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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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.

Keywords: Ozone; 1,4-dioxane; chemical industry; wastewater treatment; FTIR spectroscopy

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). 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 vapour pressure. Distillation can be employed, but it is expensive due to its boiling point of 101 ºC. 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_3) 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_3 process presents important pollutant removal efficiencies when applied to several toxic non-biodegradable compounds [20-23].

Ozonation may be produced directly by O_3 or indirectly by OH•, produced through the O_3 decomposition [24, 25], whereas OH• is a much stronger and less selective oxidant than O_3 [26, 27]. Furthermore, the O_3 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_3 with hydrogen peroxide (H_2O_2) is also known to accelerate the process [19]; however, the required H_2O_2 can be costly for high organic loads, and in industrial scale facilities the use of O_3 alone is usually preferred [15].

Few studies deal with the degradation of 1,4-dioxane by O_3, while most of the reports focus on the H_2O_2 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_3 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_3 production) [14, 24, 28]. As high initial pH was reported beneficial in the O_3/H_2O_2 oxidation of 1,4-dioxane [25], it is of great interest to study the possible improvement of the O_3 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_3 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_2O_2 (30% v/v), NaOH (98.0%) and $NaHCO_3$ (99%) were purchased from PANREAC S.A. (Barcelona, Spain).

2.2. Experimental procedure

Ozonation was conducted at 25 ºC in a jacketed cylindrical bubble reactor (height=1 m, diameter=5 cm) with a continuous feed of O_3-riched gas (4.0 $Lmin^{-1}$). The system consisted of an O_3 generator (Model 6020, Rilize, Gijon, Spain), a flow controller Bronkhorst® (Model F-201AV, Ruurlo, The Netherlands), and two on-line O_3 analyzers (Model 964C, BMT Messtechnik GMBH, Berlin, Germany). During the operation, 1000 mL of sample was recirculated in the reactor column, whereas O_3-gas was introduced continuously into the solution through a sparger from the bottom of the column (Figure 1).

The optimization experiments were carried out on a synthetic solution of 1,4-dioxane (247.8 mgL^{-1}; 450 mgL^{-1} COD_0), prepared by diluting with ultra-pure deionized water after pH adjustment to a desired value [31, 36]. The pH was controlled throughout the experiment by adding NaOH when needed to keep it at the set value, except the experiments with the single addition of $NaHCO_3$ buffer (11.9 mM) that caused the pH to increase from 9.0±0.1 to 10.0±0.1 during the experimental run. Additional experiments were carried out adding H_2O_2 at the stoichiometric ratio proposed by Kim et al. [37] (1gL^{-1} chemical oxygen demand (COD) = 2.125gL^{-1} H_2O_2). Optimal conditions were applied to treat three actual industrial wastewaters (Samples 1-3, Table 1) that were still contaminated with 1,4-dioxane and 2-methyl-1,3-dioxolane (MDO) after a biological treatment step of a particular factory. All experiments were carried out in triplicates.

In the experiments with FTIR monitoring, synthetic solution with a substantially higher initial 1,4-dioxane concentration of 6168 mgL^{-1} was used, according to Merayo et al. [35]. Instead of using NaOH, the basic conditions with the pH above 9 were maintained by a one-time addition of 23.8 mM of $NaHCO_3$ as a buffer to ensure a constant background for the FTIR measurements. In the experiment where the pH was not controlled it dropped from the initial value of 5.7±0.1 to 3.1±0.1.

2.3. Analytical methods

pH was measured on-line with a pH electrode (720 A+, Thermos Scientific, Waltham, USA). Conductivity was measured with a non ionic-selective conductivity probe (Crison, GLP 31/32, Barcelona, Spain). COD was measured, according to the Standard Methods for the Examination of Water and Wastewater [38], by the colorimetric method at 600 nm. H_2O_2 content was analyzed using the titanium sulphate spectrophotometric method [39]. Colorimetric measurements were made on an Aquamate-spectrophotometer (Thermos Scientific AQA 091801, Waltham, USA).

1,4-dioxane, MDO and EG were identified and quantified by gas−liquid chromatography (GLC) on a 7980A instrument (Agilent Technologies Inc., Palo Alto (CA), USA) equipped with a flame ionization detector. Injector and detector were respectively set up at 310 and 280°C. Samples (2 μL) were injected using the *pulsed-split* mode (*split* ratio 5:1) and analyzed in a TRB-FFAP (Teknokroma, Sant Cugat del Vallès (Barcelona), Spain) fused silica column (30 m x 0.25 mm internal diameter x 0.25 μm film thickness), with He (43 psi) as carrier gas and a temperature programme (80°C to 240°C, 9 min initial hold, 15°C min^{-1} ramp rate). Peaks were identified on the basis of sample coincidence with relative retention times of commercial standards. Quantification was performed according to peak area, corrected with the response factors calculated for each compound using 1-butanol (250 ppm) as the internal standard and the software *GC-ChemStation Rev.B.04.02 (96)* from Agilent.

Oxalic, acetic, glycolic, glyoxylic and methoxyacetic acids were identified and quantified by ion chromatography (IC) using a Dionex DX-500 instrument (Thermo Scientific, Sunnyvale, CA) equipped with a conductivity detector. A gradient of NaOH from 40 mM to 60 mM was used as eluent for the measurements keeping an eluent flow of 1.5 Lmin^{-1}. The injection loop was 75 μL. They were analysed in an AS11HC Ion Pac ionic resin column with a previous Anion Trap Column ATC3 and guard column AG11-HC.

In the waters with high bicarbonate content interfering the analysis by ion chromatography, carboxylic acids were complementary measured by High Pressure Liquid Chromatography (Model L920, Varian, CA, USA) with diode array (PDA) detection. Acetonitrile - water (50%:50%) was used as eluent. Sample injections of 20 µL were separated on a C-18 column (Vidac 250 mm x 4.6 mm ID x 5µm) at 30ºC. The target compounds, acetic acid and oxalic acid, were measured at 200 nm.

2.4. On-line FTIR analysis

FTIR spectrometer ReactIR iC10 (Mettler-Toledo, Columbia, USA) was used to monitor the ozonation reaction *in situ*. Detailed description of the equipment and the data adquisition is published elsewhere [35]. Real-time component analyses were run using ConcIRT software (Mettler-Toledo, Columbia, USA), which calculates the associated component spectra, and relative concentration profiles.

