

Experimental study of the degradation of 2,4-D induced by vacuum-UV radiation

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ABSTRACT

Vacuum-UV (VUV) photoinduced degradation of the herbicide 2,4-D was studied. A flow-through VUV photoreactor was used (i) in batch mode to study the kinetics of degradation and (ii) in continuous mode under steady state to analyze the potential utilization of this process in commercial applications. In both cases, the reactants were recycled to minimize diffusive resistances. Experimental results from the batch studies showed that the initial degradation rate of 2,4-D in ultrapure water was independent of the initial concentration of the herbicide. However, a reduction in the reaction rate was obtained over the course of the treatment, largely due to the formation of 2,4-D partial oxidation by-products which compete with 2,4-D molecules for HO (scavenging effect). Increases in water alkalinity reduced 2,4-D degradation rate as a consequence of the scavenging of HO by carbonates and bicarbonates. The degradation of 2,4-D in raw surface waters was also investigated. A noticeable reduction in the degradation rate was observed because of the presence of NOM and alkalinity, both being known HO scavengers. Additionally, the presence of inorganic species/ions that absorb VUV may also have contributed to the reduction of the overall degradation rate. High conversions were obtained in the continuous system. At a residence time of 25 seconds, conversions of 97% and 65% were achieved for inlet herbicide concentrations of 1 and 10 mg L⁻¹, respectively. Under these conditions, the received dose of 185 nm radiation was 44.8 mJ cm⁻².

Key words | 2,4-D, herbicides, photoreactor, vacuum-UV, water treatment

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INTRODUCTION

Vacuum-UV (VUV) radiation photolyzes water molecules to form hydroxyl radicals (HO), hydrogen radicals (H), and free electrons (e⁻). HO is a very reactive species, which can partially oxidize and even mineralize organic compounds. Most open literature reports on the application of VUV have focused on the reaction mechanism of different pollutants (Jakob *et al.* 1993; Gonzalez *et al.* 1994; Shirayama *et al.* 2001; Gonzalez *et al.* 2004; Han *et al.* 2004a; Quici *et al.* 2008), degradation of natural organic matter (NOM) and formation of by-products (Buchanan *et al.* 2004, 2005, 2006), and the effect of operating variables on process efficiency (Jakob *et al.* 1993; Gonzales *et al.* 1994, 1995; Han *et al.* 2004b; Alapi & Dombi 2007; Dobrović *et al.* 2007). VUV process may lead to similar results as those with H₂O₂/UV process, which also relies on the formation and action of HO, and has already

found several commercial applications in water treatment. One potential advantage of the VUV process over the H₂O₂/UV treatment is that it does not require the addition of any chemical. This would make this process very appealing to applications where the shipment and/or storage of hydrogen peroxide is problematic.

The focus of this research was to study the VUV based photoinduced degradation of a model micro-pollutant, herbicide 2,4-Dichlorophenoxyacetic acid (2,4-D). The effect of the initial contaminant concentration, alkalinity, and water matrix on the effectiveness of the process was studied in an annular photoreactor operated in batch mode. Complementary experiments were also conducted in the same photoreactor, but operated in a continuous mode, to evaluate the potential use of this technology in commercial applications.

MATERIALS AND METHODS

Water samples preparation

Diluted solutions of 2,4-D were prepared with Millipore water (MW) and 2,4-D (Sigma-Aldrich, Canada). NaHCO_3 was used to increase the alkalinity in those tests investigating the effect of alkalinity. Raw surface water samples were collected in May 2009 from Trepanier Creek (TC) and Capilano Reservoir (CR), in British Columbia, Canada. The unfiltered samples were stored at 4°C prior to use. Some important characteristics of the raw waters used in this study are presented in Table 1.

Experimental setup and operating conditions

Experiments were conducted in a flow-through annular photoreactor, which was coupled with a peristaltic pump, a storage tank, and connecting tubing (Figure 1). The reactor was operated in batch mode with the full recycle of the solution (reactants). The volume of the photoreactor was 80 cm³. The radiation was provided by a low pressure VUV-Hg lamp (Light Sources Inc. G10T51-2-VH), which was placed axially at the centre of the reactor, in contact with water. This lamp emits radiation at 185 and 254 nm. Air was sparged in the storage tank to ensure constant concentration of dissolved oxygen in the reacting solution. A heat exchanger was used in the system to ensure that the temperature of the solution stayed constant at 25°C. For each experimental run, 2000 cm³ of water was treated in the photoreactor. A relatively high recycling flow rate was used (3000 cm³ min⁻¹; Reynolds number = 1800) to ensure kinetic control. This was necessary to avoid diffusional resistances that would be introduced due to the very high absorption coefficient of water at 185 nm, causing the VUV photons to reach and the reactions to occur at regions very close to the lamp (Heit & Braun 1997).

