Chemical Engineering Journal 187 (2012) 114–122

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Kinetic study and modeling of the vacuum-UV photoinduced degradation of 2,4-D

Gustavo Imoberdorf, Madjid Mohseni*

Department of Chemical and Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver, BC, Canada V6T 1Z3[1]

ARTICLE INFO

Article history:
Received 31 October 2011
Received in revised form 20 January 2012
Accepted 23 January 2012

Keywords:
Vacuum-UV
Photoreactor
2,4-D
Water treatment
Modeling

ABSTRACT

Vacuum-UV (VUV) photoinduced degradation of a model micropollutant, herbicide 2,4-dichlorophenoxyacetic acid (2,4-D), was studied using a flow-through VUV photoreactor, operating in batch mode under kinetic control. Fast degradation rates were obtained using the VUV process, with 2,4-D concentrations lower than 1.5 mg L^{-1} being degraded by 90% after receiving a total UV/VUV fluence of 938 mJ cm^{-2}. Experimental results showed that the initial degradation rate of 2,4-D in ultrapure water was independent of the initial concentration of the contaminant. The presence of alkalinity and NOM reduced the degradation rate by up to 72% due to the hydroxyl radical scavenging effect of carbonates/bicarbonates and NOM as well as their absorption of VUV radiation. The kinetics of the VUV induced degradation of 2,4-D in ultrapure water was also investigated through a kinetic model developed in this study. This model took into account the propagation and absorption of radiative energy in the reactor, generation of hydroxyl radicals via water photolysis, and interaction between photogenerated radicals and 2,4-D.

1. Introduction

Advanced oxidation processes (AOPs) can be utilized in water treatment to degrade target micropollutants, such as pesticides, herbicides, pharmaceuticals, endocrine disrupting chemicals (EDCs), and other harmful compounds [1]. Some AOPs, such as H_2O_2/UV and H_2O_2/O_3, have already been applied in commercial scale. However, the need to add H_2O_2 or O_3 makes these processes less attractive and sometimes expensive. For the H_2O_2/O_3 process, additional complications arise since O_3 needs to be generated on site and there are potential risks associated with its use because ozone is a hazardous gas requiring many safety percussions. An alternative promising AOP involves the use of vacuum-UV (VUV) radiation to photolyze water to form hydroxyl radicals ($HO^{\bullet}$), hydrogen radicals ($H^{\bullet}$), and solvated free electrons (e_{aq}^{-}) [2]. Pollutants are mostly degraded by $HO^{\bullet}$, but they can also be degraded by other radicals or, to a limited extent, through direct photolysis by VUV radiation [3].

VUV photons can be generated commonly by excimer lamps and ozone-generating low-pressure Hg lamps (VUV-Hg lamps). Each type of lamp presents some advantages and disadvantages. Excimer lamps can emit a high power of quasi-monochromatic radiation at 126, 146, 172, 222, 282, or 308 nm (depending on the gas in the lamp). The electrical efficiency is in the order of 5–40% [4,5]. For water treatments, Xe_2-excimer lamps, which emit at 172 nm, have been considered [5]. Since water absorptivity at 172 nm is very high, about 550 cm^{-1}, [6] photons are mostly absorbed in a 10 micron layer close to the lamps, thereby generating significant mass transfer resistances that decrease the efficacy of the process significantly. Heit and Braun [7] studied mass transfer resistances generated and showed that steep profiles of oxygen concentration close to the Xe_2-excimer lamp take place.

VUV-Hg lamps emit about 10% of the radiation at 185 nm, 80–90% radiation at 254 nm, and a very low percentage in the visible range. The absorptivity of water at 185 nm is 1.80 cm^{-1}; [8] hence, radiation profiles obtained with 185 nm radiation are much less steep than those with 172 nm. In this case, 90% of 185 nm photons are absorbed in about 0.3 cm layer close to the lamp [3]. The distribution of 254 nm photons is more uniform since the absorptivity of water at 254 nm is negligible. Details of the propagation of 254 nm and 185 nm photons are presented elsewere [10]. In addition, diffusive resistances could be minimized or eliminated by increasing the turbulence in the reactor. In this regard, Dobrović et al. [9] and Imoberdorf and Mohseni [10] studied the effect of the turbulence on the mineralization of natural organic matter (NOM) and concluded that increasing the turbulence within the VUV-photoreactors is of crucial importance towards reducing diffusive resistances.

Most of the studies on the use of VUV for the degradation of pollutants have focused on the reaction mechanism of different contaminants (chlorinated hydrocarbons, [11] atrazine,[12] p-chlorobenzoic acid, [13] an organic azo dye, [14] perfluorooctanoic acid, [15] and citric and gallic acids [16]), the degradation of NOM and by-products formation, [17–19] and the effect of

---

* Corresponding author. Tel.: +1 604 822 0047; fax: +1 604 822 6003.
E-mail address: mmohseni@chbe.ubc.ca (M. Mohseni).

[1] Tel: +1 604 822 3238; fax: +1 604 822 6003.