2.5. Oxygen-equivalent Chemical-oxidation Capacity

The Oxygen-equivalent Chemical-oxidant Capacity (OCC) parameter, proposed by Cañizares et al. [40] to quantify in arbitrary units the oxidants consumed was used to compare the performance of different AOPs. This parameter is related to the O_3 and H_2O_2 consumption, according to Equations 1 and 2.

$$1\left(\frac{\mathrm{kgO_2}}{\mathrm{m^3}}\right)=[\mathrm{O_3}]\left(\frac{\mathrm{kgO_3}}{\mathrm{m^3}}\right)\cdot\frac{\mathrm{1kmolO_3}}{\mathrm{48kgO_3}}\cdot\frac{\mathrm{6kmol^-}}{\mathrm{1kmolO_3}}\cdot\frac{\mathrm{1kmolO_2}}{\mathrm{4kmol^-}}\cdot\frac{\mathrm{32kgO_2}}{\mathrm{1kmolO_2}}=1.000\cdot[\mathrm{O_3}]\left(\frac{\mathrm{kgO_3}}{\mathrm{m^3}}\right),\tag{1}$$

$$1\left(\frac{\mathrm{kgO_2}}{\mathrm{m^3}}\right)=[\mathrm{H_2O_2}]\left(\frac{\mathrm{kgH_2O_2}}{\mathrm{m^3}}\right)\cdot\frac{\mathrm{1kmolH_2O_2}}{\mathrm{34kgH_2O_2}}\cdot\frac{\mathrm{2kmol^-}}{\mathrm{1kmolH_2O_2}}\cdot\frac{\mathrm{1kmolO_2}}{\mathrm{4kmol^-}}\cdot\frac{\mathrm{32kgO_2}}{\mathrm{1kmolO_2}}=0.471\cdot[\mathrm{H_2O_2}]\left(\frac{\mathrm{kgH_2O_2}}{\mathrm{m^3}}\right),\tag{2}$$

2.6. Statistical analysis

One-way ANOVA was run (SigmaPlot 11, SPSS Inc.) to determine the significant level of differences among experimental runs. *Post hoc* all pairwise comparisons were performed using Tukey's test (P<0.05).

3. **Results and Discussion**

3.1. Ozonation treatment

3.1.1. Influence of pH

The optimization experiments carried out on synthetic 1,4-dioxane solution showed that an important turning point for the ozonation treatment of such wastewaters (COD removal >80 %) exists at pH ≈ 9 (Figure 2A). At pH 10.0±0.1, a COD removal close to 90% (P<0.050) was reached, while at pH below 9, the COD removal decreased considerably: 60% of COD was degraded at pH of 8.5±0.1, and only a 20% removal was achieved at pH=7.0±0.1. This phenomenon shows that the OH• produced in ozonation at high pH [14, 28, 41-44] is a dominant oxidant for 1,4-dioxane and its decomposition intermediates, and that the reaction by molecular O_3 at lower pH conditions has a very low efficiency in the treatment of this particular compound.

In terms of OCC (1 OCC is equivalent to $1 gL^{-1}$ of O_3, in this case), the most efficient COD removal was achieved at pH 10.0±0.1, in this case a significant 82% (P<0.050) of COD removal was obtained at 1 OCC consumed, while the further COD removal was negligible, only 6% more of the total COD was removed consuming an extra 1 gL^{-1} of O_3 (OCC = 2). Working at pH 9.0±0.1, the COD removal achieved was close to 80%, but the reaction was slower, 1.5 OCC was necessary to reach the same degradation as at pH 10.0±0.1 (Figure 2A).

The chromatographic analyses showed that 1,4-dioxane was completely removed from the water at $pH \geq 9.0$ (Figure 2B). The removal of the compound was similar ($P<0.050$) when working at pH 9.0±0.1 and 10.0±0.1; most of 1,4-dioxane was degraded with 1.25 OCC. On the contrary, in the experiments ran at pH 7.0±0.1, the 1,4-dioxane reduction was very low (<15%), in accordance with the COD removal rates. This explains why the use of O_3 as the only oxidant was ruled out for the treatment of 1,4-dioxane when the experiments were conducted in a solution of distilled water at unmodified pH below 7 [8, 19, 30]. The lower pH does not favor the decomposition of O_3 to $OH\bullet$ [14, 24, 28] that has a much greater reactivity with 1,4-dioxane than O_3 [19]. Without the presence of H_2O_2, this chain mechanism of $OH\bullet$ production is initiated by hydroxide anions at higher pH values (Equations 3 and 4) [14, 45, 46], whereat the reactions proceeds over the conversion of $O_3\bullet^-$ into $OH\bullet$ (Equations 5 and 6) [47, 48].

$$O_3 + OH^- \rightarrow O_2\bullet^- + HO_2\bullet \quad (3)$$

$$O_3 + O_2\bullet^- \rightarrow O_3\bullet^- + O_2 \quad (4)$$

$$O_3\bullet^- \rightleftharpoons O\bullet^- + O_2 \quad (5)$$

$$O\bullet^- + H_2O \rightleftharpoons OH\bullet + OH^- \quad (6)$$

For a better comparison of the drastic difference in 1,4-dioxane removal by ozonation at different pH values, the reaction kinetics are presented in Table 2. Since surplus O_3 was continuously fed into the reactor, simplified approach was taken and the oxidant species were considered to be in excess [49]. Thus, the degradation of 1,4-dioxane was considered to follow the pseudo first-order kinetics that depend on the decreasing concentration of the solute [19, 26, 49-51]. The 1,4-dioxane degradation reaction was significantly faster when the process was conducted at $pH \geq 9.0$, compared to the reaction rate at pH of 7.0±0.1. Namely, 1,4-dioxane half-life ($t_{1/2}$) was reduced about 20 times when increasing the process pH from 7.0±0.1 to the optimal pH conditions, $pH \geq 9.0$.

3.1.2. Effect of bicarbonates

Due to the fact that the industrial wastewaters under concern contained (bi)carbonates and since the carbonate and bicarbonate ions are often considered $OH\bullet$ scavengers [52-54], an additional ozonation experiment was carried out in the presence of carbonates ($9.0 \leq pH \leq 10.0$), to test the possible negative effect on the process. However, instead of producing an inhibition in the ozonation process, the presence of carbonates also enhanced the removal of COD (>90 %), compared to the experiments at neutral conditions (Figure 3), due to the carbonate buffer which kept the pH in the optimal range. The COD removal obtained in the presence of HCO_3^- ($pH \leq 10.0$) was similar, in terms of statistical significance, to the experiments where the pH was kept at 10.0±0.1 by a constant NaOH addition; whereas somewhat slower ($P<0.05$) degradation was presented at pH=9.0±0.1. This is in concordance with the study done by Barndõk et al. [55], showing that the buffering effect of (bi)carbonate alkalinity could outbalance the negative $OH\bullet$ scavenging effect during ozonation. This enhancing effect of the bicarbonate alkalinity by maintaining the desired pH is demonstrated in greater detail in Section 4.

3.2. O_3/H_2O_2 treatment

The influence of higher pH on COD and 1,4-dioxane removal by O_3/H_2O_2 process is presented in Figure 4. When compared with O_3, the oxidation of 1,4-dioxane solution with O_3/H_2O_2 at pH≥9.0 achieved final COD and 1,4-dioxane removals very similar to the sole ozonation (Figure 2). Although the oxidation with H_2O_2 was faster (Table 2), also more oxidants were consumed in terms of OCC. For example, 1 OCC by O_3 degraded more than 75% of total COD (Figure 2A) while in the O_3/H_2O_2 process only 40% of COD was removed at 1 OCC (Figure 4A). In terms of 1,4-dioxane removal, in both cases (Figures 2B and 4B), at pH≥9.0 approximately 1 OCC was needed to remove most of the compound present in the water. At pH 7.0±0.1, the elimination of 1,4-dioxane was enhanced by the addition of H_2O_2: almost all the 1,4-dioxane was removed employing 1.4 OCC (Figure 4B). There was no significant difference ($P<0.05$) in COD and 1,4-dioxane removal between experiments carried out at pH 9.0±0.1 or 10.0±0.1.

