VUV/UV/Chlorine as an Enhanced Advanced Oxidation Process for Organic Pollutant Removal from Water: Assessment with a Novel Mini-Fluidic VUV/UV Photoreaction System (MVPS)

Mengkai Li,^{†,‡} Zhimin Qiang,^{*,†,‡} Pin Hou,[§] James R. Bolton,^{||} Jiuhui Qu,^{†,‡} Peng Li,[§] and Chen Wang^{†,‡}

[†]Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuang-qing Road, Beijing 100085, China

[‡]University of Chinese Academy of Sciences, 19 Yu-quan Road, Beijing 100049, China

[§]School of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing 100083, China

^{||}Department of Civil and Environmental Engineering, University of Alberta, Edmonton, Alberta T6G 2W2, Canada

Supporting Information

ABSTRACT: Vacuum ultraviolet (VUV) and ultraviolet (UV)/chlorine processes are regarded as two of many advanced oxidation processes (AOPs). Because of the similar cost of VUV/UV and UV lamps, a combination of VUV and UV/chlorine (i.e., VUV/UV/chlorine) may enhance the removal of organic pollutants in water but without any additional power input. In this paper, a mini-fluidic VUV/UV photoreaction system (MVPS) was developed for bench-scale experiments, which could emit both VUV (185 nm) and UV (254 nm) or solely UV beams with a nearly identical UV photon fluence. The photon fluence rates of UV and VUV output by the MVPS were determined to be 8.88×10^{-4} and 4.93×10^{-5} einstein $\text{m}^{-2} \text{s}^{-1}$, respectively. The VUV/UV/chlorine process exhibited a strong enhancement concerning the degradation of methylene blue (MB, a model organic pollutant) as compared to the total performance of the VUV/UV and UV/chlorine processes, although the photon fluence of the VUV only accounted for 5.6% of that of the UV. An acidic pH favored MB degradation by the VUV/UV/chlorine process. The synergistic mechanism of the VUV/UV/chlorine process was mainly ascribed to the effective use of $\cdot\text{OH}$ for pollutant removal through formation of longer-lived secondary radicals (e.g., $\cdot\text{OCl}$). This study demonstrates that the new VUV/UV/chlorine process, as an enhanced AOP, can be applied as a highly effective and energy-saving technology for small-scale water and wastewater treatment.

INTRODUCTION

Advanced oxidation processes (AOPs) involving the generation of hydroxyl radicals ($\cdot\text{OH}$) can effectively degrade recalcitrant organic constituents in water and wastewater treatment.¹ The combined use of ultraviolet and free chlorine (UV/chlorine), two commonly applied disinfection methods, has been regarded as an effective AOP for inactivation of water-borne pathogens and decomposition of hazardous organic compounds.^{2–6} Many studies have reported the fast degradation of organic pollutants by the UV/chlorine process, which involves a series of chain reactions with the formation of both $\cdot\text{OH}$ and chlorine radicals ($\text{Cl}\cdot$) as highly reactive species:^{4,6,7}

Vacuum ultraviolet (VUV) covers a wavelength range from 100 to 200 nm. Photo-oxidation with VUV is also considered as an AOP because these photons can be absorbed by water with a high absorption coefficient (e.g., 1.8 cm^{-1} at 185 nm) to produce $\cdot\text{OH}$:⁸

It is known that low-pressure (LP) mercury lamps are typically designed to emit only 254 nm UV light (useful for disinfection), whereas the simultaneously emitted 185 nm VUV light is purposely absorbed by the lamp wall made of Ti-doped quartz to avoid the generation of ozone. However, if a high-purity synthetic quartz is used,^{9,10} then both 185 nm VUV and 254 nm UV (i.e., VUV/UV) beams can penetrate the lamp wall. Direct VUV photolysis of water can produce an

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appreciable amount of $\cdot\text{OH}$ for oxidative decomposition of organic pollutants without any additional power input. As a result, the VUV/UV process has been applied to enhance the disinfection of pathogens and the removal of dissolved organic matter and various micropollutants in water and wastewater.^{11–15} For UV-based AOPs (e.g., UV/chlorine), if a VUV/UV LP lamp (using synthetic quartz) is used as the light source, a higher efficiency can be expected than for a conventional UV LP lamp.