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 potassium iodide/potassium iodate actinometric technique (Rahn 1997). The net radiation flux of 254 nm radiation

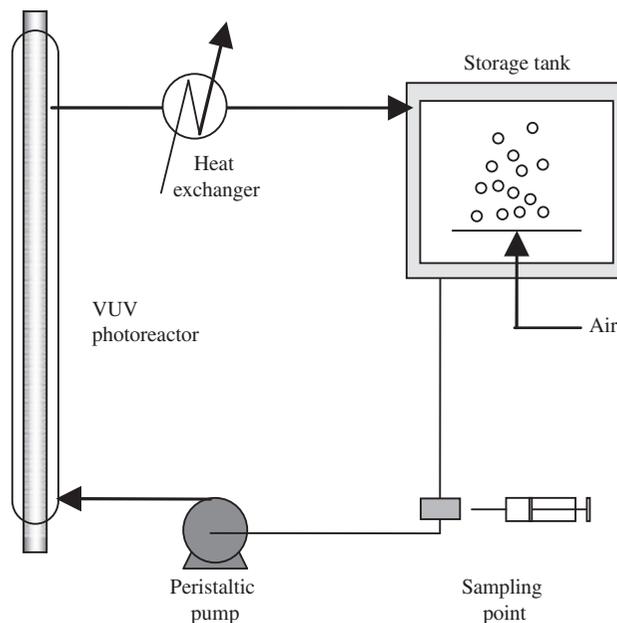


Figure 1 | Flow-through photoreactor operated in batch mode.

emitted by the VUV-Hg lamp operating at 25°C was 13.1 mW cm⁻². On the other hand, the 185 nm radiation flux emitted by the VUV-Hg lamp was determined using the cis-trans cyclooctene photoisomerisation actinometric technique (Schuchmann *et al.* 1981). The measured radiation flux at 185 nm was 1.79 mW cm⁻².

Additional experiments were carried out using a continuous setup (Figure 2). A stream of ultrapure water spiked to a given concentration of 2,4-D was fed continuously to the system, which was comprised of the flow-through annular photoreactor, a heat exchanger, a gas separator, and a recycling pump. The reactor was operated under steady state.

Analytical methods

The concentrations of 2,4-D and its oxidation by-products were quantified using a high-performance liquid chromatograph (Waters 2695 - HPLC) 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 done at $\lambda = 280$ nm via UV detection.

Table 1 | Properties of Capilano Reservoir (CR) and Trepanier Creek (TC) waters

	TOC (mg L ⁻¹)	Alkalinity (mg L ⁻¹)	pH	Abs ₂₅₄ (cm ⁻¹)	Abs ₁₈₅ (cm ⁻¹)
Capilano Reservoir water	1.81	no detected	6.3	0.065	2.13
Trepanier Creek water	5.66	55	7.4	0.17	3.20

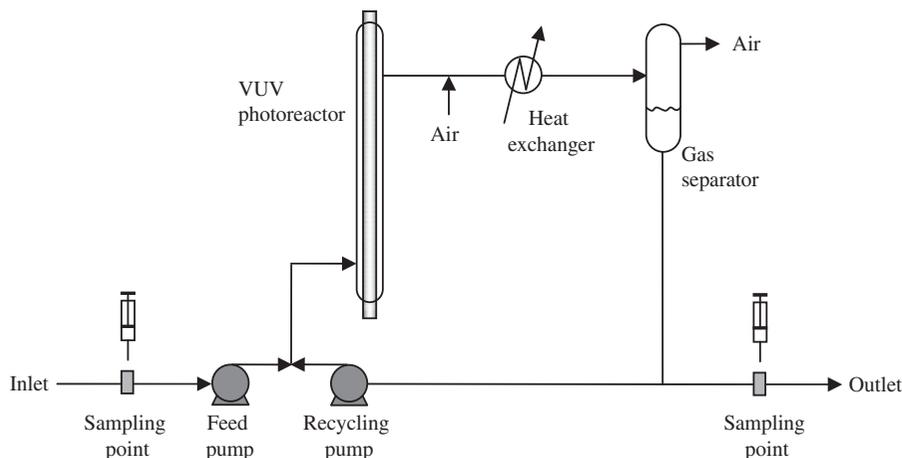
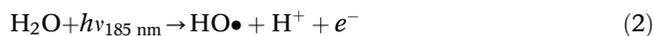


