Article type : Research Note

A Green Method to Determine VUV (185 nm) Fluence Rate Based on Hydrogen Peroxide Production in Aqueous Solution

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ABSTRACT

A mini-fluidic vacuum ultraviolet/ultraviolet (VUV/UV) photoreaction system (MVPS) was developed in our previous study. Based on the MVPS, a green method to determine VUV fluence rate has been developed using the production rate of H_2O_2 when water is exposed to 185 nm VUV. The H_2O_2 production followed pseudo-zero-order reaction kinetics well over the first 10 min of VUV/UV exposure. This new method was well calibrated with a standard *cis*-cyclooctene *cis-trans* photoisomerization actinometer as recommended by the International Union of Pure and Applied Chemistry. The apparent quantum yield for H_2O_2 production by 185 nm VUV irradiation of water was determined to be 0.024 ± 0.002. As the solution pH increased from 5.0 to 8.0, the H_2O_2 production rate decreased from 0.83 to 0.40 μM min^{-1}. Dissolved oxygen had a negligible influence on the H_2O_2 production. This study proposes a novel VUV fluence rate determination method with advantages of non-toxicity, low detection limits, low costs and convenience, and it can be used as a good alternative to traditional actinometers.

INTRODUCTION

As an advanced oxidation technology, the vacuum ultraviolet (VUV) process has been applied to water treatment, production of ultrapure water and transformation of organic materials (1–5). In the process of VUV irradiation, determination of the VUV fluence rate is crucially important, because it is an essential factor for reactor design, reaction rate determination, and operating cost calculation (6).

Several liquid-phase chemical actinometers for VUV fluence rate determination have been reported so far (7–10). Schuchmann and Sonntag (8) determined the VUV fluence rate by analyzing the H_2 production rate in the process of ethanol photolysis under 185 nm VUV irradiation (Farkas actinometer). Schuchmann et al. (9) also used the photoisomerization reaction between *cis*-cyclooctene and *trans*-cyclooctene to determine the VUV fluence rates at both 172 nm (Xe-excimer lamp) and 185 nm (low-pressure mercury lamp) with different quantum yields. Both methods have been recommended by the International Union of Pure and Applied Chemistry (IUPAC) to determine the VUV fluence rates (7). Another chemical actinometer based on water photohomolysis in methanol solution (0.2 M) was introduced by Heit et al. (10), and the quantum yield of 172 nm VUV photolysis of water was determined to be 0.42. However, in all these methods, organic solvents must be used and most of them are toxic. In addition, the analytical procedure of gas chromatograph (GC) is relatively complicated and time-consuming. Therefore, there is a need to develop an accurate, green and rapid method for VUV fluence rate determination.

As conventional VUV reactors have a relatively low accuracy for the determination of VUV photochemical kinetic parameters, a mini-fluidic VUV/UV photoreaction system (MVPS) was developed as described in our previous study (11). The MVPS provides a powerful tool for the determination of VUV photochemical kinetic parameters, such as VUV reaction rate constants and quantum yields. However, a VUV fluence rate determination method for the MVPS has not yet been developed, which limits the MVPS applications in photochemical studies. This study aimed to examine the H_2O_2 production kinetics during 185 nm VUV photolysis of water using the MVPS, to determine the apparent quantum yield for H_2O_2 production, and to evaluate its potential as a green, effective and rapid method for VUV fluence rate determination.

MATERIALS AND METHODS

Chemicals. N,N-diethyl-*p*-phenylenediamine sulfate, peroxidase from horseradish and *cis*-cyclooctene were purchased from J&K Scientific (Beijing, China). All other chemicals used were of at least analytical grade. All aqueous solutions were prepared with ultrapure water produced by a Milli-Q system (Advantage A10, Millipore, USA).

Experimental system. Irradiation experiments were conducted using the previously developed MVPS (Fig. S1) (12). In brief, a low-pressure mercury lamp with a power of 8 W was installed along the central axis of a cylindrical photoreactor. A synthetic quartz tube (the VUV/UV tube) and a Ti-doped silica tube (the UV tube) were mounted parallel to the lamp at the same radial distance (about 5 mm) to the lamp surface in the photoreactor. The reaction solution could be exposed to either the combined VUV/UV or the sole UV when flowing through the VUV/UV or UV tube, respectively, and a nearly identical UV fluence rate could be achieved in the two tubes during the exposure time. The temperature of the photoreaction system was stabilized at 25 ± 1 °C by recirculating water. The reaction solution volume was 50 mL and the solution pH was stabilized at 6.0 with 1.0 mM phosphate buffer. Water sample of 1.0 mL was taken for analysis at a time interval of 2 min during the experiment.