Because of the low penetration depth of VUV in air (about 50 mm), the traditional *quasi*-collimated beam apparatus is inapplicable to the study of bench-scale VUV reactions in aqueous solution, except that a few researchers have attempted to improve its design by placing the whole apparatus in a N_2 -filled box.^{16,17} Hence, most previous studies were conducted in annular batch reactors with a VUV/UV lamp (10–500 W) situated in the center. Moreover, these batch reactors were usually operated in a recirculating mode for sample collection at various reaction times (or photon fluences).^{18–20}

However, batch VUV/UV reactors have some problems in bench-scale studies. First, the LP lamp emits both VUV (185 nm) and UV (254 nm) beams, so it is difficult to distinguish the contribution of each wavelength. Especially for the VUV/UV-based AOPs, the UV component often plays an important role in $\cdot\text{OH}$ generation. Hence, to accurately assess the effect of the VUV component, a special apparatus is needed that can output an identical UV photon fluence for both VUV/UV and UV tests. If a VUV/UV LP lamp and a UV LP lamp are used alternately in the same apparatus, then one cannot ensure an identical UV photon fluence of the two lamps because many factors (e.g., power input, ballast quality, and operational conditions) may influence the lamp output. Moreover, because the VUV only comprises a small fraction of the total lamp output (i.e., about 5–8% of the UV output) and has a low transmittance in air, quartz sleeves are not used in many batch VUV/UV reactors so as to maximize the VUV output. However, without protection of the quartz sleeve that helps stabilize the lamp surface temperature, the fluctuation in lamp output can induce an enlarged uncertainty in bench-scale kinetic studies.^{21,22} In addition, it is difficult to determine accurately the photon fluence because of the nonuniform distribution of photon fluence rate (PFR) in batch VUV/UV reactors. Therefore, it is desirable to have a new bench-scale VUV/UV apparatus for relevant photoreaction studies.

In this study, a mini-fluidic VUV/UV photoreaction system (MVPS) was developed for bench-scale photochemical experiments, in which a lamp could deliver either the combined VUV/UV (i.e., 185/254 nm) beams or the sole UV beam with a nearly identical UV photon fluence. A UV-vis spectrophotometer was installed in the MVPS to provide online absorbance measurements or spectral scans of water samples. On the basis of the newly developed MVPS, this study further explored qualitatively the impact of VUV on the UV/chlorine process with regard to the photodegradation kinetics of organic pollutants in aqueous solution. Methylene blue (MB) was selected as a model pollutant because its concentration can be easily measured at 664 nm with the online spectrophotometer in the MVPS. The measurement at this wavelength could avoid the interference of HOCl/OCl^- . Besides, a synergistic mechanism of the VUV/UV/chlorine process was proposed and experimentally assessed. This study demonstrates that the VUV/UV/chlorine process, as an enhanced AOP, can remove

organic pollutants effectively in water and wastewater treatment.

EXPERIMENTAL SECTION

Mini-Fluidic VUV/UV Photoreaction System (MVPS).

To overcome the problems of batch VUV/UV reactors, a new apparatus, namely MVPS, was designed and fabricated for bench-scale photochemical studies, as illustrated in Figure 1.

Figure 1. Schematic diagram of the mini-fluidic VUV/UV photoreaction system (MVPS).

The core part of the MVPS was a cylindrical and jacketed quartz-wall photoreactor (length = 300 mm, outer diameter = 40 mm). Cooling water (i.e., deionized water) was recirculated through the outer chamber between two quartz walls to control a constant temperature of the photoreactor, thus ensuring stable VUV and UV outputs. An 8 W cold-cathode LP mercury lamp (arc length = 200 mm, Wanhua Co., Zhejiang, China), manufactured with a high-purity synthetic quartz wall to emit both VUV (185 nm) and UV (254 nm) beams, was installed along the central axis of the cylindrical photoreactor.

A straight synthetic quartz tube [VUV/UV tube, high VUV transmittance (i.e., 60% per millimeter)] and a straight Ti-doped quartz tube (UV tube, no VUV transmittance), both of 2 mm inner diameter and 100 mm length, were installed parallel to the lamp at the same radial distance (about 5 mm) to the lamp surface (Figure 1). By this design, the water sample in the UV tube could only receive the sole UV exposure, while that in the VUV/UV tube could receive the combined VUV/UV exposure. Furthermore, a nearly identical UV photon fluence could be achieved in the VUV/UV and UV tubes because both had a high UV (254 nm) transmittance and the same distance to the lamp surface. Note that the two tubes should avoid the end-lamp regions (i.e., the last 50 mm at each end of the lamp arc) where the PFR distribution is usually nonuniform.²³ Nitrogen gas was flushed through the inner chamber of the photoreactor, which avoided the absorption of VUV by the interior air to produce ozone and thus maximized the VUV output. A microfluorescent silica detector (MFSD) was installed at about 5 mm to the lamp surface, which could monitor online any fluctuation in the UV output in each experiment.²³