The decrease of 1,4-dioxane concentration was apparently found to fit first order kinetics, considering the oxidant species to be in excess, and the pseudo first order rate constants were found [19, 26, 49-51]. The presence of H_2O_2 significantly enhanced the oxidation process at pH=7.0±0.1 (Table 2), as the H_2O_2 contributes to the generation of OH• through adduct formation (Equations 7 and 8) proceeded by the conversion of $O_3\bullet^-$ into OH• (Equations 5 and 6) [47, 48].

$$HO_2^- + O_3 \rightleftharpoons HO_5^- \qquad (7)$$

$$HO_5^- \rightarrow HO_2\bullet + O_3\bullet^- \qquad (8)$$

As a consequence, the half-life of the compound was reduced considerably compared to the ozonation alone. However, the reaction rates also show that the positive effect of H_2O_2 was less important atpH≥9.0, because at the latter the decomposition of O_3 into OH• radical initiated by hydroxide anions [45, 46] increased significantly and, thus, the enhancement by H_2O_2 played a smaller role compared to the experiment at pH=7.0±0.1. These results demonstrate that working at the optimum pH, both high 1,4-dioxane and COD removals can be achieved with a sole O_3 treatment, while the addition of hydroxyl peroxide enhances the reaction rates for the 1,4-dioxane degradation, but also increases the oxidant consumption in terms of OCC and, thus, the treatment cost.

3.3 Treatment of industrial wastewaters

Three industrial samples were treated by both O_3 (Figure 5A) and O_3/H_2O_2 (Figure 5B). The carbonaceous alkalinity of the wastewaters ensured working at pH>9, which was also the optimal condition found previously. The percentage of COD removal as well as the quantity of COD removed depended highly on the initial organic load. The effluent containing only 1,4-dioxane at a concentration similar to the synthetic water (sample 1) showed an analogous behavior to the previous trials: 85% of COD was degraded by O_3 (Figure 5A) and 98% removal was achieved by O_3/H_2O_2 (Figure 5B).

On the other hand, samples 2 and 3 with a higher COD, containing both 1,4-dioxane and MDO (Table 1), reached a smaller COD removal percentage, but a higher total amount of COD removed. Percentage removals of 63% and 53% by O_3 (Figure 5A), and 76% and 68% by O_3/H_2O_2 (Figure 5B), were achieved for samples 2 and 3, respectively. Nevertheless, in terms of OCC consumed to degrade 1 g of COD, the treatment of samples 2 and 3 by ozonation was more efficient (2 and 1 OCC, respectively), while sample 1 needed more than 4 OCC per g of COD. This is probably due to the high MDO content that was degraded more readily than 1,4-dioxane [8]. However, in the combined process of O_3/H_2O_2, a similar amount of oxidants was consumed per COD for all three wastewaters (Figure 5B). Although the overall COD removal was increased considerably by the addition of H_2O_2, the process efficiency, in terms of OCC, remained more or less the same because the higher initial COD required a greater amount of oxidant (H_2O_2), and, thus, increased the ratio $OCC/COD_{removed}$.

According to the chromatography (Table 3), a high degradation of 1,4-dioxane from the samples 2 and 3 was achieved after approximately 1 OCC. The degradation intermediates were mainly EG and volatile fatty acids, which are more biodegradable, meaning they could be removed in a traditional biological process. However, the MDO was almost completely degraded, even being in much higher quantities, which proves that it is oxidized more readily than 1,4-dioxane, and thus, it is competing for the available oxidants [8]. However, the combination of O_3/H_2O_2 allows a complete degradation of 1,4-dioxane as well as MDO from sample 3 at the same experimental time. This implies that for the complete removal of 1,4-dioxane in the presence of MDO, longer treatment times are required when using O_3 alone, or an additional oxidant, such as H_2O_2, should be added. Both options would increase the OCC per COD removal, thus, their cost-effectiveness should be studied and compared.

4. On-line FTIR monitoring of the 1,4-dioxane decomposition

For the better understanding of the differences between the ozonation of 1,4-dioxane under basic and acidic conditions, experiments were carried out, monitoring the evolution of the FTIR spectra. The 3D surface of the reaction evolution in the experiment conducted at pH<5.7 without no pH control (Figure 6A) shows a moderate decrease of 1,4-dioxane in time, the peak of 1118 cm^{-1} being the most illustrative, as emphasized in the graph. The slow degradation of the 4 main peaks of 1,4-dioxane in relative absorbance units is pointed out in the insert placed in the header, indicating with an arrow the foremost curvature at 1118 cm^{-1} in the spatial surface. On the other hand, much faster decrease of 1,4-dioxane can be observed in the experiment carried out at pH>9 in the presence of bicarbonate buffer (Figure 6B). The chromatography analysis supports this tendency: 93% of 1,4-dioxane (66% of the COD) was removed in the FTIR experiment at pH>9, whereas only 63% removal of 1,4-dioxane (40% of the COD) was achieved in the acidic conditions.

According to the intermediate compounds identified by the ConcIRT software that associates the important organic bonds to the different organic molecules, it is clear that the basic conditions favoured faster kinetics of 1,4-dioxane degradation (Figure 7). At pH<5.7 (Figure 7A), the 1,4-dioxane degradation was slower and intermediates like ethylene glycol diformate (EGDF), and acetic, glycolic and glyoxylic acids, could be observed; whereas less oxalic acid was produced (this tendency is also supported by the chromatographic analyses of carboxylic acids). At pH>9 (Figure 7B), the major intermediate identified by ConcIRT software as well as by the chromatography analysis was EG which was subsequently degraded into oxalic acid.

Considering these results and taking into account the literature, the decomposition of 1,4-dioxane by molecular O_3 in acidic conditions (Figure 7A) follows a pathway of EGDF formation as a primary intermediate, similarly to several UV assisted AOPs [31, 32, 56-58]. EGDF is generated by an oxidative ring opening mechanism through peroxyl radical [32, 35]. In addition, a parallel route occurs through the formation of methoxyacetic acid [32], but in a lesser extent, since the chromatography analysis detected metoxyacetic acid only in the first quarter of the experiment. Likewise, while generated in the beginning, the concentration of EGDF decreases during the experiment, as the amount of several decomposition products increases along the reaction (Figure 7A). According to the chromatography, the further oxidation of EGDF leads mainly to the formation of glycolic acid, in accordance with Maurino et al. and Stefan and Bolton [31, 32]. In the relative absorbance profiles, glyoxylic acid appears concurrently with glycolic acid, most likely as a decomposition product of the latter [32], and when its concentration decreases, more oxalic acid appears (Figure 7A). Oxalic acid could be generated from both the degradation of glycolic and glyoxylic acids [31, 32]. The moderate increment of acetic acid, although visualized jointly with glycolic acid, is most certainly a decomposition product of methoxyacetic acid [32].

