol L^{-1} NO_2^-.

In the three surface waters, the wetland water was found to have the highest generation rate of hydroxyl radial ($1.69 \pm 0.12\times10^{-11}$ mol L^{-1} s^{-1}). The higher hydroxyl radical generation rate in wetland water under light than other waters was also found in previous studies[34], possibly owning to the difference of the constituents of various natural waters. The constituents of the waters used in this study were shown in Table 4. It could be seen that in wetland water, the concentration of DOM, NO_3^-, NO_2^- and metal ions, which are the precursors of the hydroxyl radical in natural water under sunlight, were much higher than those in the lake water and sea water. To verified the influence of water constituents on the generation rate of hydroxyl radical, the generation of hydroxyl in the water samples appended with NO_3^- (0.8 mmol L^{-1}) and NO_2^- (0.2 mmol L^{-1}) was also investigated. It could be seen that the generation rate of hydroxyl radical in the waters appended with NO_3^- (0.8 mmol L^{-1}) and NO_2^- (0.2 mmol L^{-1}) was about ten and one hundred times higher than that of waters without addition of NO_3^- and NO_2^-, respectively.

Table 3 Generation rate of hydroxyl radical (10^{11} mol L^{-1} s^{-1}) in different natural water

	No additives	NO_3^-, 0.8 mmol L^{-1}	NO_2^-, 0.2 mmol L^{-1}	Ref.
Lake water	0.75 ± 0.081	7.50 ± 0.42	138 ± 10	this work
Sea water	0.94 ± 0.047	6.67 ± 0.17	159 ± 7	this work
Wetland water	1.69 ± 0.12	10.3 ± 0.8	127 ± 10	this work
Estuarine waters	1.52 ± 0.01 -1.93 ± 0.01	na	na	35
Wetland waters	0.14 ± 0.01 -4.49 ± 0.22	na	na	34
Sea waters	0.055 ± 0.06 -1.05 ± 0.02	na	na	34
Lake waters	0.69 ± 0.05 -5.9 ± 0.4	na	na	14

Table 4 Chemical characteristics of different surface waters

Parameters	Lake water	Sea water	Wetland water
pH	6.8	8.1	6.7
TOC, μmol L^{-1}	313.33	249.67	113
NO_3^-, μmol L^{-1}	< 0.1	0.582	9.85
NO_2^-, μmol L^{-1}	< 0.2	0.659	3.24
Cl^-, mmol L^{-1}	3.421	547.23	2.029
Cu, μg L^{-1}	3.90	3.87	7.53
Mn, μg L^{-1}	5.76	13.37	3.75
Fe, μg L^{-1}	< 0.5	< 0.5	1120

4. Conclusions

A simple and sensitive method for determination of hydroxyl radical generated in surface water under sunlight was developed. The method is based on the trapping of hydroxyl radical by DMSO to produce formaldehyde quantitatively and then quantitative measurement of formaldehyde indirectly by using HPLC-fluorescence detection. In comparison with the previous reported method, the present method has the following advantages. Firstly, the using of DMSO, which is highly water soluble and has an appreciable reaction rate with hydroxyl radical, makes it easier to get a high trapping reagent concentration to inhibit the side reaction of hydroxyl radical with other constituents in natural water. Secondly, formaldehyde was found to be stable and could not react with hydroxyl radical further in the irradiation process. Thirdly, the derivatization reagent of formaldehyde is available readily, which make the determination of hydroxyl radical very easy. The available readily derivatization reagent and only one quantitative product produced in this method, make the separation and quantification much easier. The present method has been demonstrated for the determination of hydroxyl radical generated in typical natural water under sunlight with satisfactory results.

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Notes and references

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