A UV-vis spectrophotometer (UV2600, Shimadzu, Japan) with a continuous injection cell was connected to the VUV/UV and UV tubes to provide online spectrophotometric analysis. The water sample was pumped by a peristaltic pump

sequentially through the exposure portion of the MVPS (i.e., the VUV/UV or UV tube) and through the spectrophotometer, and then recirculated to receive additional exposure until a desired photon fluence was reached. It should be pointed out that for a certain exposure time, only a part of water sample could receive the VUV/UV or UV irradiation, while the remaining part was in the dark. Hence, by defining a reduction equivalent exposure time (t_{ree} , s) as the total reaction time (t , s) multiplied by the ratio of the exposure volume of the operation tube ($\pi r^2 L$, m³) to the total sample volume (V , m³), the VUV ($F_{\text{p,o,VUV}}$, einstein m⁻²) or UV ($F_{\text{p,o,UV}}$, einstein m⁻²) photon fluence can be readily calculated as follows:²⁴

$$t_{\text{ree}} = \frac{\pi r^2 h}{V} t \quad (6)$$

$$F_{\text{p,o,UV}} = E_{\text{p,o,UV}} t_{\text{ree}} \quad (7)$$

$$F_{\text{p,o,VUV}} = E_{\text{p,o,VUV}} t_{\text{ree}} \quad (8)$$

where r and h are the radius and length of the VUV/UV (or UV) tube (m), respectively; and $E_{\text{p,o,UV}}$ and $E_{\text{p,o,VUV}}$ are the UV PFR in the UV or VUV/UV tube and the VUV PFR in the VUV/UV tube (einstein m⁻² s⁻¹), respectively. Hence, the total exposure photon fluence ($F_{\text{p,o}}$, einstein m⁻²) in the VUV/UV tube is equal to the sum of $F_{\text{p,o,VUV}}$ and $F_{\text{p,o,UV}}$. In other words, t_{ree} can be regarded as the exposure time when the whole sample receives the exposure with the same UV or VUV/UV PFR(s) in the relevant tube.

Chemicals and Analysis. Milli-Q water (Advantage A10, Millipore, U.S.A.) was used in all experiments and analytical determinations. MB and uridine were purchased from Sigma-Aldrich (St. Louis, U.S.A.), whose concentrations were determined by absorbance measurements at 664 and 262 nm using the online spectrophotometer, respectively. The concentration of methanol (Sigma-Aldrich) was determined by gas chromatography equipped with a flame ionization detector (GC-FID, Shimadzu 2010, Japan). The concentration of H₂O₂ (Beijing Chemical Reagents Co., Beijing, China) was determined by the titanium oxysulfate (TiOSO₄, Fluka) method with a detection limit of 0.01 mg L⁻¹.²⁵ Active chlorine (HOCl/OCl⁻) was prepared freshly from a stock NaOCl solution (10–15% by weight, Sigma-Aldrich), and its concentration was measured by the *N,N*-diethyl-*p*-phenylenediamine colorimetric method on a UV-vis spectrophotometer (Hach DR5000, U.S.A.).²⁶ To scavenge •OH, 5 mM *tert*-butanol (TBA, Sigma-Aldrich) or 0.5 mM nitrobenzene (NB, Sigma-Aldrich) was added to relevant reaction solutions in advance.

Experimental Procedures. Each experiment was initiated after warming up the lamp for about 15 min until the MFSD signal reached a constant value. Uridine²⁷ (0.12 mM) or methanol^{28,29} (95 mM) was used as the chemical actinometer to determine the $F_{\text{p,o,UV}}$ and $F_{\text{p,o,VUV}}$ in the MVPS, respectively. To assess the enhancement on MB degradation by the VUV/UV/chlorine process as compared to the UV/chlorine process, an unbuffered MB solution (5 mg L⁻¹) was spiked with 25 mg L⁻¹ (as active chlorine) NaOCl and immediately pumped through the VUV/UV and UV tubes to receive the irradiation. The solution pH decreased approximately from an initial value of 6.4 to a final value of 5.5 during the course of reaction. To examine the effect of pH, the MB solution was buffered at either pH 5 (with phosphate) or 10 (with borate) and then subjected to photodegradation in the VUV/UV/chlorine and

UV/chlorine processes. According to its pK_a at 25 °C (i.e., 7.5), active chlorine at pH values of 5 and 10 consist of 99.7% and 0.3% HOCl, respectively. The MB concentration was measured by the online spectrophotometer at a time interval of 0.5 min during photodegradation experiments that lasted for 10 min each.