Analytical methods. H_2O_2 concentration was analyzed by a photometric method (13) with a low detection limit of 3 μg L^{-1}. VUV fluence rate was determined by a standard *cis*-cyclooctene *cis*-*trans* photoisomerization actinometer as recommended by the IUPAC (7,9). The *cis*-cyclooctene and *trans*-

cyclooctene concentrations were analyzed by GC (Shimadzu, 2010 Plus), equipped with a flame ionization detector (FID). The separation column (DB-1701, 30 m × 0.25 mm, 0.25 μm) was from Agilent Technologies. The injector temperature was 80 °C and the injection volume was 1.0 μL with a split ratio of 5:1. The oven temperature was started at 50 °C, held for 5 min, and then ramped at 25 °C min^{-1} to 250 °C.

RESULTS AND DISCUSSION

H_2O_2 production

The bond dissociation enthalpy of water is 498 kJ mol^{-1}, so the threshold wavelength that is defined as "the maximum wavelength for which the photon energy matches the bond energy of the bond that breaks in the photolysis reaction" (14) is 240 nm. When water is exposed to 185 nm VUV, it is readily photolyzed into hydroxyl radicals ($HO^\bullet$) and hydrogen atoms ($H^\bullet$) [Eq. (1)], which was confirmed by a spin-trapping electron paramagnetic resonance (EPR) experiment (Fig. S2). The characteristic $HO^\bullet$ spin-trapping peaks were detected within 30 s after the solution was exposed to VUV/UV, while such peaks were not observed when the solution was exposed to UV alone. Two hydroxyl radicals can merge into one H_2O_2 molecule [Eq. (2)], and two other terminal reactions [Eqs. (3) and (4)] can also occur at the same time. The H_2O_2 concentration increased with increasing reaction time until it reached a maximum value after 2 h exposure (Fig. 1 inset). Then the H_2O_2 concentration decreased slightly and leveled off at a *quasi*-stationary concentration of 41 μM after 5 h exposure. The *quasi*-stationary state was reached when the production rate of H_2O_2 [Eq. (2)] was equal to its consumption rate [Eqs. (5) and (6)] (15).

$$H_2O \xrightarrow{\text{VUV}} HO^\bullet + H^\bullet \qquad \Phi_{185\,nm} = 0.33 \text{ (16)} \qquad (1)$$

$$HO^\bullet + HO^\bullet \rightarrow H_2O_2 \qquad k_2 = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ (16)} \qquad (2)$$

$$HO^\bullet + H^\bullet \rightarrow H_2O \qquad k_3 = 1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \text{ (17)} \qquad (3)$$

$H^{\bullet} + H^{\bullet} \rightarrow H_2$ $\qquad k_4 = 1 \times 10^{10}\ M^{-1}\ s^{-1}$ (16) $\qquad$ (4)

$H_2O_2 \xrightarrow{UV} HO^{\bullet} + HO^{\bullet}$ $\qquad \Phi_{H_2O_2} = 0.555$ (18) $\qquad$ (5)

$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O$ $\qquad k_6 = 3.3 \times 10^{7}\ M^{-1}\ s^{-1}$ (16) $\qquad$ (6)