Figure 2 | Flow-through photoreactor operated with recycle in continuous mode.

Complete mineralization of 2,4-D was assessed by measuring total organic carbon (TOC) content of the solution using a TOC-VCPH Shimadzu analyzer. The 254 nm absorbance (Abs_{254}) was determined using a UV-vis spectrophotometer (Shimadzu 1240), whereas the 185 nm absorbance (Abs_{185}) was measured in 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 with a dissolved oxygen meter (YSI 52 meter, YSI 5909 probe) and H_2O_2 concentration was measured using the triiodide method (Klassen *et al.* 1994).

EXPERIMENTAL RESULTS

Two of the most important reactions taking place in VUV/water systems are the photochemical homolysis and photochemical ionization of water:



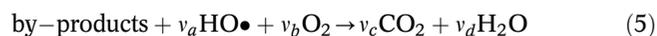
The quantum yields for the photochemical homolysis and ionization of water at 185 nm are 0.33 and 0.045, respectively (Gonzalez *et al.* 2004). The generated HO can subsequently react with 2,4-D:



In addition to the degradation of 2,4-D through the reaction with HO, the photolysis of 2,4-D by 185 nm radiation is also expected to take place:



The products of the partial oxidation or direct photolysis will go through further reactions, potentially leading to the complete mineralization:



where ν_x are the stoichiometric coefficients involved in the mineralization of by-products.

Radiation at 254 nm plays a minor role in the system since it cannot lead to the photolysis of water nor a significant degradation of 2,4-D (Kwan & Chu 2003).

Given the high absorption coefficient of water at 185 nm (1.80 cm^{-1}), VUV photons can only penetrate 3 mm in the aqueous phase; thus, only the region close to the lamp receives VUV radiation. Besides, taking into account the diffusion coefficient of HO (about $2.3 \times 10^{-5}\text{ cm}^2\text{ s}^{-1}$; Buxton *et al.* 1988) and its average life time in water (10^{-9} to 10^{-6} seconds; LaVerne 1989), hydroxyl radicals are expected to react close to the place where they are generated. Therefore, the degradation of the pollutants takes place in the VUV illuminated area of the photoreactor.

Effect of the initial concentration of 2,4-D

Experiments were conducted by treating 2 litres of ultrapure Millipore water (MW) spiked with different concentrations of 2,4-D. Figures 3 (a) and (b) show changes in the concentrations

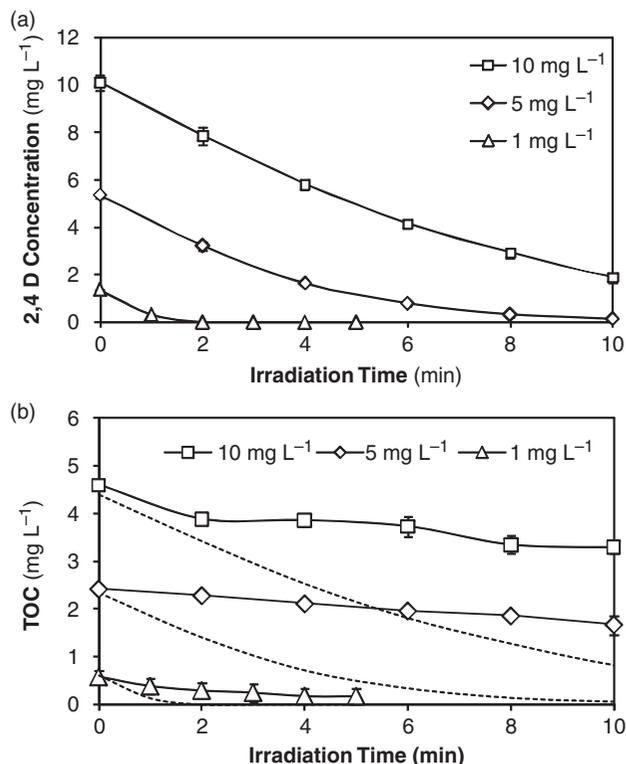


Figure 3 | Effect of the initial concentration: (a) 2,4 D concentrations against irradiation time and (b) TOC against irradiation time. Error bars represent the standard deviation of the results of two experiments and the dotted line represent the expected contribution of 2,4 D and 2,4 DCP to the TOC.