1385-8947/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2012.01.107

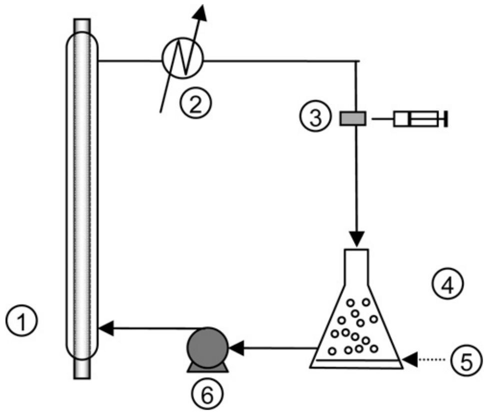

Fig. 1. Flow-through photoreactor operated in batch mode: (1) annular photoreactor, (2) heat exchanger, (3) sampling point, (4) storage tank, (5) air, (6) recycling pump.

operating variables on the efficiency of the process [9,12,20–22]. There have been studies that analyzed the kinetics of VUV-induced degradation of complex micropollutants through simplified kinetic expressions [23,24]. Also, the degradation of simple pollutants, such as formic acid, was studied with a detailed model [3]. However, kinetics are not fully understood due to the complexity of the reactions taking place in the VUV process. In the simplest case, which occurs when just pure water receives VUV radiation, several radicals are generated ($HO^\bullet$, e^-_{aq}, $H^\bullet$, $HO_2{}^\bullet$, $O_2{}^{\bullet-}$) and can interact among themselves leading to more than 30 reactions taking place simultaneously [2]. The system is even more complex in the presence of organics because some of these radicals can react with organic compounds to initiate an intricate reaction mechanism.

The focus of this research is to study the kinetics of the VUV-photoinduced degradation of a model micropollutant, herbicide 2,4-chlorophenolaceticacid (2,4-D). Experiments were conducted in a VUV annular flow-through photoreactor operating in batch mode. The effect of recycling flow rate, initial contaminant concentration, alkalinity, and water matrix on the effectiveness of 2,4-D degradation was studied. A model was developed to describe the degradation of 2,4-D in pure water. The specific phenomena incorporated into the model include the radiation propagation within the reactor, a kinetic scheme that considers the main reactions occurring in the system, and the corresponding mass balances. The model was used to analyze the kinetics of the degradation of 2,4-D. Once the main reactions governing the process are identified, they could be extrapolated to different pollutants, and the kinetic model could be solved if the corresponding kinetic constants between the pollutants and OH radicals are known. This would allow the development of detailed and comprehensive models that could help with the optimization of the process and the design of larger scale prototypes.

2. Material and methods

2.1. Experimental setup

Experiments were conducted in a flow-through annular VUV photoreactor operating in batch mode with full recycle of the reactants. The photoreactor was coupled with a peristaltic pump, a storage tank, and connecting tubing (Fig. 1). An ozone-generating low-pressure VUV-Hg lamp (Light Sources Inc. G10T51-2-VH) was used as the source of radiation. The volume of the photoreactor was 0.085 L, its length was 27.5 cm, its internal diameter was 1.5 cm (lamp diameter) and its external diameter was 2.5 cm. A heat exchanger was used to control and stabilize the temperature of the solution at 25 °C. Air was sparged in the storage tank to maintain saturated and constant concentration of dissolved oxygen in the reacting solution.

The 254 nm radiation flux of the VUV-Hg lamp was measured using a research radiometer (IL 1700, SED240 sensor, and NS254 filter), which was calibrated with the ferrioxalate actinometric technique [25]. The net radiation flux of 254 nm radiation emitted by the lamp operating at 25 °C was 13.1 mW cm^{-2}. On the other hand, the 185 nm radiation flux was determined using the cis–trans cyclooctene photoisomerisation actinometric technique [26]. The measured radiation flux at 185 nm was 1.79 mW cm^{-2}.

2.2. Water samples preparation

Contaminated water samples were generated by adding 2,4-D (Sigma–Aldrich) into either Millipore (MP) water or raw surface water. For experiments involving raw surface water, samples were collected from Trepanier Creek (TC), Josephine lake in Bowen Island (BI), and Capliano reservoir (CR), all in British Columbia, Canada. The unfiltered samples were stored at 4 °C prior to use. Some important parameters of the raw waters used in this study are presented in Table 1. In some tests, $NaHCO_3$ (Fisher, Canada) was used to increase the alkalinity of water.

2.3. Experimental procedure

For each experimental run, 2.0 L of the water spiked with 2,4-D was placed in the tank, the pump was turned on, and water was recirculated for 10 min to equalize the temperature at 25 °C. Then, the lamp was turned on and samples were taken at set intervals for monitoring the concentrations of 2,4-D, total organic carbon (TOC), H_2O_2, pH, and temperature. For most of the experiments, the recycle flow rate was relatively high at 3000 cm^3 min^{-1} (Reynolds number = 1800). Separate tests conducted at different recycling flow rates indicated that diffusional resistances were negligible at this flow rate, and reactions occurred under kinetic controlled conditions.

2.4. Analytical methods

The concentrations of 2,4-D and oxidation by-products were quantified using a high-performance liquid chromatograph (HPLC, Waters 2695) equipped with C-18 column (4-μm particle diameter) and a UV-detector. Methanol/water/acetic acid (58:40:2%, v/v) were used as the mobile phase. The flow rate of mobile phase was 1 mL min^{-1} and the analysis was conducted at $\lambda = 280$ nm via UV detection. Mineralization extent of 2,4-D was assessed by measuring the concentration of TOC using a TOC-VCPH Shimadzu analyzer. The UV absorption at 254 nm (Abs_{254}) was determined using a UV–vis spectrophotometer (Shimadzu 1240), whereas that at 185 nm (Abs_{185}) was measured using a VUV-UV–vis spectrophotometer (Cary 4000 Varian). pH was measured using a pH meter (Thermo Orion PerpHecT LogR 1330 meter, 9206BN electrode). The concentration of dissolved oxygen was monitored using a dissolved oxygen meter (YSI 52 meter, YSI 5909 probe) and the concentration of H_2O_2 was measured using the triiodide method [27].

3. Experimental results and discussions

3.1. Description of the reacting system

The primary and most important reactions resulting from the VUV irradiation of water are the photochemical homolysis and the photochemical ionization of water:

$$H_2O + h\nu_{185\,nm} \rightarrow HO^\bullet + H^\bullet \qquad (1)$$