In basic conditions (Figure 7B), however, the degradation of 1,4-dioxane by ozonation seems to be somewhat different. No EGDF could be detected along the reaction, but EG was identified as the primary reaction intermediate by both ConcIRT software and chromatography, simultaneously with the increment of oxalic acid as its final decomposition product [32, 35]. EG is most likely produced by the hydrolysis of its formate esters [31, 32, 35], implicating the same initial mechanism of the EGCF formation as in the case of pH<5.7. However, like proposed in a previous study on Fenton oxidation [35], EGDF is not detected, as it is quickly hydrolyzed to EG. Moreover, high pH conditions could also promote the fast hydrolysis of EGDF to EG, like reported for UV/TiO_2 oxidation [31]. Kishimoto [59] also reports EG as the main intermediate of 1,4-dioxane in an electrolysis/O_3 treatment, although suggesting a route through an unknown molecule “chemical I” over p-dioxanol and p-dioxanone.

Both the chromatography analysis and the relative absorbance profiles (Figure 7B) indicate that when most of the 1,4-dioxane is consumed, the concentrations of EG and, subsequently, oxalic acid start to decrease as well. As oxalic acid is one of the last intermediates expected [31, 32, 35], its disappearance indicates that the reaction has reached a stage where total mineralization of the organics starts taking place. This is not the case at pH<5.7 where the increment of oxalic acid was still very low in the end of the reaction (Figure 7A).

Conclusions

O_3 was proven efficient as a sole oxidant to degrade 1,4-dioxane from wastewaters in controlled basic conditions. pH was the key parameter to make the ozonation a viable process, since the production of OH• increases at higher pH, and 1,4-dioxane and its by-products are degraded preferentially by OH•. The FTIR study of decomposition pathways demonstrates that the faster degradation at pH>9 occurs through the formation of EG as a primary intermediate; whereas the decomposition in acidic conditions consist in the formation and slow degradation of EGDF.

Working at pH 10.0±0.1, close to 90% of the COD was removed and almost a complete degradation of 1,4-dioxane was reached. The presence of (bi)carbonates enhanced the process, due to their buffer effect, which kept the pH at optimal conditions. Although addition of H_2O_2 enhanced the kinetics of the 1,4-dioxane degradation process even more; this improvement was more relevant at pH 7.0±0.1 than at pH over 9.

The treatment of industrial wastewater where 1,4-dioxane was the only organic contaminant showed a similar behaviour to the synthetic water. 85% of COD was degraded by O_3 and 90% removal was achieved by O_3/H_2O_2. The treatment of industrial samples containing both 1,4-dioxane and MDO reached a higher reduction of COD, although smaller percentage removal. The MDO was degraded more easily than 1,4-dioxane and, therefore, its presence offered competition for the OH• radicals and reduced the efficiency of the 1,4-dioxane degradation. Adding H_2O_2 to the process, a complete elimination of 1,4-dioxane and MDO was reached; however, also a higher amount of oxidants in terms of OCC was consumed.

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TABLE 1

	Units	Sample 1	Sample 2	Sample 3
1,4-dioxane	mgL^{-1}	250	280	300
MDO	mgL^{-1}	0	669	606
pH		8.7 – 9.0	7.8 – 8.1	6.7 – 6.9
Conductivity	μScm^{-1}	2000	2000	1800
Redox	MV	8	12	5
Hardness	mgL^{-1} $Ca^{2+} + Mg^{2+}$	50	25	60
Alkalinity	$mgCaCO_3$ L^{-1}	1045	865	983
COD_t	mgO_2 L^{-1}	463	1319	2230
N_{total}	mgL^{-1}	0	0	0
P_{total}	mgL^{-1}	2.48	3.57	1.49
Fe_{total}	mgL^{-1}	0.030	0.000	0.067

Table 1. Characterization of industrial wastewaters.

TABLE 2

Treatment	**O_3**			**O_3/H_2O_2**		
pH	***$t_{1/2}$ min***	***k min^{-1}***	***R^2***	***$t_{1/2}$ min***	***k min^{-1}***	***R^2***
7.0	578	1.2	0.99	29	24	0.92
9.0	29	24	0.91	19	36	0.99
10.0	23	30	0.94	14	48	1.00

Table 2. Kinetics of 1,4-dioxane degradation in O_3 and O_3/H_2O_2 processes.

TABLE 3

	1,4-dioxane mgL^{-1}	MDO mgL^{-1}	EG mgL^{-1}	VFA mgL^{-1}
Sample 1	0	-	0	36
Sample 2	<5	<15	22	204
Sample 3	65	<5	267	237

Table 3. Chromatography analysis. Samples 2 and 3: initial composition and composition after 1 OCC for O_3 experiments and 2.5 for O_3/H_2O_2 experiments at original pH and $[H_2O_2]_0$=2.125*COD (mgL^{-1}). EG = ethylene glycol, VFA = volatile fatty acids.

FIGURE CAPTIONS:

Figure 1. Schematic of experimental setup.

Figure 2. Ozonation at different pH: removal of COD (A) and 1,4-dioxane (B) with respect to OCC. $[1,4\text{-dioxane}]_0 = 247.8$ mgL^{-1}. Letters (a,b,c,d) identify different statistically significant groups (Tukey's test, $P < 0.05$).

Figure 3. Ozonation in different alkaline wastewater matrices: removal of COD with respect to OCC. Basic conditions maintained either by on-line control with NaOH or punctual addition of $NaHCO_3$ (11.9 mM). $[1,4\text{-dioxane}]_0 = 247.8$ mgL^{-1}. Letters (a,b) identify different statistically significant groups (Tukey's test, $P < 0.05$).

Figure 4. O_3/H_2O_2 at different pH: removal of COD (A) and 1,4-dioxane (B) with respect to OCC. $[1,4\text{-dioxane}]_0 = 247.8$ mgL^{-1}; $[H_2O_2]_0 = 2.125*COD$ (mgL^{-1}). Letters (a,b) identify different statistically significant groups (Tukey's test, $P < 0.05$).

Figure 5. COD removal from industrial samples by O_3 (A) and O_3/H_2O_2 (B). $[H_2O_2]_0 = 2.125*COD$ (mgL^{-1}). Sample 1 consumed 4.27 (O_3) and 4.77 (O_3/H_2O_2) $OCC/gL^{-1}COD$; sample 2, 2.29 (O_3) and 3.24 (O_3/H_2O_2) $OCC/gL^{-1}COD$, and sample 3, 1.07 and 3.57 (O_3/H_2O_2) $OCC/gL^{-1}COD$.