of 2,4-D and TOC over the course of treatment. When the initial concentration of 2,4-D was 1 mg L⁻¹, neither 2,4-D nor its known oxidation by-products were detected by HPLC after two minutes of irradiation. However, the TOC reduced by 66% over the same time, indicating that organic by-products were still present in the solution. After 5 minutes of irradiation, greater extent of mineralization was obtained since the TOC reduced by 84%. When the initial concentration of 2,4-D was 5 mg L⁻¹, 2,4-D and TOC concentrations

reduced by 98% and 31%, respectively, after 10 minutes of irradiation. An even smaller extent of degradation was observed for the initial concentration of 10 mg L⁻¹, since 2,4-D and TOC concentrations reduced by 81% and 28%, respectively, after 10 minutes of treatment. Control experiments were conducted using a UV-Hg lamp (Light Sources Inc. G10T5-1/2 L), which has the same emission power at 254 nm to that of the VUV-Hg lamp. No significant degradation of 2,4-D was observed, confirming that this compound cannot be efficiently eliminated by photolysis at 254 nm.

Figure 4 (a) shows the initial reaction rate of 2,4-D obtained for different concentrations. No significant changes were obtained for the initial 2,4-D concentrations of 1, 5, and 10 mg L⁻¹, suggesting an overall zero order kinetics. However, according to the intrinsic kinetics of the degradation of 2,4-D (reaction 3), this reaction should follow first order kinetics with respect to the concentrations of 2,4-D. This discrepancy is largely explained by the fact that the process is limited by the rate of HO formation and availability. Note that for the reaction (3) to occur, both 2,4-D and HO should be simultaneously available. Given that the expected concentration of HO is very low due to the very reactive nature of this radical, 2,4-D molecules will be in excess with respect to HO. Under such conditions, the degradation of 2,4-D would be limited by the availability of HO. At the same time, the rate of HO formation is limited by the rate of photon absorption at 185 nm, which itself depends on the emission power of the lamp, reactor geometry, and optical properties of the propagating medium. Further, the rate of HO formation does not depend on 2,4-D concentration which is relatively low and does affect the radiation distribution in the reactor. As a result, the rate of HO formation is expected to be independent of the 2,4-D concentration, giving an overall apparent zero order kinetics to the degradation of 2,4-D.

Figure 4 (b) shows the rate of 2,4-D degradation versus irradiation time. In all the cases, 2,4-D degradation rate

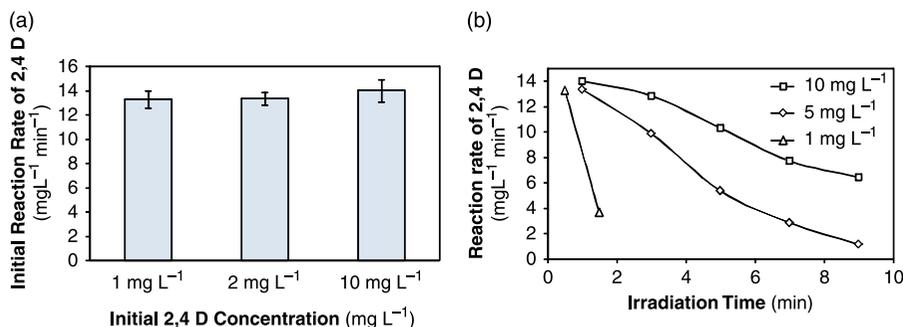


Figure 4 | (a) Initial reaction rate for different initial 2,4 D concentrations and (b) 2,4 D reaction rate for against irradiation time. Error bars represent the standard deviation of the results of two experiments.

