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# Pilot-scale treatment of 1,4-dioxane contaminated waters using 185 nm radiation: Experimental and CFD modeling

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## ABSTRACT

This work investigates the feasibility of a 185 nm advanced oxidation process (AOP) for the degradation of 1,4-dioxane from contaminated waters using a pilot-scale system operating at 6–30 L/min. Using synthetic and natural water samples with less than 20 L/min, the 185 nm pilot system was able to reduce 1,4-dioxane concentration from 100 ppb to below the WHO guideline limit (i.e., 50 ppb) with no need for an exogenous chemical oxidant/catalyst. The electrical energy-per-order (EEO) analysis of the system demonstrated the cost-effectiveness of the process for 1,4-dioxane removal with EEO values close to 0.8 kWh/m$^3$/order. Further, 1,4-dioxane degradation rate decreased by 3%-13%, depending on the flow rate, when the raw water was spiked by a second micropollutant, atrazine, which competes for hydroxyl radicals. To provide an in-depth understanding of 1,4-dioxane removal, a mechanistic computational fluid dynamic (CFD) model was developed and validated experimentally. Sensitivity analysis of the operational variables underlined the significance of flow characteristics within the photoreactors as well as the natural organic matter (NOM) concentration of the water as the key factors controlling the degradation of 1,4-dioxane. The proposed model predicted the impact of the flow rates, $\cdot$OH scavenging of atrazine and water matrix (NOM and alkalinity) on 1,4-dioxane degradation with less than 2% average absolute deviation, demonstrating its potential as a viable tool for the design, optimization, and scale-up of 185 nm AOP systems.

## 1. Introduction

The polar cyclic diether 1,4-dioxane is a widely used solvent in a wide range of industrial organic products (e.g., fabric cleaners, paper, electronics and pharmaceuticals, paints, varnishes, inks and dyes). It is a known carcinogen to animals and a suspected carcinogen to humans and is thus classified as a priority pollutant [1,2]. Owing to 1,4-dioxane's very high hydrophilicity and water solubility along with low vapor pressure, it does not interact with soil particles and easily evaporate, and therefore it permeates surface and groundwater sources. In addition, conventional treatment processes are limited in their effectiveness for the treatment of 1,4-dioxane-contaminated water [1]. Numerous studies have confirmed the presence of 1,4-dioxane in landfill leachate [3], effluents from domestic and industrial sewage plants [4,5], surface water and groundwater [6,7] and even drinking water [1,7].

The World Health Organization (WHO) has established guideline values for various chemical contaminants in drinking water with a recommended value for 1,4-dioxane of less than 50 µg/L. The USEPA National Center for Environmental Assessment proposed a health-based advisory level of 3 µg/L in tap water [8]. Meanwhile, it is difficult to remove it from drinking water supplies using conventional treatment technologies consisting of coagulation, sedimentation and sand filtration [9,10]. Adsorption on activated carbon is also not effective because of the hydrophilic nature of this compound [10]. Further, 1,4-dioxane is not biodegradable because of its heterocyclic structure [1], rendering conventional bio-treatment technologies as ineffective/limited in their application for the degradation of 1,4-dioxane [10,11]. In recent years, ultraviolet (UV) based advanced oxidation processes (AOPs) and in particular, $H_2O_2$/UV AOP, have demonstrated to be very promising and applied at large-scale treatment facilities [12,13].

Despite its wide applications, the $H_2O_2$/UV process is very costly because of the high price of hydrogen peroxide and its transportation and storage requirements [14]. Additionally, the need for regular monitoring and post treatment of the surplus peroxide imposes further costs and complexity to the $H_2O_2$/UV process making it onerous for applications in small to medium-sized water treatment facilities with stringent operational and financial constraints [15]. An alternative and effective UV-based AOP is vacuum-UV (VUV) with 185 nm irradiation that eliminates the demanding need for an auxiliary chemical oxidant,

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e.g., hydrogen peroxide. This can result in a more environmentally friendly and operationally simpler process with potentially greater economic benefits. The effectiveness of the 185 nm VUV irradiation for the decomposition of a wide range of micropollutants under small batch-recirculating reactors has been studied extensively [16–20]. However, their large scale implementation has been stymied, in part, by a lack of pilot scale studies demonstrating the practicality and feasibility of the 185 nm AOP systems under continuous-flow degradation of refractory pollutants in real water. To the best of our knowledge, this is the first study that investigates the practicality of 185 nm AOP for degradation of 1,4-dioxane under continuous-flow operation.

The primary objective of this work was to study the feasibility of 185 nm VUV-based AOP for the degradation of 1,4-dioxane in synthetic and natural water samples using a continuously operating pilot-scale system. A descriptive computational fluid dynamics (CFD) model was developed and experimentally validated to gain a better understanding of the 1,4-dioxane removal in the photoreactors. A sensitivity analysis allowed for the study of the operational parameters variations such as flow rate and main water matrix constitutes (e.g., natural organic matter and alkalinity).