Figure 6. Evolution of FTIR spectra (1800-800 cm^{-1}) along the ozonation treatment of 1,4-dioxane ($C_0=6168$ mgL^{-1}) under (A) basic conditions at $pH>9$ in the presence of $NaHCO_3$ buffer (23.8 mM), and (B) acidic conditions at $pH<5.7$. Inserts point out the evolution of the representative peaks of 1,4-dioxane along its degradation.

Figure 7. FTIR-absorbance profiles of the main by-products produced during the O_3 oxidation of 1,4-dioxane ($C_0=6168$ mgL^{-1}), identified in relative absorbance units of the ConcIRT software, under (A) basic conditions at $pH>9$ in the presence of $NaHCO_3$ buffer (23.8 mM), and (B) acidic conditions at $pH<5.7$.

FIGURE 1

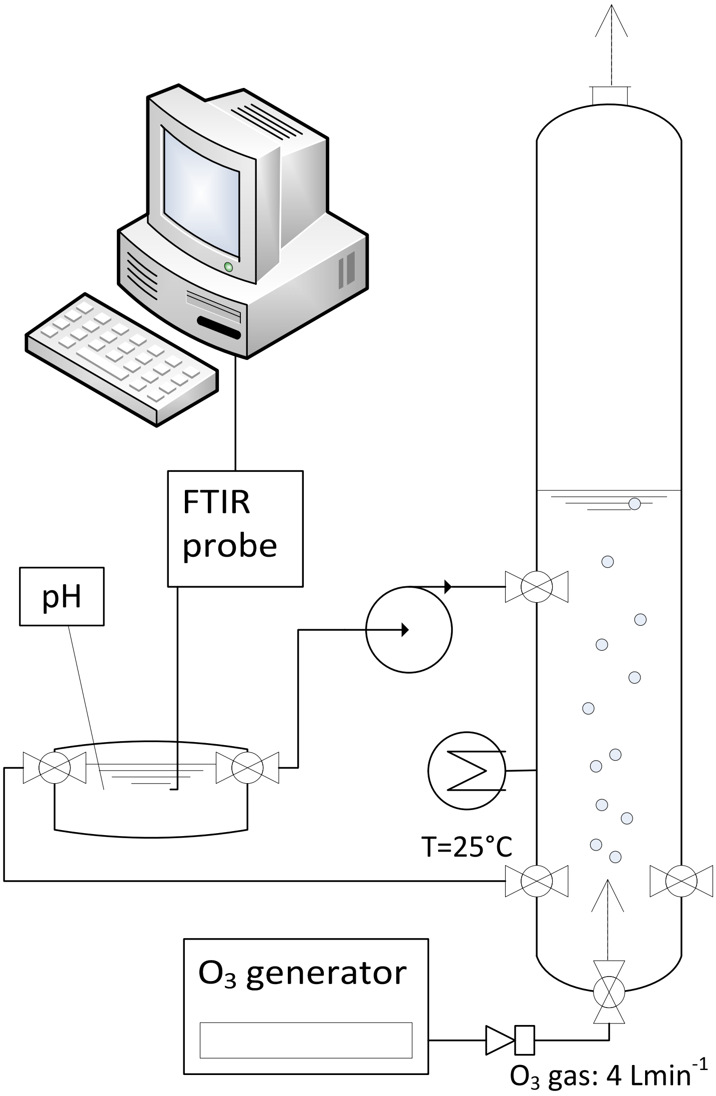


FIGURE 2

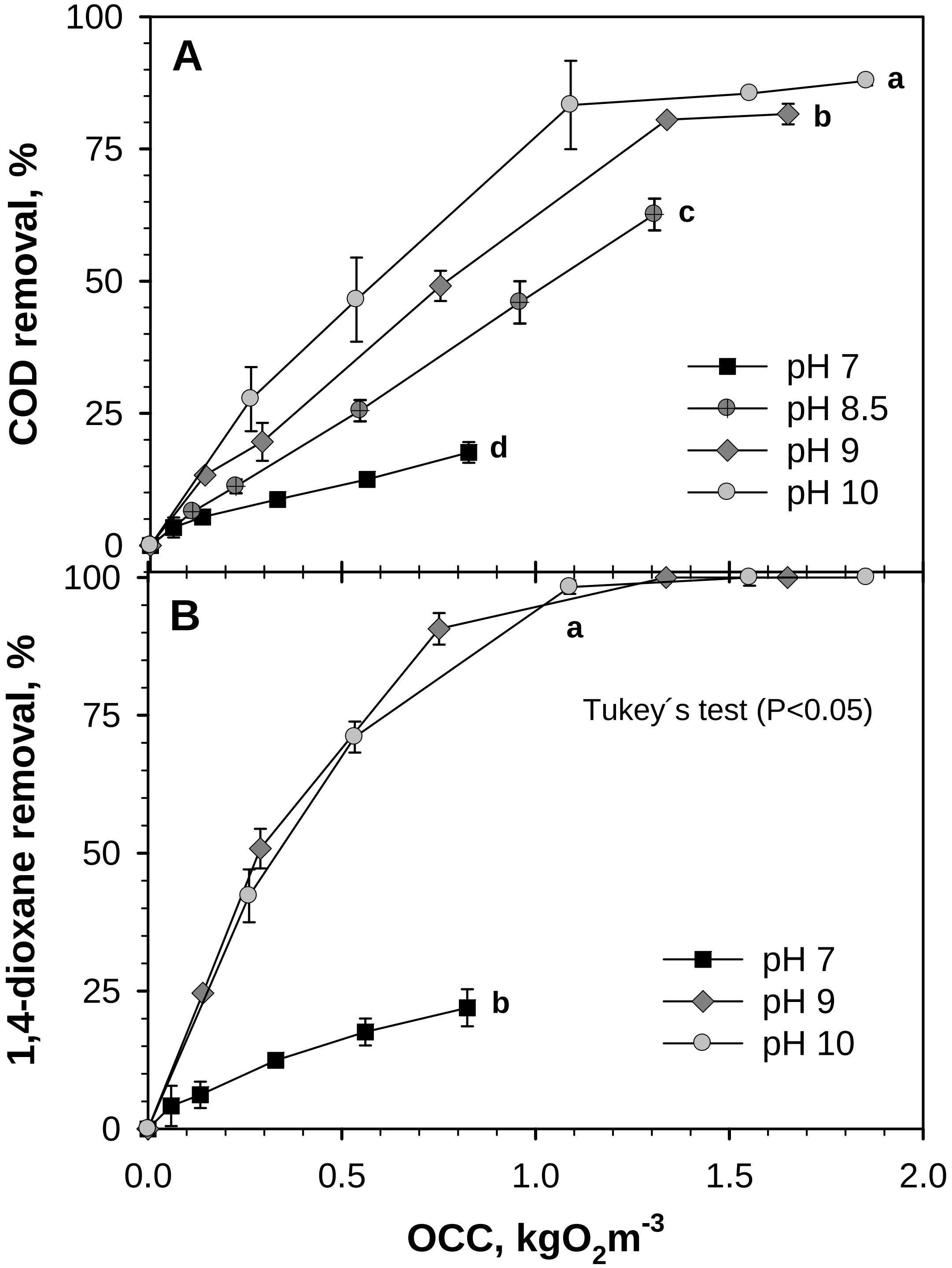

A
COD removal, %
100
75
50
25
0
a
b
c
d
pH 7
pH 8.5
pH 9
pH 10
B
1,4-dioxane removal, %
100
75
50
25
0
a
b
Tukey´s test (P<0.05)
pH 7
pH 9
pH 10
0.0
0.5
1.0
1.5
2.0
OCC, kgO2m-3

