



# On-line monitoring of photolysis reactions using electrospray ionization mass spectrometry coupled with pressurized photoreactor



Hong Zhang<sup>b, c</sup>, Xiaodi Li<sup>d</sup>, Kai Yu<sup>a</sup>, Na Li<sup>a</sup>, Jing He<sup>a</sup>, Hong You<sup>a, b, c</sup>, Jie Jiang<sup>a, \*</sup>

<sup>a</sup> School of Marine Science and Technology, Harbin Institute of Technology at Weihai, Weihai 264209, China

<sup>b</sup> School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China

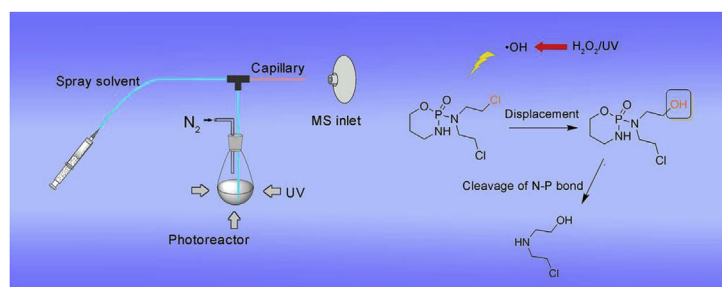
<sup>c</sup> State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China

<sup>d</sup> School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

## HIGHLIGHTS

- Electrospray ionization coupled with pressurized photoreactor was developed.
- It enables on-line monitoring of photolysis reactions.
- It can capture and characterize reactive photolysis reaction intermediates.
- Two new intermediates of cyclophosphamide in H<sub>2</sub>O<sub>2</sub>/UV were identified.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 21 October 2017

Received in revised form

30 December 2017

Accepted 20 January 2018

Available online 3 February 2018

### Keywords:

Photolysis reaction intermediates

Real-time monitoring

Mass spectrometry

Electrospray ionization

Cyclophosphamide

H<sub>2</sub>O<sub>2</sub>/UV

## ABSTRACT

A simple method by coupling a spray capillary with pressurized photoreactor for on-line monitoring of photolysis reactions was reported. In this method, only an inert gas is used to transfer the reaction solution, which avoids potential sample loss and contamination. The photolysis reaction is online quenched, and therefore, it has advantages of on-line detection and characterization of photolysis reaction intermediates. The assembly is easy to achieve, low-cost, and robust. Different from off-line methods, the photolysis reaction solution is directly transferred to a capillary tip for ionization, avoiding the delay in the detection of reactive intermediates. With this setup, this technique has been applied for on-line monitoring of degradation of cyclophosphamide (CP) in H<sub>2</sub>O<sub>2</sub>/UV for which two new intermediates were intercepted and structurally characterized for the first time by tandem mass spectrometry. In H<sub>2</sub>O<sub>2</sub>/UV, the degradation of CP occurred via hydroxylation, dehydrogenation, chlorine substitution reaction, and cleavage of the chloroethyl group. These results indicate that the coupling of electrospray ionization mass spectrometry with pressurized photoreactor can detect and characterize the key photolysis reaction intermediates, which render it a potential tool for elucidating the mechanism of water remediation.

© 2018 Elsevier B.V. All rights reserved.

## 1. Introduction

Advanced oxidation processes (AOPs) utilizing reactive species (e.g.,  $\cdot\text{OH}$ ,  $\text{SO}_4^{\cdot-}$ , etc.) have been widely used for water remediation in recent years [1,2]. The most popular one is photolysis oxidation

\* Corresponding author.

E-mail address: [jiejiang@hitwh.edu.cn](mailto:jiejiang@hitwh.edu.cn) (J. Jiang).

techniques including  $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{TiO}_2/\text{UV}$ ,  $\text{K}_2\text{S}_2\text{O}_8/\text{UV}$ , etc. Such methods can completely destroy the refractory organics owing to its excellent degradation efficiency and complete mineralization of the refractory organics [3,4]. Elucidation of the photolysis reaction mechanism generally requires the isolation and characterization of reaction intermediates [5,6], which is usually not easy and is often time-consuming. However, an effective method for on-line isolation and characterization of the photolysis reaction intermediates is lacking. This results in that the degradation mechanism of refractory organics is particularly complex, being still a matter of debate.

To date, several methods have been developed to capture and characterize the photolysis reaction intermediates and/or products. But chromatography [7] and UV spectroscopy [8] based methods provide limited structure information on the detected intermediates. This impedes accurate elucidation of the reaction mechanism. Electro-spin resonance (ESR) spectroscopy [9] and capillary electrophoresis (CE) [10] have been also used to intercept and characterize the photolysis reaction intermediates. However, the multiple handling steps of these methods such as liquid-liquid extraction, filtration and dilution make that the key photolysis reaction intermediates are difficult or even impossible to isolate and detect. In addition, with inappropriate reagent used, sample may suffer inevitable loss and contamination.

Mass spectrometry (MS) has been widely used to reveal the mechanistic details of chemical reactions [11], which greatly profits from the development of electrospray ionization (ESI) [12,13]. In ESI, the sample present in liquid phase is gently transferred to gas phase, where they can be analyzed and eventually characterized, with little or no fragmentation. ESI-MS has been applied to investigate the mechanism of water remediation, for example, with the photoelectrocatalytic oxidation of  $\text{Cu}(\text{II})$ -EDTA [14], oxidation of 5-fluorouracil [15], and with the photocatalytic degradation of methyl orange [5]. However, these investigations are performed offline, which is difficult to capture and characterize the key photolysis reaction intermediates. This results in the mechanism of the photolysis reaction unclear. Although a number of groups have used various reactors coupled with ESI for the condensed phase analysis [16–19], on-line monitoring of photolysis reaction is yet a challenge.

