Impact of Small Organic Molecules on the Degradation of Methylene Blue in VUV/UV Irradiation System

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Abstract. Generally, small organic molecules (SOM) in waters are always as the ·OH scavengers in the AOPs and reduce its efficiency. In this paper, the studies are focused on the impact of small organic molecules on the degradation of methylene blue (MB) in VUV/UV irradiation system. Results show that the degradation of MB in VUV/UV process were divided into two section: the inhibition and acceleration with SOM addition. MB completely degraded at 30 min in VUV/UV system with addition of SOM, but the degradation was significantly inhibited in UV/H2O2/SOM system. The result show that the formation of H2O2 in water under VUV/UV irradiation and the addition of SOM improved the generation of H2O2. The decomposition of H2O2 at the maximum accumulated contents accelerate the MB degradation. This study provides an efficient VUV/UV process for reduce the interference of SOM, which could be applied in water treatment.

1. Introduction

Advanced oxidation process (AOPs) is one of the most efficient method to remove organic pollutions in aqueous. AOPs are almost all rely on the highly oxidative radical species, such as ·OH with a redox potential of 2.8 V[1]. Over the last decades, many AOPs such as Fenton[2], electrochemical advanced oxidation processes[3] and photocatalysis[4] were studied. Among them, UV based AOPs is a kind of promising advanced treatment technology that have been used in engineering. Recent years, VUV-AOP is regarded as a novel UV based AOPs and focused by more and more researchers. VUV (Vacuum ultraviolet) covers the wavelength range from 100 nm to 200 nm, which can produce ·OH, eaq and ·H through photochemical ionization water molecules. Compared with traditional UV based AOPs, VUV-AOP could save energy as well as chemicals and more and has been considered as the next generation UV based AOPs.

A small molecule is a low molecular weight organic compound (SOM, mall organic molecules), usually within a mass less than 1500 Daltons. Rate coefficients of ·OH reactions with small organic molecules so high that they were used as the ·OH scavengers in the AOPs[5]. Generally, small organic molecules are always been contained in water and wastewater and retarded the efficiency of AOPs. That is the most important problem for AOPs applications.

The objective of this study was to evaluate the effect of small organic molecules such as methanol, formaldehyde and formic acid on the degradation of methylene blue in VUV/UV irradiation system. The efficiency of the different processes was compared and the concentration of H2O2 produced in
different processes was measured. The mechanisms of the impact of small organic molecules on methylene blue degradation were assessed.

2. Materials and methods

2.1. Materials

Methylene blue, MeOH, HOCH, HCOOH, potash iodide and ammonium molybdate were purchased from Chron Chemical, China. Chemicals used for experiments were reagent grade and without further purification. All solutions were prepared with ultrapure water produced from a Direct-Pure UP water purification system (RephiLe Bioscience, China).

2.2. Degradation of methylene blue

All the batch experiments for MB degradation were performed in a lab scale annular photo reactor, and the photo reactor setup is shown in Fig. 1. A glass column (50mm×250mm) with a working volume of 300 mL, reaction temperature was kept at 25 ℃ with a thermostatic water bath (THD-1015, Ningbo Tianheng, China). A 8 W low pressure mercury lamp (Beijing Aerospace Hong Da Optoelectronics Technology Co., China) as the experimental light source could emit VUV/UV (10-08100, emitting at both 185 nm and 254 nm) or UV (10-08000, emitting only at 254 nm) spectrum. The lamps were inserted into a quartz sleeve and placed in the axes of the glass column. Initial solution pH was uncontrolled but was measured and remained around 6.23 during the reactions. Samples were withdrawn from the photo-reactor at predetermined time intervals and analyzed timely.

2.3. Analytical methods

The concentration of methylene blue (MB) and UV-Vis absorption spectra of aqueous was analyzed by UV-vis spectroscopy (Specord® 200 plus, Analytik Jena, Germany). The hydrogen peroxide generated during VUV/UV photolysis was by KI method[6].