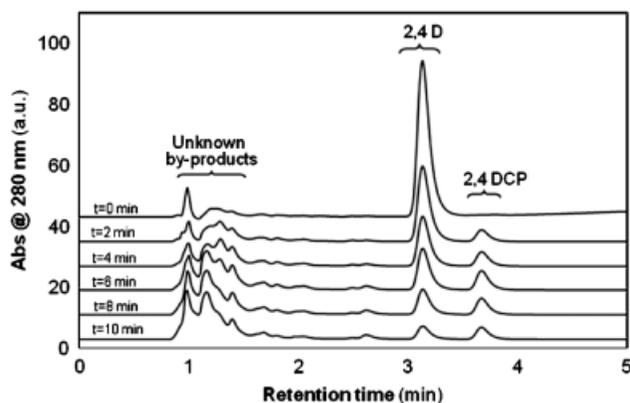


Figure 5 | Chromatograms showing the degradation of 2,4-D over time.

decreased with irradiation time. This reduction cannot be explained only by taking into account the reduction in the concentration of 2,4-D because, as already mentioned, the degradation rate of the contaminant was independent of concentration (Figure 4 (a)). It is postulated that formation of by-products plays an important role from the kinetics point of view. Figure 5 shows the chromatograms obtained. Only 2,4-DCP was identified being a by product of the degradation. According to Djebbar & Sehili (2008), 2,4-DCP was the main by-product in the photocatalytic (HO induced) degradation of the herbicide.

In Figures 3 (b), the difference between the TOC concentration (solid line) and the contribution of the 2,4-D and 2,4-DCP to the TOC (dashed line) represents unidentified organic by-products formed due to partial oxidation of 2,4-D. From these results, it is possible to note that the concentration of by-products increased over the course of treatment. The gradual increases in by-product concentration may be responsible for the observed reduction in the degradation rate of 2,4-D (shown in Figures 3 (b)). It is speculated that these by-products react with HO (reaction 5), acting as scavengers, thereby reducing the overall degradation rate of 2,4-D.

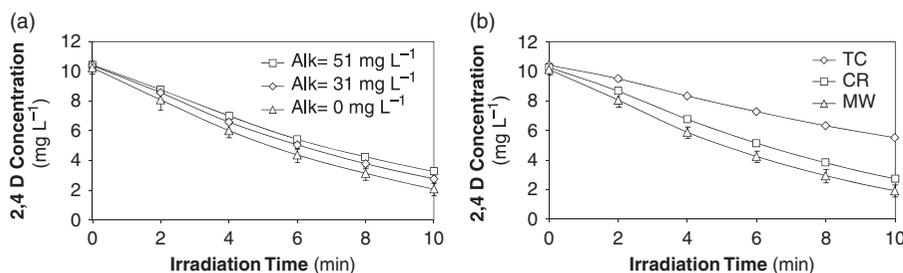


Figure 6 | (a) Effect of the alkalinity. (b) Effect of the water matrix: 10 mg L⁻¹ of 2,4 D in Trepanier Creek water (TC), Capilano Reservoir water (CR), and ultrapure water (MW). Error bars represent the standard deviation of the results of two experiments.

Effect of the alkalinity

Samples of ultrapure water with 10 mg L⁻¹ of 2,4-D were supplemented with different concentrations of NaHCO₃ to increase the alkalinity of water. Increasing the alkalinity led to the reduced degradation rate of 2,4-D (Figure 6 (a)) by up to about 23%. This reduced rate was clearly due to the fact that carbonates and bicarbonates can react with HO, reducing the concentration of HO available to react with 2,4-D (Gultekin & Ince 2004; Wu *et al.* 2007):



Effect of water matrix

The effect of water matrix and source was investigated by testing two raw surface waters (TC and CR) with 10 mg L⁻¹ of 2,4-D in the batch system (Figure 1), and by comparing the results with those in ultrapure water. Experimental results in Figure 6 (b) show that the effectiveness of VUV for the degradation of 2,4-D decreased significantly when TC water was used. The contaminant degradation rate in TC decreased by 72% when compared with that in MW water. A high scavenging effect was expected for this water due to the relatively high natural organic matter (NOM) content and high alkalinity (Table 1). In addition, Abs₁₈₅ for the TC water was high, resulting in a very poor propagation of 185 nm radiation in the reactor. The high Abs₁₈₅ was associated with the presence of VUV absorbing inorganic species/ions in natural waters. On the other hand, as shown in Figure 6 (b), the degradation rate of 2,4-D in CR water only decreased by about 22% when compared to that in ultrapure water, indicating a smaller reduction in the VUV effectiveness. This demonstrates that CR water with its low background TOC