RESULTS AND DISCUSSION

Determination of $F_{\text{p,o,UV}}$ and $F_{\text{p,o,VUV}}$ in the MVPS. A uridine solution (0.12 mM) was used as the chemical actinometer to determine the $F_{\text{p,o,UV}}$ in the MVPS. Figure 2

Figure 2. Photolysis of uridine in the presence or absence of TBA (5 mM) in the VUV/UV and UV tubes.

shows the logarithmic decay of uridine with reaction time in each tube in the presence or absence of TBA (i.e., •OH scavenger). The fit lines indicate that each reaction could be well expressed by pseudo-first-order kinetics. In the UV tube, TBA addition had little impact on the reaction rate constant because of the negligible •OH generation during the direct UV photolysis of uridine. In the VUV/UV tube, because VUV photons preferred to react with water (with a high concentration of 55.6 M) than with uridine, the direct VUV photolysis of uridine was insignificant. The total uridine decay was ascribed to both the direct UV photolysis and the oxidation by •OH generated from the direct VUV photolysis of water. As a result, the uridine decay in the VUV/UV tube was obviously faster than in the UV tube (Figure 2). After scavenging •OH with TBA in the VUV/UV tube, the reaction rate constant of uridine ($2.74 \times 10^{-4} \text{ s}^{-1}$) was close to that in the UV tube ($2.51 \times 10^{-4} \text{ s}^{-1}$), demonstrating that the UV and VUV/UV tubes had nearly identical $F_{\text{p,o,UV}}$ values.

On the basis of the UV photolysis rate constant of uridine determined above, the $F_{\text{p,o,UV}}$ (einstein m⁻²) could be calculated as follows:

$$F_{\text{p,o,UV}} = \frac{k_u}{\ln(10) \times 0.1 \times \epsilon_\lambda \times \Phi_u} \times t \quad (9)$$

where k_u (s⁻¹) is the time-based pseudo-first-order rate constant for UV photolysis of uridine; and ϵ_λ (M⁻¹ cm⁻¹) and Φ_u are the decadic molar absorption coefficient and quantum yield of uridine at an exposure wavelength (λ), respectively. The ϵ_{254} and Φ_u values were reported to be 8,775 M⁻¹ cm⁻¹ and 0.020, respectively.²⁷ Therefore, the UV PFR

(i.e., $E_{p,o,UV}$) was calculated to be 8.88×10^{-4} einstein $m^{-2} s^{-1}$ (or a fluence rate of 41.8 mW cm^{-2}) at 254 nm from eqs 6 and 7 ($r = 1 \text{ mm}$, $h = 100 \text{ mm}$, $V = 44 \text{ mL}$).

In addition, a methanol solution (95 mM) was used as another chemical actinometer to determine the $F_{p,o,VUV}$ in the VUV/UV tube. Figure 3 shows that the VUV photolysis of

Figure 3. Photolysis of methanol (MeOH) in the VUV/UV tube.

methanol could be well expressed by zero-order kinetics, and the rate constant of methanol degradation (k_{MeOH}) was $7.0 \times 10^{-8} \text{ M s}^{-1}$. Hence, the VUV photon flux could be calculated with eq 10:²⁸

$$q_{VUV} = \frac{k_{MeOH}V}{0.946(\Phi_{H_2O}f_{H_2O} + \Phi_{MeOH}f_{MeOH})} \quad (10)$$

where q_{VUV} is the absorbed VUV photon flux (einstein s^{-1}); Φ_{H_2O} and Φ_{MeOH} are the total quantum yields of $\bullet OH$ generated from VUV photolysis of water ($\Phi_{H_2O} = 0.375$) and methanol ($\Phi_{MeOH} = 1$), respectively; f_{H_2O} and f_{MeOH} are the incident photon fractions absorbed by water ($f_{H_2O} = 0.9962$) and methanol ($f_{MeOH} = 0.0038$), respectively; and the factor of 0.946 refers to the production of methanol by the disproportionation reaction of hydroxymethyl radicals which slows down the $\bullet OH$ -induced degradation of methanol.²⁸ The VUV PFR (i.e., $E_{p,o,VUV}$) at the outer surface of the VUV/UV tube was equal to the q_{VUV} divided by the cross-sectional area of the tube [i.e., 4.93×10^{-5} einstein $m^{-2} s^{-1}$ (or a fluence rate of 3.19 mW cm^{-2})], which accounted for 5.6% of the UV PFR. With the $E_{p,o,VUV}$ available, the $F_{p,o,VUV}$ could be readily calculated with eq 8.