Herein, we introduce a method by coupling of a spray capillary with pressurized photoreactor, which allows on-line detection and characterization of photolysis reaction intermediates. In this method, only a pressurized inert gas is used to drive the sample solution to a capillary for ionization. It simplifies the operation and avoids potential loss and contamination of the samples. The photoreaction solution is diluted and quenched online, thus making the sample solution is detected on the order of less than 1 s. With this setup, this method is capable of continuously sampling reaction solution from the pressurized photoreactor allowing dynamic changes in the system to be followed. It is also suitable for detection of intermediates in a photoreactor at different site by simply adjusting the tubing that is immersed in the sample solution. In addition, the photoreactor and the spray is integrated, and the assembly is easy to achieve, low-cost, and robust. In this work, the coupling of a spray capillary with pressurized photoreactor was demonstrated for on-line monitoring of the degradation of cyclophosphamide (CP) in  $\text{H}_2\text{O}_2/\text{UV}$ . CP was selected because it belongs to the most commonly used alkylating agent in anti-cancer therapy [20]. It is frequently detected in water and soil sources, has a potential threat to the environment and human health [21], and undergoes negligibly direct UV photolysis [2,22]. With this method, two key intermediates were detected and characterized by tandem mass spectrometry for the first time, which gave new insights into the oxidation mechanism of CP in  $\text{H}_2\text{O}_2/\text{UV}$ .

## 2. Materials and methods

### 2.1. Reagents

Methanol (MS grade) was purchased from Sigma-Aldrich (Darmstadt, Germany). Cyclophosphamide (purity  $\geq 99.5\%$ ) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (30% w/w) was purchased from Aike Co. (Chengdu, China). All the inert gases including He, Ar and  $\text{N}_2$  were purchased from Jinghua Industry Co. (Hangzhou, China). Low-pressure Hg lamps were purchased from Philips Co. (4 W, 254 nm, Shanghai, China). Ultrapure water was obtained from a Milli-Q water purification system, (Milford, MA).

### 2.2. Electrospray ionization coupled with pressurized photoreactor

As shown in Fig. 1, the photolysis reaction solution was driven by pressurized inert gas to a T-piece for on-line dilution and quenching, and then ionized via a capillary tip. In detail, a custom-built quartz bottle (8 mL) was placed in a dark box containing three low-pressure Hg lamps, and was connected to a source of pressurized inert gas via a short length of Teflon tubing (i.d. 1.0 mm, o.d. 2.0 mm). One end of a PEEK tube (i.d. 0.013 mm, o.d. 1.53 mm) was immersed in the sample solution in the quartz bottle, and another side of the tube was connected to the T-piece. A fused silica spray capillary (i.d. 0.10 mm, o.d. 0.19 mm) used for sample ionization was connected with the T-piece and positioned in front of the inlet of a mass spectrometer. The lengths of the PEEK tubing and the spray capillary were 120 and 20 mm, respectively. The spray solvent (methanol) was introduced to the T-piece via a PEEK tubing, and was controlled by a syringe pump (WPI, Sarasota, FL). The inert gas

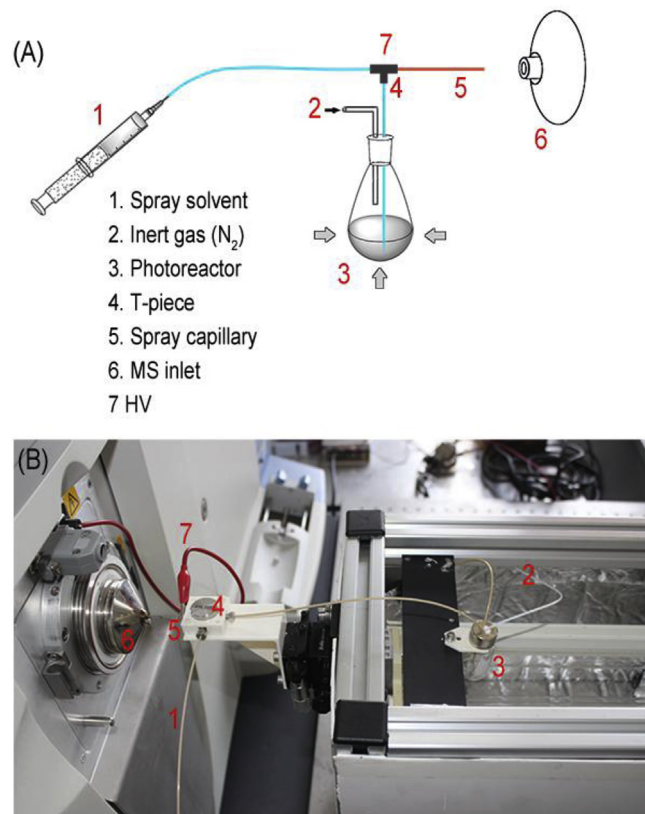


Fig. 1. (A) Schematic diagram; (B) photograph of the apparatus marked by the same labels with (A).

Download English Version:

<https://daneshyari.com/en/article/7553944>

Download Persian Version:

<https://daneshyari.com/article/7553944>

[Daneshyari.com](https://daneshyari.com)