## 2. Materials and methods

### 2.1. Experimental design and procedures

Experiments were conducted in a pilot-scale VUV/UV system comprised of two photoreactors installed in series (Fig. 1). The reactors were made of stainless-steel, with an annular configuration, an equipped with a 145 W low-pressure mercury amalgam ozone-generating lamp (Strahler NAQ 170/90 XL, Heraeus Noblelight GmbH) with a 19 mm diameter and illuminated length of 800 mm. The internal and external diameters of the annular photoreactor and synthetic quartz sleeve (Heraeus Quartz America LLC, SUPRASIL310) were 5.5 cm and 2.8 cm, respectively, yielding a radial gap of 1.35 cm, corresponding to a hydraulic diameter of 2.7 cm for treating the water. Each reactor included two perforated baffles, with the first one placed within 5 cm from the inlet cone and the next one at 50 cm from the first baffle.

**Table 1**
Natural water properties (Capilano Reservoir, BC).

| Properties | Values |
|---|---|
| $DOC_0$ [mg/L] | 1.8 |
| UV $_{254,0}$ [$cm^{-1}$] | 0.066 |
| $SUVA_0$ | 3.6 |
| $pH_0$ | 6.5 |
| Conductivity [μS/cm] | 11 |
| Chloride [mg/L] | 0.6 |
| Alkalinity [mg/L $CaCO_3$] | 2.6 |

Besides, it should be noted that a 4-μm filtration unit was utilized to limit the interference of large particles (e.g., in the natural water samples) from entering the VUV pilot system.

Fig. 1 Natural water samples were collected from Capilano Reservoir (CR), in British Columbia, Canada. The unfiltered samples were stored at 4°C and spiked with 100 ppb 1,4-dioxane prior to use. The main properties and characteristics of the natural water used in this study are presented in Table 1. Synthetic waters were prepared using distilled water (DW) supplemented with isolated NOM from Suwannee River (1R101N), purchased from the International Humic Substances Society. The synthetic water samples were buffered at pH 7 using a mixture of monosodium phosphate and disodium phosphate. The synthetic water samples were purged with pure oxygen to ensure an oxygen content close to saturation level at 20 ( ± 1) °C.

### 2.2. Analytical methods

The concentration of 1,4-dioxane was analyzed with a gas chromatograph equipped with a mass spectrometer (GC/MS, Saturn 2200, Varian). The instrument was also equipped with a CombiPal autosampler. Atrazine concentration was quantified by high-performance liquid chromatography (Dionex UltiMate™ 3000, US) with the detection wavelength set at 222 nm. Using a TOC Analyzer (Shimadzu TOC-VCPH), concentrations of NOM and its oxidation by-products were quantified by dissolved organic matter (DOC) as $mg_{carbon}$ per L. The concentration of hydrogen peroxide was determined via UV

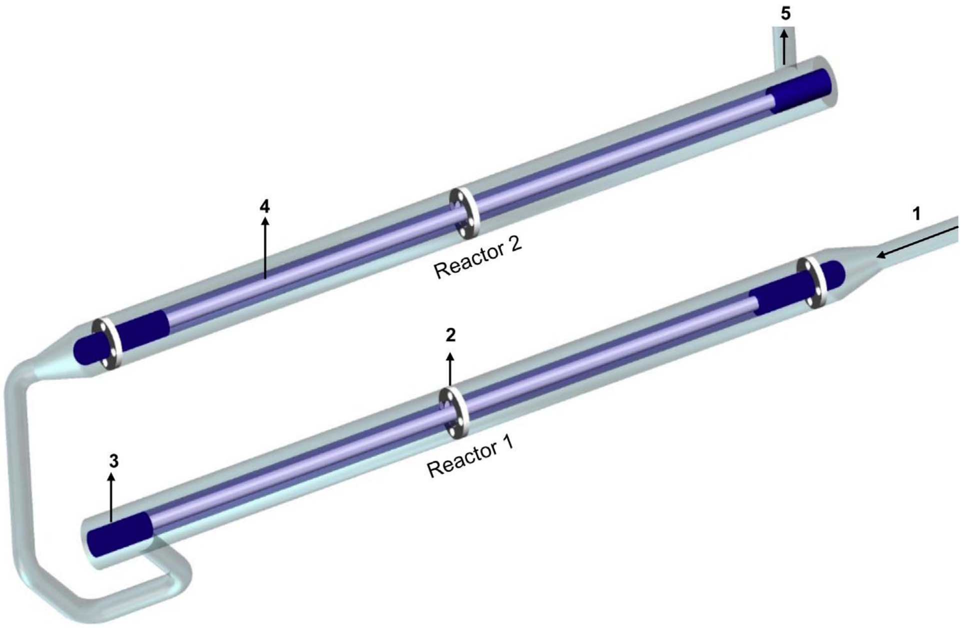

**Fig. 1.** Schematic of utilized 185 nm pilot set-up for experiments.

1. Contaminated water
2. Perforated baffle
3. Quartz sleeve (Suprasil 310)
4. Ozone-generating low pressure mercury amalgam lamp (185 nm + 254 nm)
5. Treated effluent