The H_2O_2 production followed pseudo-zero-order reaction kinetics well over the first 10 min of VUV irradiation (Fig. 1). The H_2O_2 production rate in that time period was determined to be 0.80 μM min^{-1} with a good correlation coefficient (r^2 = 0.9992). When water was exposed to VUV/UV irradiation up to 10 min, the produced H_2O_2 had a very low concentration (≤8.0 μM). As the H_2O_2 concentration increased, its UV photolysis rate also increased, but only 4.4% of H_2O_2 was photolyzed at a concentration of 10 μM after 10 min UV exposure (Fig. S3). Therefore, the UV photolysis of H_2O_2 [Eq. (5)] could be neglected at the beginning of the VUV/UV exposure (i.e., in the first 10 min). The H_2O_2 consumption reaction [Eq. (6)] was also insignificant, because its rate constant is only $3.3 \times 10^7\ M^{-1}\ s^{-1}$ (16), which is much smaller than that of Eq. (2). Without regard to its consumption at the beginning of the VUV/UV exposure, the H_2O_2 production was dependent only on the concentration of $HO^{\bullet}$ which has a high diffusion-controlled second-order reaction rate constant [Eq. (2)] (16). Therefore, Eq. (1) becomes the bottleneck reaction to the H_2O_2 production from VUV-generated $HO^{\bullet}$. As the concentration of water is excessively high (55.6 M), the VUV photolysis of water follows pseudo-zero-order reaction kinetics (19). Consequently, the H_2O_2 production also followed pseudo-zero-order reaction kinetics corresponding to that of the VUV photolysis of water at the beginning of the VUV/UV exposure.

Calibration of the new method

Since the H_2O_2 production rate [$r_{H_2O_2}$ (μM min^{-1})] followed pseudo-zero-order reaction kinetics, it would be proportional to the absorbed VUV photon flux [q (einstein s^{-1})] at the beginning of the VUV/UV exposure. Accordingly, q could be determined using Eq. (7):

$$q = \frac{r_{H_2O_2} V}{\Phi} \tag{7}$$

where q can be converted to photon fluence rate ($E_{o,p}$) by a conversion coefficient (11,14) and is used here for simplicity; Φ is the apparent quantum yield for H_2O_2 production; and V is the reaction volume (50 mL).

To determine the apparent quantum yield, the H_2O_2 production rates were determined at different VUV photon fluxes (Fig. 2). The horizontal coordinate represents the VUV photon fluxes that were determined by the standard *cis*-cyclooctene *cis*-*trans* photoisomerization actinometer, and the vertical coordinate represents the corresponding H_2O_2 production rates. As expected, a good linear correlativity ($r^2 = 0.993$) was achieved between the VUV photon flux and the H_2O_2 production rate. The apparent quantum yield for H_2O_2 production was determined to be 0.024 ± 0.002 according to the linear slope. Based on the apparent quantum yield for H_2O_2 production, Eq. (7) could be conveniently used to determine the VUV photon flux.

Effects of pH and oxygen

Because of the pH variation of ultrapure water, phosphate buffer was used during the experiments. The pH of the ultrapure water used in this study was determined to be about 6.5. After the ultrapure water was buffered with phosphate (1.0 mM) and adjusted to the same pH, the H_2O_2 production rate was almost the same as when no buffer was used (data not shown). It demonstrates that the phosphate itself had little influence on the H_2O_2 production. The influence of solution pH on the H_2O_2 production is shown in Fig. 3a. When the solution pH increased from 5.0 to 8.0, the H_2O_2 production rate decreased from 0.83 to 0.40 μM min^{-1}. This is probably because $HO^{\bullet}$ has a higher oxidation potential under acidic conditions (12), which favored the production of H_2O_2. Oxygen is ubiquitous in water. The influence of dissolved oxygen (DO) on the H_2O_2 production rate was examined by purging nitrogen or oxygen gas, separately. DO at concentrations ranging from 0.05 to 14.0 mg L^{-1} had little influence on the H_2O_2 production rate (Fig. 3b), which means that Eqs. (8) and (9) were insignificant for the H_2O_2 production at the beginning of the VUV/UV exposure. In fact, the rate constant of Eq. (9) is only 2×10^6 M^{-1} s^{-1}, which is much smaller than that of Eq. (2) (i.e., 4×10^9 M^{-1} s^{-1}) (16).

$$H^\bullet + O_2 \rightarrow HO_2^\bullet \qquad k_8 = 1 \times 10^{10}\ M^{-1}\ s^{-1}\ (16) \qquad (8)$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \qquad k_9 = 2 \times 10^{6}\ M^{-1}\ s^{-1}\ (16) \qquad (9)$$

CONCLUSIONS

A novel VUV fluence rate determination method using the MVPS has been developed based on the H_2O_2 production by VUV photolysis of water. The method was well calibrated with a standard actinometer and the apparent quantum yield for H_2O_2 production was determined to be 0.024 ± 0.002. The H_2O_2 production rate decreased with increasing solution pH, but was almost unaffected by the DO concentration. This novel method has advantages of non-toxicity, low detection limits, low costs and convenience, and thus can be used as a good alternative to traditional actinometers that commonly use organic solvents.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (51525806, 21590814, 51611540344), Ministry of Science and Technology of China (2016YFC0400802), and National Geographic Air and Water Conservation Fund of US (GEFC23-15).