FIGURE 3

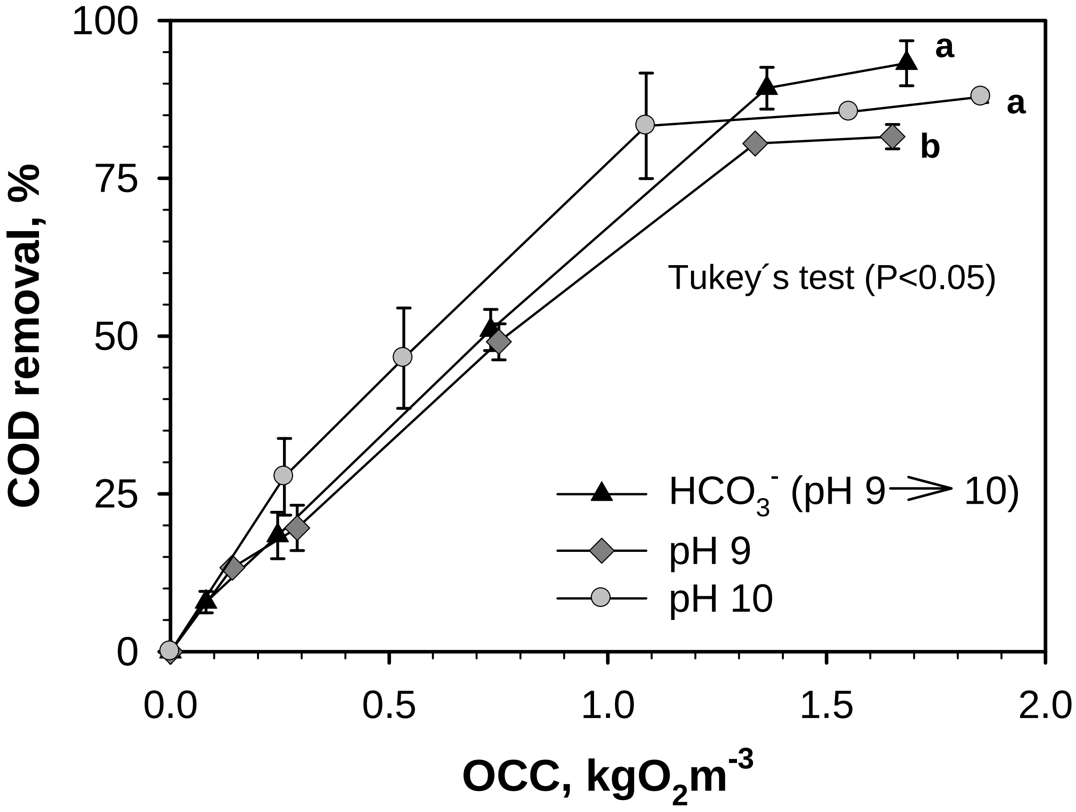
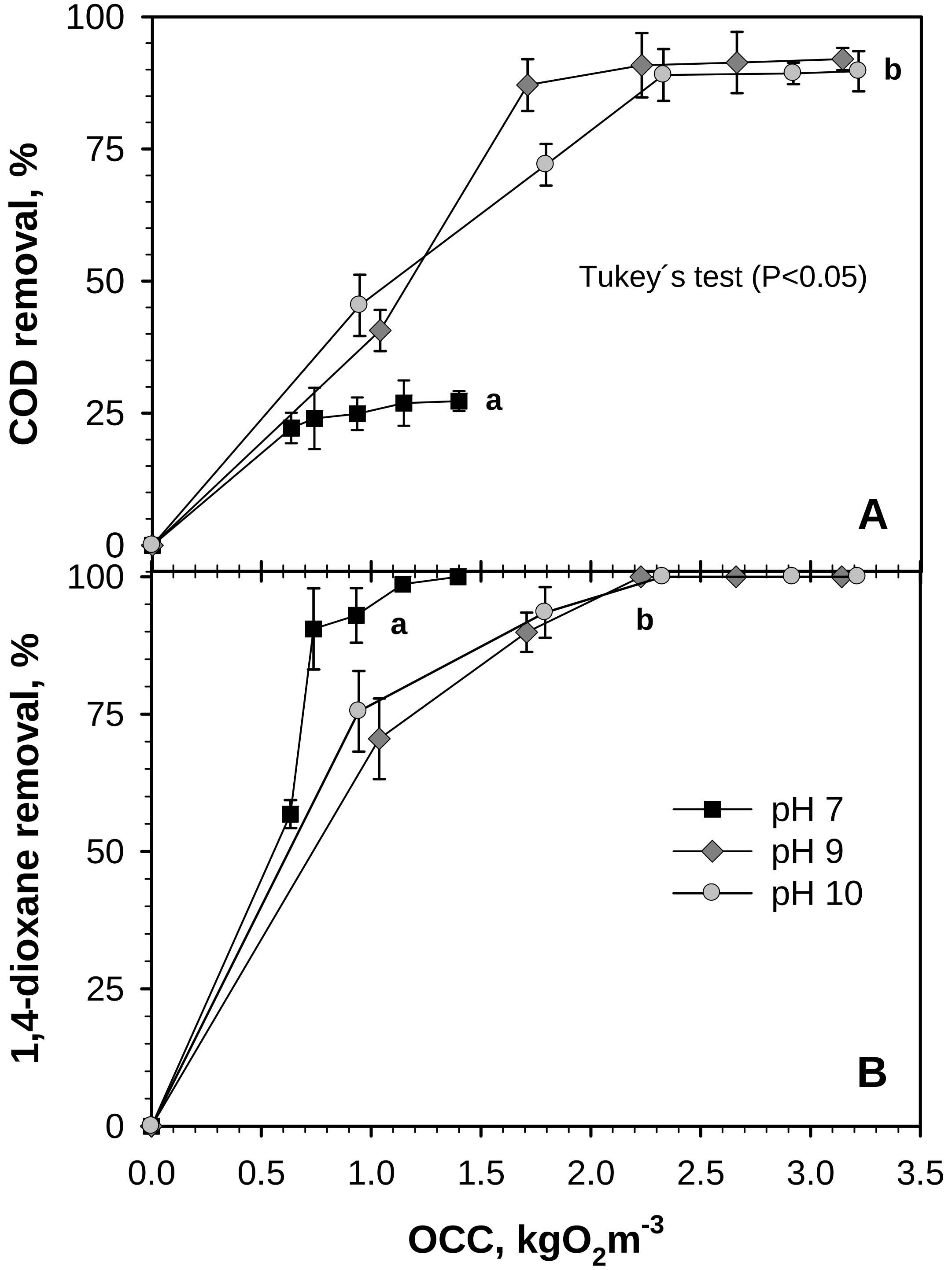