VUV/UV/Chlorine Process. Figure 4 shows the degradation of MB in the UV/chlorine and VUV/UV/chlorine processes with pH uncontrolled (pH decreased approximately from 6.4 to 5.5 over the reaction course). The fit lines indicate that all reactions followed pseudo-first-order kinetics. Only a slight degradation was found if the MB solution was exposed to UV or active chlorine alone ($k'_U = 9.0 \text{ m}^2 \text{ einstein}^{-1}$, $k_{Cl} = 3.17 \times 10^{-4} \text{ s}^{-1}$). However, a notably higher photon fluence-based reaction rate constant ($k'_{V/U} = 268 \text{ m}^2 \text{ einstein}^{-1}$) was observed in the VUV/UV process because of the additional advanced oxidation by $\bullet OH$. After spiking active chlorine, the photon fluence-based reaction rate constant increased considerably to $352 \text{ m}^2 \text{ einstein}^{-1}$ ($k'_{U/Cl}$) in the UV/chlorine process and to

Figure 4. MB degradation by UV/chlorine and VUV/UV/chlorine. Conditions: $[MB]_0 = 5 \text{ mg L}^{-1}$, $[chlorine]_0 = 25 \text{ mg L}^{-1}$.

$1,180 \text{ m}^2 \text{ einstein}^{-1}$ ($k'_{V/U/Cl}$) in the VUV/UV/chlorine process.

Since little MB was degraded under UV exposure alone and the direct VUV photolysis of MB was also negligible, the degradation of MB in the VUV/UV/chlorine process could arise from only two parts: (1) oxidation by active chlorine and radicals (e.g., $\bullet OH$ and $Cl^\bullet$) generated from active chlorine exposed to UV (254 nm), and (2) oxidation by $\bullet OH$ generated from VUV (185 nm) photolysis of water. The former part was equivalent to the MB degradation by UV/chlorine (i.e., in the UV tube), considering that the UV photon fluence was nearly identical in both tubes. The latter part was equivalent to the MB degradation by VUV/UV (i.e., in the VUV/UV tube) without active chlorine addition. Therefore, in theory, the photon fluence-based rate constant of MB degradation in the VUV/UV/chlorine process ($k'_{V/U/Cl}$) should be equal to the sum of those in the UV/chlorine and VUV/UV processes (i.e., $k'_{U/Cl} + k'_{V/U}$). Nevertheless, the $k'_{V/U/Cl}$ ($1,180 \text{ m}^2 \text{ einstein}^{-1}$) was actually 1.9 times the sum of $k'_{V/U}$ ($268 \text{ m}^2 \text{ einstein}^{-1}$) and $k'_{U/Cl}$ ($352 \text{ m}^2 \text{ einstein}^{-1}$), manifesting a significant enhancement of the MB degradation by the combined VUV/UV/chlorine process. Similar tests were also performed by substituting active chlorine with H_2O_2 , whereas the MB degradation rate constant in the VUV/UV/ H_2O_2 process ($k'_{V/U/H} = 271 \text{ m}^2 \text{ einstein}^{-1}$) was almost equal to the sum of those in the UV/ H_2O_2 ($k'_{U/H} = 77 \text{ m}^2 \text{ einstein}^{-1}$) and VUV/UV ($k'_{V/U} = 185 \text{ m}^2 \text{ einstein}^{-1}$) processes (Figure S1).

Effect of Active Chlorine Dose. The effect of active chlorine dose on MB degradation by VUV/UV/chlorine, UV/chlorine, VUV/UV/ H_2O_2 , and UV/ H_2O_2 is shown in Figure 5a. As the active chlorine dose was raised from 0 to 50 mg L^{-1} , both $k'_{V/U/Cl}$ and $k'_{U/Cl}$ increased obviously with the former increasing relatively faster. By contrast, both $k'_{V/U/H}$ and $k'_{U/H}$ increased slowly with increasing H_2O_2 dose at a similar pace. To quantitatively assess the enhancement of the combined process (i.e., VUV/UV/chlorine or VUV/UV/ H_2O_2) on MB degradation as compared to the total performance of the two relatively simpler processes [i.e., UV/chlorine (or UV/ H_2O_2) plus VUV/UV], an enhancement factor (R , with its subscript denoting a chemical added) was defined as follows:

Figure 5. MB degradation by UV/chlorine, VUV/UV/chlorine, UV/ H_2O_2 , and VUV/UV/ H_2O_2 as a function of active chlorine or H_2O_2 dose: (a) the photon fluence-based rate constants and (b) the enhancement factor (R). Conditions: $[\text{MB}]_0 = 5 \text{ mg L}^{-1}$.

$$R_{\text{Cl}} = \frac{k'_{\text{V/U/Cl}}}{k'_{\text{U/Cl}} + k'_{\text{V/U}}} - 1 \quad (11)$$

$$R_{\text{H}} = \frac{k'_{\text{V/U/H}}}{k'_{\text{U/H}} + k'_{\text{V/U}}} - 1 \quad (12)$$