SUPPORTING INFORMATION

Additional Supporting Information is available in the online version of this article:

Figure S1. Schematic diagram of the mini-fluidic VUV/UV photoreaction system (MVPS).

Figure S2. Electron paramagnetic resonance (EPR) spectrum of $HO^{\bullet}$ formed during the VUV/UV exposure, with 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 0.1 M) used as a spin trapping agent.

Figure S3. UV photolysis of H_2O_2 at different initial csoncentrations.

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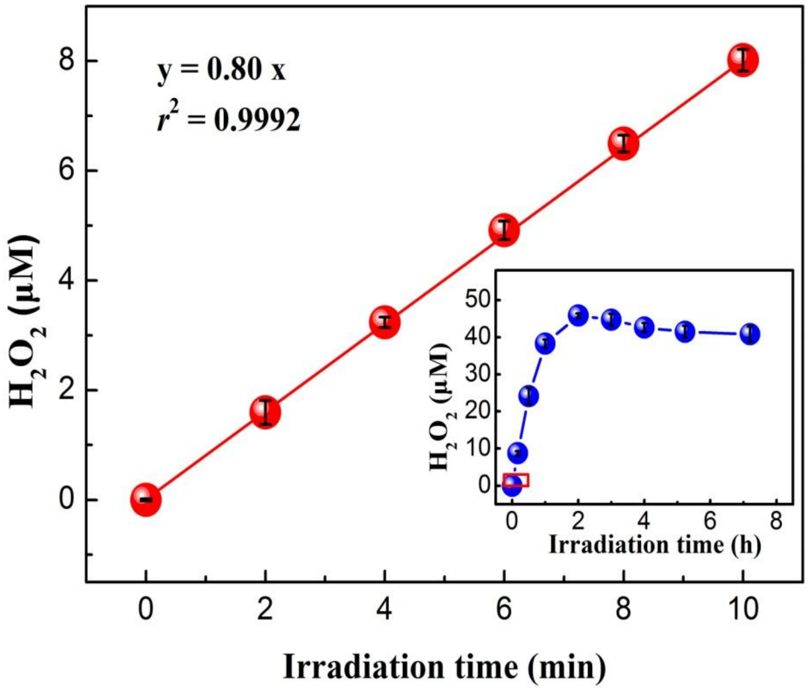
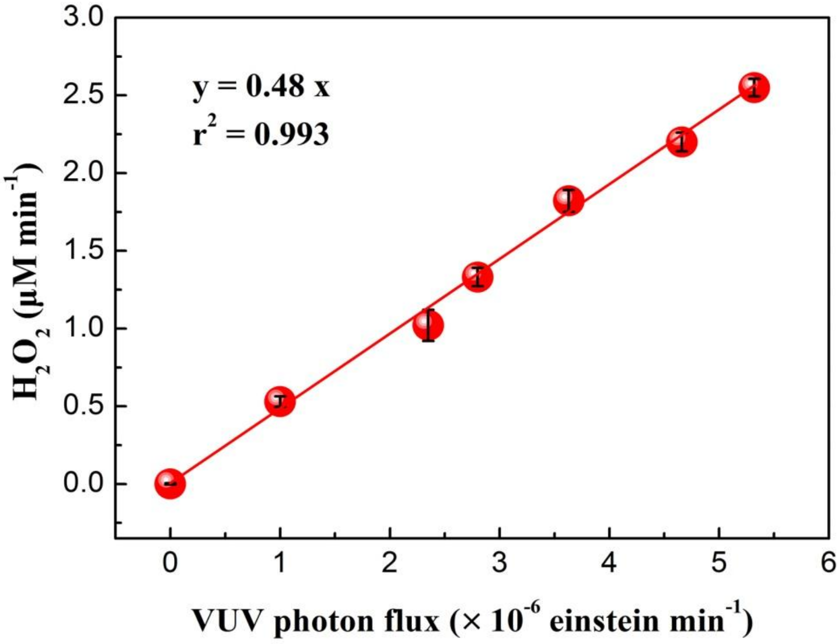
FIGURE CAPTIONS