3. Results

3.1. The kinetics of MB degradation

Degradation kinetics of MB in different process were summarized in Fig.2. The degradation of MB under UV irradiation was negligible, but that was very fast in VUV/UV irradiation process and the pseudo first order kinetic constants was 0.1729 min⁻¹ (Fig.1 A). In VUV/UV irradiation system, ·OH were generated mainly through photoionization of H₂O molecules, and ·OH was the main free radical degrading MB. However, the degradation process were different from in only VUV/UV irradiation system when the small organic molecules addition such as MeOH, HOCH and HCOOH. The MB degradation process were divided into two section: the inhibition and acceleration. In the first section, the degradation of MB was inhibited as MeOH, HOCH and HCOOH addition, and the pseudo first
order kinetic constants was 0.0179, 0.0191 and 0.0193 min⁻¹, respectively. In the second section, the
degradation of MB was accelerated as MeOH, HOCH and HCOOH addition, the pseudo first order
kinetic constants was 0.3029, 0.4485 and 0.3557 min⁻¹, respectively. The degradation rate of the
second section was higher than the merely VUV/UV irradiation markedly. That was different from the
previous reports of acetamiprid degradation in UV/H₂O₂ and UV/PS system[7].

3.2. Effect of SOM on MB degradation in different systems
To assess the effect of SOM on degradation efficiency of MB, we selected four reaction systems, i.e.,
UV alone, VUV/UV alone, UV/ H₂O₂ and VUV/UV/H₂O₂, to study MB degradation with different
SOM addition (Fig. 3). As seen in Fig. 3A, the degradation of MB in UV alone was slightly and the
effect of three SOMs were negligible. MB was degraded in 30 min due to the H₂O₂ addition in
UV/H₂O₂ system, but the degradation rate was reduced when the SOM addition (Fig. 3B).

Figure 3. Effect of small organic molecules on MB degradation in different systems (A)
VUV/UV, (B) VUV/UV/H₂O₂, (C) UV, (D) UV/H₂O₂. Reaction conditions: MB dosages=30
mg/L, SOM (MeOH, HOCH or HCOOH) dosages=5 mM, H₂O₂ dosages=5 mM.
In the UV/ H2O2 system, ·OH was generated from the H2O2 photolysis under UV irradiation. This result can be attributed to the ·OH scavenged by SOM. However, MB degradation rate was accelerated after incipient inhibition, and all removed at 30 min in VUV/UV/H2O2 system (Fig. 3D). It is worth noting that, the same phenomenon occurs in VUV/UV system without the H2O2 addition (Fig. 3C). The results indicated that VUV was the primary role that reduce the inhibitory effect of SOM. Under VUV irradiation, the inhibiting effect of SOM was weakened and MB could be degraded.

3.3. The more H2O2 generated with SOM presence

The formation of H2O2 in different process are shown in Fig. 4. The concentration of H2O2 increased to 38.56×10^-6 M at 5 min and decreased 15.15 ×10^-6 M at 30 min. In the VUV/UV process, H2O2 will be generated in situ because of the ·OH recombination. At the same time, H2O2 was decomposing by VUV and UV irradiation. With the addition of MeOH, HCOH and HCOOH, more H2O2 was generated and the maximum accumulated H2O2 concentration rose to 139.40×10^-6 M, 221.67×10^-6 M and 167.95×10^-6 M, respectively. However, no H2O2 was detected in the solution containing the MeOH and HCOH under UV irradiation. In the UV/HCOOH system, H2O2 produced continuously and the concentration of H2O2 increased to 56.67×10^-6 M at 30 min. In the VUV/UV system, SOM enhanced the H2O2 generation, and VUV play a key role in this process.

![Figure 4. The concentration of H2O2 as a function of time production in different process. Reaction conditions: MB dosages=30 mg/L, SOM (MeOH, HOCH or HCOOH) dosages=5 mM.](image)

It should be note that the time of maximum accumulated H2O2 concentration was identical to the time of start accelerating degradation of MB. As addition of SOM in VUV/UV system, the ·OH reacted with SOM and the degradation of MB was reduced. Meanwhile the H2O2 produced and accumulated in the aqueous solution. As the SOM was consumed up and the H2O2 concentration reached its maximum, H2O2 starts to break down and produced a good deal of ·OH. MB was attracted by ·OH and degradation rate was accelerated (Fig. 5).

![Figure 5. Schematic of the MB degradation mechanism in VUV/UV system with SOM addition.](image)
4. Conclusions
In this study, MB degradation in an aqueous solution with addition of SOM by the VUV/UV process was investigated. In the VUV/UV system, \( \text{OH} \) was participated in the degradation of MB and play the primary contribution. Degradation of MB was inhibited by SOM in UV/H\(_2\)O\(_2\) system, but that was accelerated at second section in VUV/UV and VUV/UV/H\(_2\)O\(_2\) system. H\(_2\)O\(_2\) was generated in VUV/UV irradiation system and that was enhanced by the addition of SOM. Specifically, VUV reduced the inhibitory effect of SOM attributed to produced more H\(_2\)O\(_2\).

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