



# Removal of 1,4-dioxane from industrial wastewaters: Routes of decomposition under different operational conditions to determine the ozone oxidation capacity



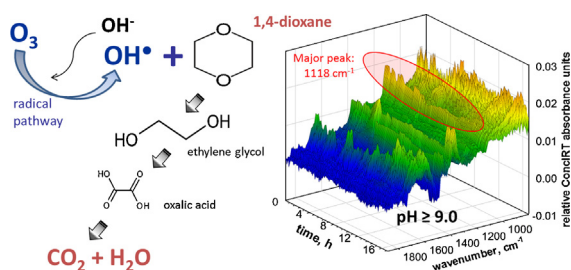
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## HIGHLIGHTS

- Wastewaters containing 1,4-dioxane were successfully degraded by ozone.
- Ozonation alone has been formerly considered insufficient for such effluents.
- The key for the 1,4-dioxane removal by ozone was to maintain the pH above 9.
- FTIR spectroscopy was applied as a powerful tool to monitor the intermediate species.
- Decomposition of 1,4-dioxane was shown to follow different routes at different pH.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 27 March 2014

Received in revised form 19 July 2014

Accepted 28 July 2014

Available online 14 August 2014

### Keywords:

Ozone  
1,4-Dioxane  
Chemical industry  
Wastewater treatment  
FTIR spectroscopy

## ABSTRACT

This paper denotes the importance of operational parameters for the feasibility of ozone ( $O_3$ ) oxidation for the treatment of wastewaters containing 1,4-dioxane. Results show that  $O_3$  process, which has formerly been considered insufficient as a sole treatment for such wastewaters, could be a viable treatment for the degradation of 1,4-dioxane at the adequate operation conditions. The treatment of both synthetic solution of 1,4-dioxane and industrial wastewaters, containing 1,4-dioxane and 2-methyl-1,3-dioxolane (MDO), showed that about 90% of chemical oxygen demand can be removed and almost a total removal of 1,4-dioxane and MDO is reached by  $O_3$  at optimal process conditions. Data from on-line Fourier transform infrared spectroscopy provides a good insight to its different decomposition routes that eventually determine the viability of degrading this toxic and hazardous compound from industrial waters. The degradation at  $pH > 9$  occurs faster through the formation of ethylene glycol as a primary intermediate; whereas the decomposition in acidic conditions ( $pH < 5.7$ ) consists in the formation and slower degradation of ethylene glycol diformate.

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## 1. Introduction

1,4-Dioxane is widely used in industry as a solvent in the production processes of various pharmaceuticals, pesticides, magnetic tapes, paper, cotton, textile, adhesives, cosmetics, dyes, oils, waxes, resins, cellulosic esters and ethers. It is also a common by-product of chemical processes, like those involving ethylene glycol (EG).

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Nowadays, the environmental interest of 1,4-dioxane is growing since it is listed as a priority pollutant, and a hazardous waste for humans and environment, classified as a probable human (B2) carcinogen [1–3].

1,4-Dioxane was considered non-biodegradable by microorganisms [3–5], although some recent investigations have shown its biodegradation under certain conditions; Han et al. [6] obtained appreciable eliminations of 1,4-dioxane at low initial concentrations, using an up-flow biological aerated filter; Shin et al. [7] reported that the biodegradation of 1,4-dioxane by different bacteria depends strongly on the community structure and the presence of an extra carbon source. Adsorption on activated carbon and air-stripping cannot remove 1,4-dioxane from water due to its high solubility and low vapor pressure. Distillation can be employed, but it is expensive due to its boiling point of 101 °C. Traditional oxidation methods are not effective eliminating this contaminant from water, as the oxidation of 1,4-dioxane using chlorine produces other compounds more toxic than 1,4-dioxane [3,4,8].

Many researchers have studied the application of advanced oxidation processes (AOPs) in the treatment of refractory organic pollutants in water [9–12]. AOPs involve the generation of hydroxyl radicals (OH•) with very high oxidation capacity, capable of mineralizing different organic pollutants into carbon dioxide [13,14]. Among the different AOPs, ozone (O<sub>3</sub>) is particularly promising for treating recalcitrant materials at industrial scale, firstly, due to its capability to produce high levels of OH• without producing residues and, secondly, because of the possibility of treating large water flows at full scale [15–19]. O<sub>3</sub> process presents important pollutant removal efficiencies when applied to several toxic non-biodegradable compounds [20–23].

Ozonation may be produced directly by O<sub>3</sub> or indirectly by OH•, produced through the O<sub>3</sub> decomposition [24,25], whereas OH• is a much stronger and less selective oxidant than O<sub>3</sub> [26,27]. Furthermore, the O<sub>3</sub> does not react strongly with the 1,4-dioxane molecule and the removal is mainly produced by OH• radicals [19]. Thus, it is possible to increase its degradation, working with a higher pH at which OH• radicals are more effectively formed [14,24,28]. Combination of O<sub>3</sub> with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is also known to accelerate the process [19]; however, the required H<sub>2</sub>O<sub>2</sub> can be costly for high organic loads, and in industrial scale facilities the use of O<sub>3</sub> alone is usually preferred [15].

