Research article

Impact of hydrodynamics on pollutant degradation and energy efficiency of VUV/UV and H_2O_2/UV oxidation processes

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ABSTRACT

The Vacuum-UV/UV process, an incipient catalyst/chemical-free advanced oxidation process (AOP), is potentially a cost-effective solution for the removal of harmful micropollutants from water. Utilizing a novel mechanistic numerical model, this work aimed to establish a thorough understanding of the degradation mechanisms in the VUV/UV process operating under continuous flow conditions, when compared with the widely applied H_2O_2/UV AOP. Of particular interest was the examination of the impact of flow characteristics (hydrodynamics) on the degradation efficacy of a target micropollutant during the VUV/UV and H_2O_2/UV AOPs. While hydroxyl radical (•OH) oxidation was the dominant degradation pathway in both processes, the degradation efficacy of the VUV/UV process showed much stronger correlation with the extent of mixing in the photoreactor. Under a uniform flow regime, the degradation efficiency of the target pollutant achieved by the H_2O_2/UV process with 2- and 5 ppm H_2O_2 was greater than that provided by the VUV/UV process. Nonetheless, introduction of mixing and circulation zones to the VUV/UV reactor resulted in superior performance compared with the H_2O_2/UV AOP. Based on the electrical energy-per-order (EEO) analysis, incorporation of circulation zones resulted in a reduction of up to 50% in the overall energy cost of the VUV/UV AOP, while the corresponding reduction for the 5-ppm H_2O_2/UV system was less than 5%. Furthermore, the extent of •OH scavenging of natural organic matter (NOM) on energy efficiency of the VUV/UV and H_2O_2/UV AOPs under continuous flow conditions was assessed using the EEO analysis.

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1. Introduction

Ultraviolet (UV) based advanced oxidation processes (AOPs), and in particular H_2O_2/UV AOP, have demonstrated great promise for the removal of organic micropollutants in water (Aleboyeh et al., 2012; Zuorro et al., 2014). Despite large-scale applications, H_2O_2/UV AOP suffers from the high cost of hydrogen peroxide including acquisition, transportation and storage (Von Gunten, 2003). More importantly, since a significant portion of utilized H_2O_2 will remain unreacted within the system, regular monitoring and post treatment of the residual peroxide are essential (Zoschke et al., 2012). The need for quenching the residual peroxide imposes further costs and complexity to the H_2O_2/UV process, specifically for applications in small-to medium-sized water treatment facilities. Vacuum-UV/UV AOP is an alternative competitive technology that eliminates the need for an auxiliary chemical oxidant, e.g., hydrogen peroxide,

resulting in a simpler and more environmentally sustainable process with greater economic potential for commercial applications.

The effectiveness of VUV/UV process for the removal of a wide range of contaminants under small batch recirculating reactors has been studied extensively (Arany et al., 2013; Crapulli et al., 2014; Imoberdorf and Mohseni, 2011, 2012; Kim and Tanaka, 2009; Zoschke et al., 2014). The experimental comparison of the H_2O_2/UV and VUV/UV AOPs in small batch recirculating reactors indicates superior performance of the VUV/UV process. Mouamfon et al. (2011) reported up to 20% greater performance for the VUV/UV process when compared with the widely applied H_2O_2/UV AOP for degrading a target pharmaceutical, sulfamethoxazole, in a lab-scale batch reactor. Similarly, Zoschke et al. (2012) evaluated the treatment cost of the VUV/UV and H_2O_2/UV AOPs for remediation of taste and odor compounds (e.g., geosmin and 2-methyl isoborneol) in terms of the electrical energy-per-order (EEO). The authors underlined the cost competitiveness of VUV/UV over H_2O_2/UV process, with up to 50% lower EEO for small batch recirculating reactors.

Despite the promising results obtained through lab-scale batch experiments, the practical implementation of the VUV/UV AOP within the water industry has not been fulfilled. The lack of experimental and modeling studies demonstrating the treatment capability of the VUV/UV systems under continuous flow operations is among the key impediments hindering their large-scale implementation. Furthermore, the impact of hydroxyl radical (•OH) scavengers on the performance of the VUV/UV AOP needs to be evaluated under continuous-flow operation. This is of paramount importance, since the very high absorption coefficient of water for 185 nm VUV radiation limits the oxidation power of the process to a thin film optical path (Barrett and Mansell, 1960; Price et al., 1960) (e.g., less than 1 cm). Finally, there is a significant need for investigating the impact of flow characteristics (reactor hydrodynamics) on the competiveness of the VUV/UV systems, when compared with the more established H₂O₂/UV process. Hydrodynamic studies have often been conducted through incorporation of baffles (Duran et al., 2011) or static mixers (Oppenländer et al., 2005), modification of the reactor geometry (Santoro et al., 2010) or injection of gas bubbles into the reactor (Azimi et al., 2014). Among these, the implementation of baffles has received greater attention due to its technical feasibility, operational practicality and cost-effectiveness.

The main objective of this work was to utilize computational fluid dynamics (CFD) modeling for an in-depth comparative study of the VUV/UV and H₂O₂/UV AOPs for the removal of para-chlorobenzoic acid as a target model pollutant in a conventional continuously operating photoreactor. A core aspect of this work included exploring the role of flow characteristics (hydrodynamics) in the competiveness of VUV/UV systems when compared with the H₂O₂/UV process. Furthermore, the extent of •OH scavenging of natural organic matter (NOM) and its influence on the energy-efficiency of the VUV/UV and H₂O₂/UV AOPs were assessed in terms of EEO. To date, no similar study that employs a mechanistic model for an in-depth comparative study of the VUV/UV and H₂O₂/UV AOPs under continuous-flow conditions has been reported.