Figure 5b shows that spiking active chlorine to the VUV/UV process yielded obviously higher R values than spiking H_2O_2 . Moreover, the R_{Cl} kept increasing with increasing active chlorine dose until reached a maximum value (i.e., 0.9) at 25 mg L^{-1} active chlorine, thereafter it decreased at a higher active chlorine dose (50 mg L^{-1}). By contrast, the R_{H} kept increasing with increasing H_2O_2 dose, but its increase was much slower than that of R_{Cl} . It is well-known that H_2O_2 competes for $\cdot\text{OH}$,⁷ and the self-recombination of $\cdot\text{OH}$ resulting from VUV photolysis of water (to form additional H_2O_2) could further exacerbate this scavenging effect in the VUV/UV/ H_2O_2 process. However, in the UV/chlorine process, the quantum yield of active chlorine (to produce radicals) increased with increasing active chlorine dose.⁵

Effect of pH. MB degradation by UV/chlorine and VUV/UV/chlorine was comparatively examined at pHs 5 and 10. Without irradiation, the solution pH only showed a slight impact on MB degradation by active chlorine (Figure S2). However, after exposure to UV or VUV/UV light, the solution pH could significantly impact MB degradation (Figure 6). Specifically, under UV exposure alone, MB was degraded more quickly at pH 10 ($k'_{\text{U}} = 62 \text{ m}^2 \text{einstein}^{-1}$) than at pH 5 ($k'_{\text{U}} = 13 \text{ m}^2 \text{einstein}^{-1}$). By contrast, the VUV/UV process removed MB more effectively at pH 5 ($k'_{\text{V/U}} = 365 \text{ m}^2 \text{einstein}^{-1}$) than at pH 10 ($k'_{\text{V/U}} = 245 \text{ m}^2 \text{einstein}^{-1}$). This could be attributed to two opposite aspects. On the one side, when abundant $\cdot\text{OH}$ was generated by VUV photolysis of water, the following reactions could occur:^{31–33}

Figure 6. MB degradation by UV/chlorine and VUV/UV/chlorine as a function of photon fluence at: (a) pH 5; and (b) pH 10. Conditions: $[\text{MB}]_0 = 5 \text{ mg L}^{-1}$, $[\text{chlorine}]_0 = 25 \text{ mg L}^{-1}$.

Reactions 13, 15, and 16 would shift toward the right with increasing pH. Because $\cdot\text{OH}$ was consumed to produce $\text{O}_2^{\bullet-}$ and $\text{O}_2^{\bullet-}$, which have lower oxidation potentials than $\cdot\text{OH}$, the MB degradation would be retarded correspondingly. On the other side, the pH increase promoted the deprotonation of two side amine moieties in the MB structure (Figure S3), thus facilitating the electrophilic attack of oxidative radicals. The net effect came out to be that MB degradation by VUV/UV slowed down at pH 10 as compared to that at pH 5.

For the UV/chlorine process, its photon fluence-based rate constant at pH 5 ($k'_{\text{U/Cl}} = 517 \text{ m}^2 \text{einstein}^{-1}$) was about 3.3 times that at pH 10 ($k'_{\text{U/Cl}} = 155 \text{ m}^2 \text{einstein}^{-1}$), which could arise from the dissociation of HOCl to OCl^- ($\text{p}K_{\text{a}} = 7.5$, 25°C). It was reported that under UV exposure, HOCl has a higher quantum yield for radical production than does OCl^- ,^{4,7} thus the pH decrease enhanced MB degradation by UV/chlorine. For the VUV/UV/chlorine process, the photon fluence-based rate constant (i.e., $k'_{\text{V/U/Cl}}$) at pH 5 was also significantly higher (2.9 times) than that at pH 10. Overall, the synergistic effect of the VUV/UV/chlorine process was stronger at pH 5 ($R_{\text{Cl}} = 0.4$) than at pH 10 ($R_{\text{Cl}} = 0.1$).