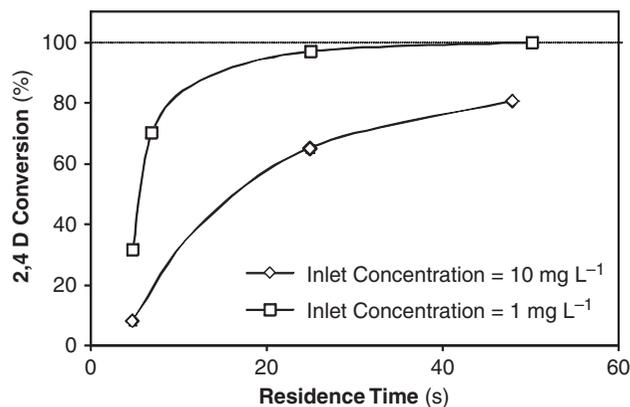


Figure 7 | Degradation of 2,4 D in the continuous VUV system. The standard deviation of three replicated measurements was lower than 3%.

(i.e., NOM content) and nearly negligible alkalinity (see Table 1) would be a suitable candidate for treatment with VUV.

Continuous experiments

The flow-through photoreactor was also used in continuous mode, as shown in Figure 2. Water samples were recycled to minimize diffusional resistances. The system was operated for 20 minutes prior to sampling to ensure that steady state operation was reached. For these experiments, ultrapure water with 1 or 10 mg L⁻¹ of 2,4-D was used. Figure 7 shows the conversions of 2,4-D obtained at different inlet flow rates. When the system was operated at residence time of 25 seconds, 97% and 65% conversions were obtained for the inlet herbicide concentrations of 1 and 10 mg L⁻¹, respectively. Regardless of the residence time, higher conversions of 2,4-D were obtained with inlet concentration of 1 mg L⁻¹. This result is in agreement with the apparent zero order reaction rate obtained from batch experiments since, for the reaction rate being independent of the herbicide concentration, higher conversions are expected with lower initial concentrations of 2,4-D.

To analyze the energetic requirements of the system, the received dose was calculated as the product between the radiation flux at 185 nm and the hydraulic residence time:

$$\text{Dose}_{185\text{nm}} = \text{Radiation Flux}_{185\text{nm}} \times \text{HRT} \quad (8)$$

As mentioned in the experimental section, the radiation flux emitted by the VUV lamp was determined by actinometry. Radiation at 254 nm was not considered for the calculation of the dose, since it does not play an important role in this system. The received dose at 185 nm for a residence time of 25 seconds

was 44.8 mJ cm⁻². Typical UV doses at 254 nm for the H₂O₂/UV process are in the range of 1000 to 2000 mJ cm⁻² (Kim *et al.* 2009). Using this relatively low dose, it was possible to degrade completely all 1 mg L⁻¹ of 2,4-D or degrade 65% of the 10 mg L⁻¹ of 2,4-D in ultrapure water, making this process attractive from the economic point of view.

CONCLUSIONS

VUV radiation (185 nm) showed to be highly effective at degrading herbicide 2,4-D. This was largely due to the action of 185 nm photons, photolyzing water molecules to generate hydroxyl radicals (HO). Experimental results obtained in a batch flow-through reactor indicated that the initial degradation rate of 2,4-D in ultrapure water was independent of the initial concentration of the contaminant. However, by-products generated during the partial oxidation of 2,4-D competed with 2,4-D molecules for HO, and caused a reduction in the degradation rate over the course of the treatment. Batch experiments also showed that the presence of alkalinity reduced the effectiveness of the degradation process. Similarly, 2,4-D degradation rate decreased significantly when raw surface water was used. This effect was particularly important for raw water with relatively high TOC (5.66 mg L⁻¹) and high alkalinity (55 mg L⁻¹). High 2,4-D conversions were obtained in experiments involving continuous operation of the reactor under steady state regime. Conversion rates of 97% and 65% were obtained for the inlet concentrations of 1 and 10 mg L⁻¹, respectively, when the residence time was 25 seconds, and the 185 nm dose was 44.8 mJ cm⁻².

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