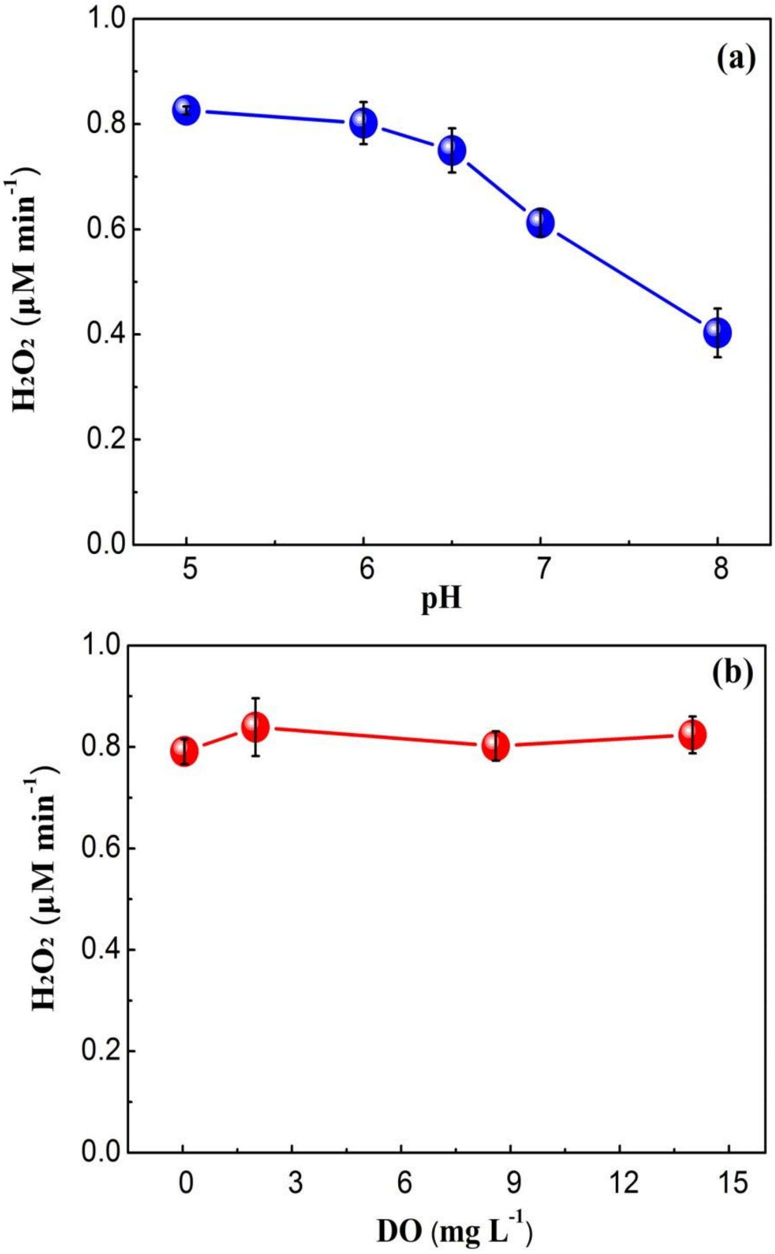
Figure 1. H_2O_2 production as a function of VUV irradiation time (pH = 6.0).

Figure 2. H_2O_2 production rate as a function of VUV photon flux.

Figure 3. Effects of pH (a) and DO (b) on H_2O_2 production rate.


y = 0.80 x
r^2 = 0.9992
H_2O_2 (μM)
Irradiation time (min)
0
2
4
6
8
10
0
2
4
6
8
H_2O_2 (μM)
Irradiation time (h)
0
10
20
30
40
50
0
2
4
6
8


y = 0.48 x
r^2 = 0.993
H_2O_2 (μM min^{-1})
VUV photon flux (× 10^{-6} einstein min^{-1})
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
1
2
3
4
5
6


(a)
1.0
0.8
0.6
0.4
0.2
0.0
H_2O_2 (μM min^{-1})
5
6
7
8
pH
(b)
1.0
0.8
0.6
0.4
0.2
0.0
H_2O_2 (μM min^{-1})
0
3
6
9
12
15
DO (mg L^{-1})