100
75
50
25
0
COD removal, %
0.0
0.5
1.0
1.5
2.0
OCC, kgO2m-3
a
a
b
Tukey´s test (P<0.05)
HCO3- (pH 9 ⇒ 10)
pH 9
pH 10

FIGURE 4



COD removal, %
100
75
50
25
0
Tukey´s test (P<0.05)
a
b
A
1,4-dioxane removal, %
100
75
50
25
0
a
b
pH 7
pH 9
pH 10
B
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
OCC, kgO$_2$m^{-3}

FIGURE 5

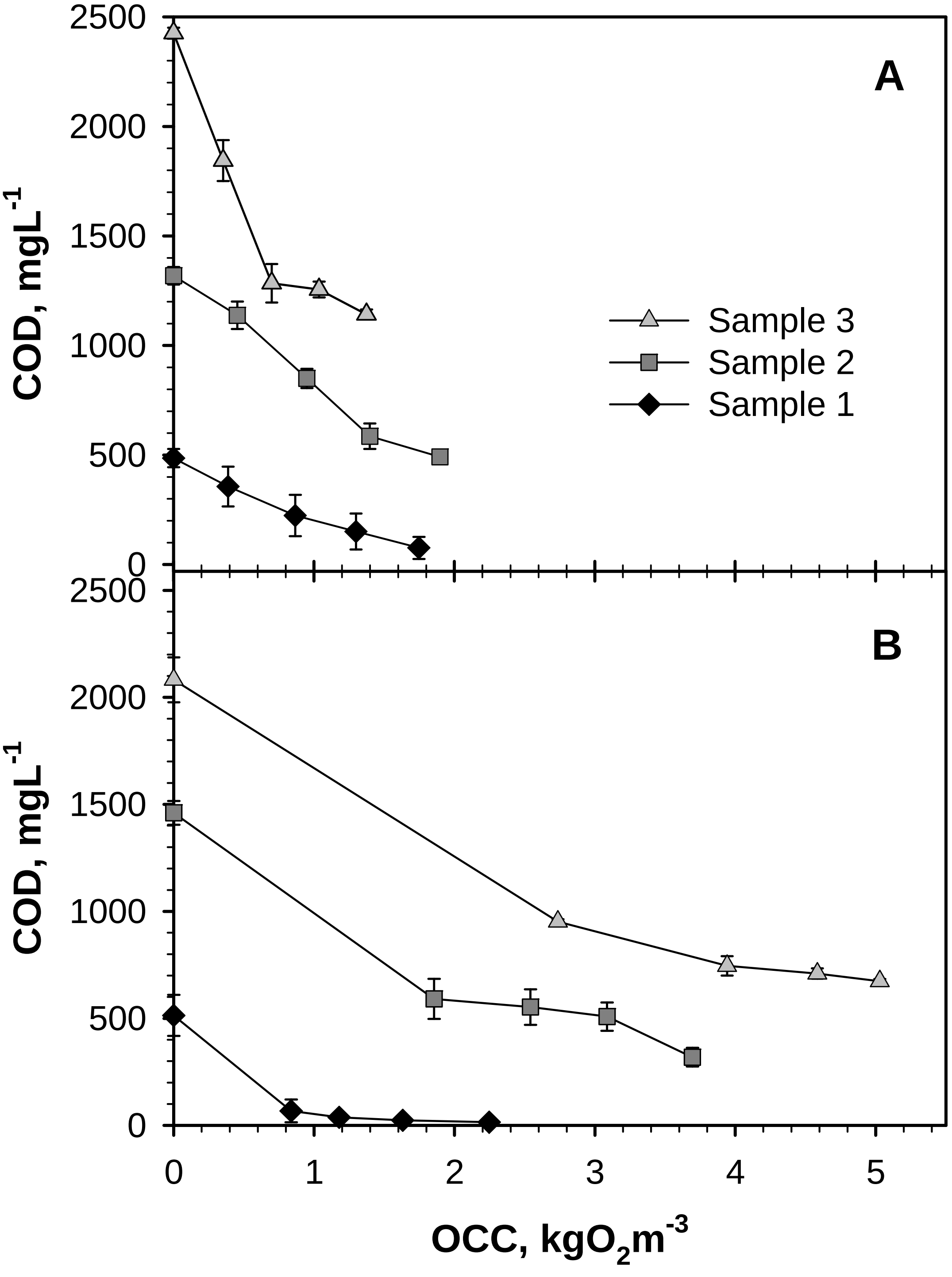

A
B
Sample 3
Sample 2
Sample 1
COD, mgL-1
COD, mgL-1
0
500
1000
1500
2000
2500
0
1
2
3
4
5
OCC, kgO2m-3