Effect of NB. Because NB reacts very fast with $\cdot\text{OH}$ ($k_{\text{NB},\cdot\text{OH}} = 3.9 \times 10^9 \text{ s}^{-1}$) but hardly reacts at all with reactive chlorine species (e.g., $\text{Cl}^\bullet$),⁴ the contributions of $\cdot\text{OH}$ and the reactive chlorine species to MB degradation could be clarified by adding NB as an $\cdot\text{OH}$ scavenger. In the presence or absence of 0.5 mM NB, the photon fluence-based rate constants of MB degradation by VUV/UV, UV/chlorine and VUV/UV/chlorine at pHs 5 and 10 are listed comparatively in Table 1. As expected, under VUV/UV exposure, little MB was degraded

Table 1. Pseudo-First-Order Photon Fluence-Based Rate Constants of MB Degradation (k' , $\text{m}^2 \text{einstein}^{-1}$) by VUV/UV, UV/Chlorine and VUV/UV/Chlorine

process	pH 5		pH 10	
	without NB	with NB ^a	without NB	with NB ^a
VUV/UV	365 ^b	26	245	17
UV/chlorine	517	149	155	51
VUV/UV/chlorine	1222	432	447	130

^a[NB]₀ = 0.5 mM. ^bEach number in this table is a result of the linear regression of 7–20 experimental data points ($R^2 > 99\%$).

with NB addition in both acidic and alkaline conditions. Furthermore, in the presence of NB, the photon fluence-based rate constants for MB degradation by UV/chlorine and VUV/UV/chlorine also decreased. However, a notable portion of MB was still degraded, because NB could not scavenge the reactive chlorine species generated in the two processes. In the VUV/UV/chlorine process, it can be calculated that the relative contributions of $\bullet\text{OH}$ and the reactive chlorine species to MB degradation were 63% and 35% at pH 5, and 67% and 29% at pH 10, respectively. The direct photolysis only contributed to 2% and 4% of MB degradation at pHs 5 and 10, respectively.

Synergistic Mechanism of VUV/UV/chlorine. In most AOPs (e.g., UV/H₂O₂ and UV/O₃), reactive species are distributed quite uniformly in aqueous solution. Nevertheless, for the VUV/UV process, because of the low penetration depth of the 185 nm VUV in water, a majority of reactive species (i.e., $\bullet\text{OH}$ and $\text{H}^\bullet$) are formed in the region near the quartz sleeve (i.e., the near-field region), whereas much less reactive species are formed in the region with a larger distance from the quartz sleeve (i.e., the far-field region). Hence, in the near-field region, the $\bullet\text{OH}$ and $\text{H}^\bullet$ with a high local concentration tend to induce the formation of H₂O₂ (eq 14) and H₂ (eq 17)³⁴ arising from their self-recombination reactions.

To test the formation of H₂O₂, Milli-Q water was exposed to VUV/UV irradiation in the MVPS, and 0.59 mg L⁻¹ H₂O₂ was detected at a photon fluence of $2.28 \times 10^{-2} \text{ einstein m}^{-2}$ (Figure 7). Imoberdorf and Mohseni¹² also reported that up to 0.32 mM H₂O₂ was generated in an annular VUV/UV reactor after a long exposure time of 40 min. By contrast, with addition

Figure 7. Chlorine consumption and H₂O₂ formation in the VUV/UV, UV/chlorine, and VUV/UV/chlorine processes. Conditions: [chlorine]₀ = 25 mg L⁻¹.

of 25 mg L⁻¹ active chlorine to the VUV/UV process (i.e., VUV/UV/chlorine), the formation of H₂O₂ was greatly inhibited until the depletion of active chlorine (Figure 7). Thereafter, H₂O₂ started to appear and reached 0.21 mg L⁻¹ at a photon fluence of $2.28 \times 10^{-2} \text{ einstein m}^{-2}$. Accordingly, active chlorine was consumed much faster in the VUV/UV/chlorine process than in the UV/chlorine process. This implies that in the VUV/UV/chlorine process, the abundant $\bullet\text{OH}$ in the near-field region could further react with HOCl/OCl⁻ to produce secondary radicals such as $\bullet\text{OCl}$ (eqs 18 and 19)⁴ instead of forming H₂O₂ (eq 14). These secondary radicals could live longer and migrate for a larger distance to attack MB molecules available in the far-field region of the bulk solution. Hence, through addition of active chlorine, the $\bullet\text{OH}$ generated from VUV photolysis of water was mostly used for pollutant removal rather than ending up in the ineffective H₂O₂. This may explain the synergistic effect observed in the VUV/UV/chlorine process.

The effect of active chlorine dose is also manifested in Figure 5. When the active chlorine dose increased from 0 to 25 mg L⁻¹, the primary radicals ($\bullet\text{OH}$) could react with HOCl/OCl⁻ to produce the secondary radicals (e.g., $\bullet\text{OCl}$) as aforementioned, thus causing a rapid increase in the R_{Cl} due to their larger migration distance (Figure 5b). However, when the active chlorine dose further increased to 50 mg L⁻¹, the R_{Cl} decreased to some extent. This probably arises from three aspects: (1) at a high active chlorine concentration, the primary $\bullet\text{OH}$ in the near-field region was completely consumed by MB and HOCl/OCl⁻, so the secondary radicals already reached a maximum concentration; (2) the secondary radicals had a relatively weaker oxidation potential than $\bullet\text{OH}$ (e.g., $\bullet\text{OCl}$ vs $\bullet\text{OH}$); and (3) with the availability of abundant HOCl/OCl⁻, some tertiary reactive species (e.g., Cl₂ $\bullet^-$) might be formed, which could only react slowly with MB.