Few studies deal with the degradation of 1,4-dioxane by O<sub>3</sub>, while most of the reports focus on the H<sub>2</sub>O<sub>2</sub> assisted ozonation [8,19,25,29]; and there is even less literature on the treatment of industrial effluents, as most studies report the removal of low-concentration of 1,4-dioxane from synthetic solutions. The use of O<sub>3</sub> as a sole oxidant to remove the 1,4-dioxane has been discarded by several authors due to the low elimination reached at chosen process conditions [8,19,30]. However, ozonation of organics is strongly affected by process pH, depending on the compounds dissociation as well as on the dominant oxidation mechanism (OH• vs. O<sub>3</sub> production) [14,24,28]. As high initial pH was reported beneficial in the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> oxidation of 1,4-dioxane [25], it is of great interest to study the possible improvement of the O<sub>3</sub> process when adequate pH conditions are maintained throughout the experiment. No reports have been published on the decomposition pathways of 1,4-dioxane by classical ozonation process, although the understanding of the degradation mechanism could play a great role in the process optimization. So far, the intermediates and by-products of 1,4-dioxane degradation have been studied based on chromatography analyses for UV-based AOPs [31,32].

Fourier transform infrared (FTIR) spectroscopy is an alternative method to analyze different molecule groups and structures [33,34]. Recently, Merayo et al. [35] demonstrated the advantages of on-line FTIR spectroscopy to monitor the evolution of reaction intermediates during the Fenton oxidation of aqueous 1,4-dioxane,

showing that a good calibration could provide valuable information *in situ*, avoiding expensive and time-consuming sample preparation and analyses. For ozonation process, this on-line method presents an appealing opportunity to track the different reaction pathways under varying process conditions, as different degradation by-products of 1,4-dioxane could be expected to dominate depending on the reaction pH [31].

Therefore, the objective of this paper was to study the feasibility of O<sub>3</sub> oxidation of 1,4-dioxane and, consequently, to treat real industrial wastewaters at optimal conditions. FTIR spectroscopy was applied as a powerful tool to monitor the intermediate species generated during the decomposition of 1,4-dioxane for the better understanding of the degradation mechanisms under different operational conditions.

## 2. Materials and methods

### 2.1. Reagents

1,4-Dioxane (99.99%) was supplied by Sigma–Aldrich Chemie® GmbH, Steinheim, Germany). H<sub>2</sub>O<sub>2</sub> (30%, v/v), NaOH (98.0%) and NaHCO<sub>3</sub> (99%) were purchased from PANREAC S.A. (Barcelona, Spain).

### 2.2. Experimental procedure

Ozonation was conducted at 25 °C in a jacketed cylindrical bubble reactor (height = 1 m, diameter = 5 cm) with a continuous feed of O<sub>3</sub>-riched gas (4.0 L min<sup>-1</sup>). The system consisted of an O<sub>3</sub> generator (Model 6020, Rilize, Gijón, Spain), a flow controller Bronkhorst® (Model F-201AV, Ruurlo, The Netherlands), and two on-line O<sub>3</sub> analyzers (Model 964C, BMT Messtechnik GMBH, Berlin, Germany). During the operation, 1000 mL of sample was recirculated in the reactor column, whereas O<sub>3</sub>-gas was introduced continuously into the solution through a sparger from the bottom of the column (Fig. 1).

The optimization experiments were carried out on a synthetic solution of 1,4-dioxane (247.8 mg L<sup>-1</sup>; 450 mg L<sup>-1</sup> COD<sub>0</sub>), prepared by diluting with ultra-pure deionized water after pH adjustment

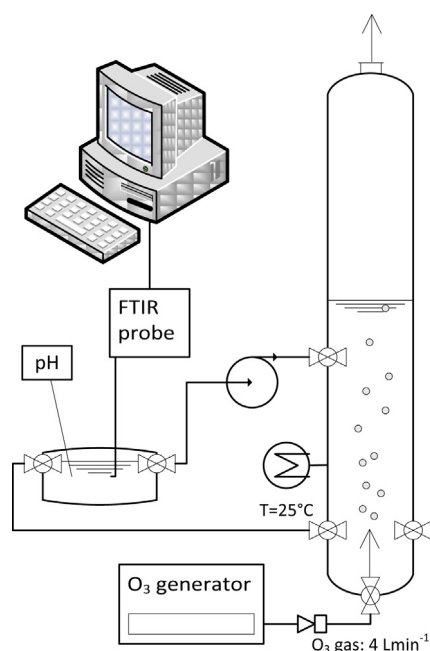


Fig. 1. Schematic of experimental setup.

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