2. Materials and methods

2.1. Experimental setup and procedure

Experimental tests were conducted in a prototype annular photoreactor operating under continuous flow conditions (Fig. S1, presented as Supplemental Information). The reactor was made of Plexiglas®, with an annular configuration, equipped with a 42 W low-pressure mercury amalgam lamp, longitudinally placed at the axial center of the reactor. The internal and external diameters of the annular photoreactor and synthetic quartz sleeve (Heraeus Quartz America LLC, SUPRASIL310) were 7 cm and 2.8 cm, respectively, yielding a radial gap of 2.1 cm corresponding to a hydraulic diameter of 4.2 cm for treating the water. The presence of approximately 10 hydraulic diameters between the reactor inlet and lamp (e.g., ~40 cm) ensured that the flow was fully developed before the irradiated zone. Meanwhile, the operating temperatures at the amalgam position, lamp envelope surface and water at 0.5 cm distance from the reactor body were monitored using K-type thermocouples (OMEGA®, US).

An ozone-generating lamp (GPHVA357T5VH, Light Sources Inc.) was utilized for experiments involving VUV/UV AOP, whereas an ozone-free lamp (GPHVA357T5L, Light Sources Inc.) with identical dimension and power requirement was employed for UV and or H₂O₂/UV processes. The diameter and arc length of the lamps were 15 mm and 278 mm, respectively. The operating amalgam temperature of the utilized lamps during the degradation experiments were approximately $65 \pm 2.0\,°C$ depending upon the flow rates of water. Knowing the amalgam temperature, 185 nm VUV and 254 nm UV irradiances of the lamps were calculated using a radiometer (Bagheri and Mohseni, 2014). Details of the utilized radiometry technique for the 185 nm and 254 nm lamp power measurements can be found elsewhere (Bagheri and Mohseni, 2014; Sasges et al., 2012).

2.2. Analytical methods

The concentration of p-CBA was directly analyzed with HPLC (Dionex UltiMate™ 3000, US). Separation was accomplished using a reverse phase Nova Pak C18, 4 µm 3.9 × 150 mm separator column. A sample volume of 20 µL with a flow rate of 0.45 mL/min (55% acetonitrile/44% water/1% phosphoric acid) was injected to the system and the detection wavelength was set at 235 nm. For pH adjustment, a phosphate buffer solution (a mixture of monosodium phosphate and disodium phosphate (Sigma—Aldrich, Canada) was employed. Concentration of hydrogen peroxide was determined via UV spectrophotometry utilizing the I_3^- method (Klassen et al., 1994). Hydrogen peroxide was purchased as 35 wt. % solution (Sigma—Aldrich, Canada) in water. Using a TOC Analyzer (Shimadzu TOC-VCPH) with the non-purgeable organic carbon (NPOC) method, concentrations of methanol and its oxidation by-products were quantified as an aggregate and reported as mg carbon per L.

3. Model development

CFD simulation of the VUV/UV process necessitates simultaneous resolution of hydrodynamics, fluence rate at both 185 nm and 254 nm wavelengths and a comprehensive kinetic scheme (Bagheri and Mohseni, 2014; Bagheri et al., 2013). It should be noted that since the kinetic scheme and radiation system governing H₂O₂/UV process are already part of VUV/UV multiphysics, the developed model can be utilized for both VUV/UV and H₂O₂/UV AOPs. ANSYS® 14.5 simulation platform was employed to build and discretize the simplified 2D axisymmetric reactor geometry via 15,418 structured hexahedral cells. As well, ANSYS® Fluent 14.5 was employed to read the exported mesh and perform the CFD computations. As for the hydrodynamics sub-models, the laminar hydrodynamics equation was utilized under laminar flow conditions (e.g., Re < 2100), whereas the Realizable k-epsilon (k-ε) sub-model was utilized and compared under turbulent flow conditions (Duran et al., 2011; Elyasi and Taghipour, 2010; Santoro et al., 2010). The utilized kinetic rate equations for the degradation of the target pollutant, p-CBA, is described in Tables S1 (submitted as Supplemental Information to this manuscript). To simulate •OH scavenging impact of NOM, methanol was utilized as a surrogate •OH scavenger. Based on earlier investigations (Gonzalez et al., 2004), methanol undergoes a widely studied sequential oxidation kinetic scheme which can be well summarized via three main reactions (see Tables S1). Based on the •OH reaction rate constant of Suwannee River NOM of $1.56 \times 10^4\,(mgC/L)^{-1}s^{-1}$ (Westerhoff et al., 2007), the concentration of methanol corresponding to •OH scavenging of 2-ppm NOM was calculated. Fluence rate fields for 185 nm and 254 nm photons were computed by solving the radiative transport equation (RTE) using a non-gray discrete ordinate (DO) sub-model. Furthermore, the reflection, refraction and absorption of photons within the air gap (separating the lamp and the quartz sleeve region) and on the quartz sleeve were incorporated within the radiation sub-model (Duran et al., 2010). Moreover, to account for the dependency of 185 nm water absorption coefficient on temperature $(+0.05\,cm^{-1}/°C)$, a linear function which corresponds to $1.4\,cm^{-1}$ at 25 °C was coupled with the RTE (Bagheri and Mohseni, 2014). Measured UV254 transmittance of the samples was found to be 98%, and this value was used in the simulations.