In addition, the synergistic effect of the VUV/UV/chlorine process could also arise from the VUV photolysis of HOCl/OCl⁻ (eq 20), although VUV photons react much faster toward H₂O. Table 1 shows that in the presence of NB, the $k'_{\text{VUV/Cl}}$ was 2.9 and 2.5 times the $k'_{\text{UV/Cl}}$ at pH 5 and 10, respectively. This implies that after completely scavenging $\bullet\text{OH}$, a higher Cl $\bullet$ concentration could be expected in the VUV/UV/chlorine process than in the UV/chlorine process, which led to a much faster MB degradation.

Discussion on MVPS. The MVPS is a new bench-scale apparatus for fundamental photoreaction studies. Although it cannot solely deliver VUV (185 nm) irradiation, it can output VUV/UV and UV beams with a nearly identical UV photon fluence in the two test tubes through special design of the optical structure, thus enabling studies on the net effect of VUV irradiation. Hence, the MVPS provides a powerful tool to compare quantitatively the treatment efficiencies of UV- and VUV/UV-based AOPs in the presence or absence of an assistant chemical (e.g., active chlorine), where UV often plays an important role in pollutant removal by forming reactive species and by direct photolysis as well. In addition, the two test tubes (i.e., VUV/UV and UV tubes) are installed close to the lamp (about 5 mm to the lamp surface), which gives rise to a

high UV PFR [8.88×10^{-4} einstein $\text{m}^{-2} \text{s}^{-1}$ (or a fluence rate of 41.8 mW cm^{-2}) at 254 nm] and a short reaction time correspondingly. Further assisted with an online spectrophotometer, the MVPS can quickly determine the reaction kinetics under VUV/UV exposure, with a significant reduction in both experimental workload and operational error.

Compared with a cylindrical batch VUV/UV reactor, the MVPS has a much shorter optical path-length (2 mm inner diameter, and even a thinner tube can be selected). Because the background UV absorbance of water sample induces a PFR attenuation along the radial distance of the lamp according to the Lambert–Beer Law, a smaller variance of UV PFR (i.e., $E_{\text{p,0,UV}}$) within the cross-section of the test tube in the MVPS can be reasonably expected than that in a batch reactor. Moreover, by recirculating water of a constant temperature through the outer chamber of the photoreactor (to maintain a stable mercury vapor pressure in the lamp) and online monitoring the lamp output with an MFSD as well, a stable UV output is ensured during each experiment. Therefore, the UV photon fluence in the MVPS can be determined more accurately than that in a batch reactor.

Note that the MVPS adopts an operation mode of intermittent light exposure, that is, t_{ree} is only a part of the total reaction time (t). For some complex reactions whose photoreaction (dependent on light) and dark-reaction (independent of light) rates are comparable, intermittent light exposure may induce a certain error in kinetic measurements. Under this circumstance, the dark-reaction rate needs to be measured separately by a control experiment, and then the overall kinetic parameters obtained from the MVPS should be corrected based on relevant kinetic model calculations. In the present study, because the rate constant of MB degradation by active chlorine in the dark was much smaller than those of photoreactions (Figure 4), intermittent light exposure would not induce a problem.

Discussion on VUV/UV/Chlorine. The low VUV output has long been regarded as the principal limitation for its practical applications to water treatment.⁹ Hence, a majority of research efforts have been made to enhance the VUV output, such as increasing the VUV transmittance of the quartz used for lamp wall and sleeve, raising the total power of the lamp, and inventing new light sources for VUV irradiation. However, unfortunately, to date, no significant progress has been made. This study, for the first time, demonstrates that the treatment efficiency of the VUV/UV process can be simply but greatly improved by addition of active chlorine. Because the new VUV/UV/chlorine process is easy to apply, highly efficient, and energy saving, it has a promising prospect for small-scale water and wastewater treatment.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b00133.

(Figure S1) MB degradation by UV/H₂O₂ and VUV/UV/H₂O₂; (Figure S2) MB degradation by active chlorine in the dark; and (Figure S3) molecular structure of MB; and additional references (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +86 10 62849632; fax: +86 10 62923541; e-mail: qiangz@rcees.ac.cn (Z. Qiang).

Notes

The authors declare no competing financial interest.

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