FIGURE 6

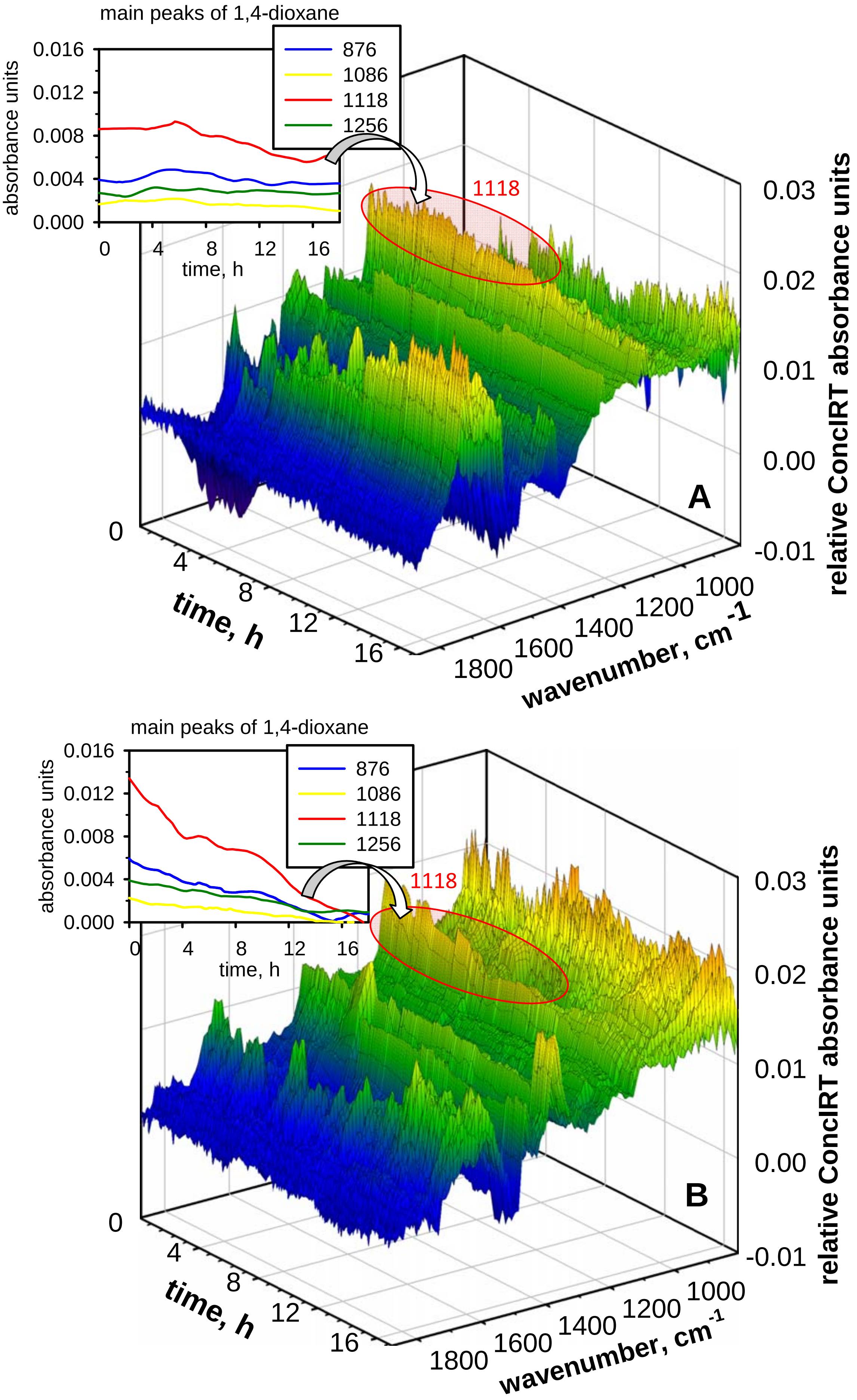
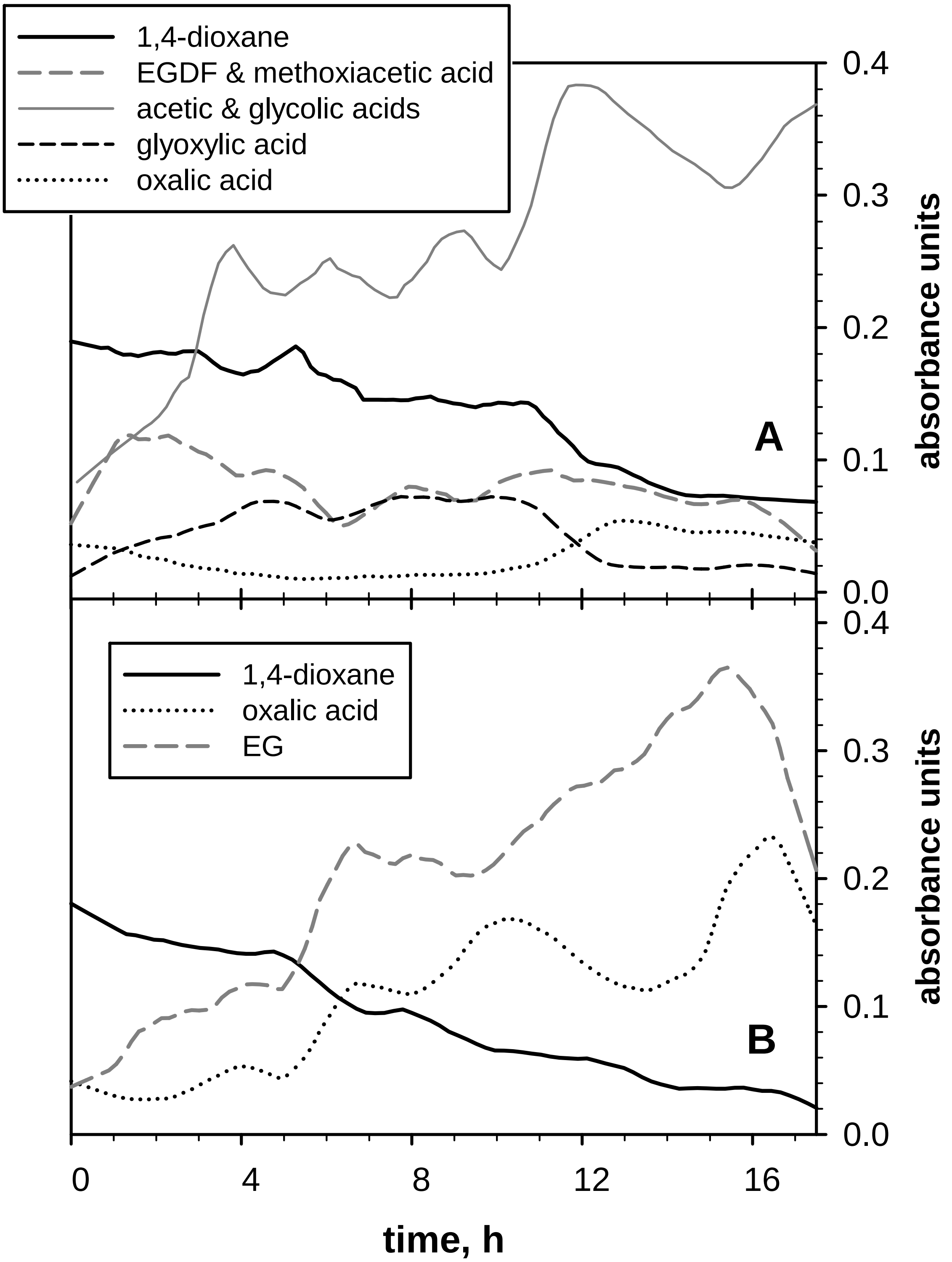

main peaks of 1,4-dioxane
absorbance units
0.016
0.012
0.008
0.004
0.000
0
4
8
12
16
time, h
876
1086
1118
1256
1118
0.03
0.02
0.01
0.00
-0.01
relative ConcIRT absorbance units
A
0
4
8
12
16
time, h
1800
1600
1400
1200
1000
wavenumber, cm-1
main peaks of 1,4-dioxane
absorbance units
0.016
0.012
0.008
0.004
0.000
0
4
8
12
16
time, h
876
1086
1118
1256
1118
0.03
0.02
0.01
0.00
-0.01
relative ConcIRT absorbance units
B
0
4
8
12
16
time, h
1800
1600
1400
1200
1000
wavenumber, cm-1

FIGURE 7


1,4-dioxane
EGDF & methoxiacetic acid
acetic & glycolic acids
glyoxylic acid
oxalic acid
A
0.0
0.1
0.2
0.3
0.4
absorbance units
1,4-dioxane
oxalic acid
EG
B
0.0
0.1
0.2
0.3
0.4
absorbance units
0
4
8
12
16
time, h