Optimization of the Fenton treatment of 1,4-dioxane and on-line FTIR monitoring of the reaction

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ABSTRACT

1,4-dioxane is a non-biodegradable, toxic, hazardous, and priority pollutant widely used in the chemical industry as a solvent; as well as it is a resulting by-product of many industrial processes. The optimization of the Fenton treatment of 1,4-dioxane, and the on-line FTIR monitoring of its degradation route, including the assessment of the enhancement of the biodegradability of the solution along treatment are herein addressed. Besides the full removal of 1,4-dioxane, an 80% reduction of the chemical oxygen demand (COD) was achieved at the best tested treatment conditions. Whether the used concentration of H_2O_2 was expectedly addressed as the reaction factor most influencing the achieved COD removal at the end of the process; the performance of the treatment under acid pH conditions showed to have just a slight influence, thus supporting this process may suitably be performed at neutral pH value. On-line FTIR monitoring of the process novelly provided the degradation route of 1,4-dioxane along its oxidation treatment, as well as a comprehensive optimization of the Fenton process based on the increase of the biodegradability of the solution and the reduction of the consumption of reagents.

KEYWORDS: Advanced oxidation processes; Fenton method; FTIR; on-line reaction monitorization; 1,4-dioxane oxidation.

1. Introduction

1,4-dioxane is an organic compound used as solvent in many industrial processes, as well as it is generated as a by-product in several industrial chemical reactions [1]. The main environmental concern regarding the potential release of this compound to the environment has recently increased due to its major negative effects on health. Correspondingly, 1,4-dioxane is classified as a priority pollutant by the US EPA [2]. Furthermore, it is a bio-recalcitrant and persistent organic molecule that cannot be treated by conventional bio-treatment technologies [1,3]. In fact, physical treatments, such as adsorption on activated carbon or air striping, have not been successful removing dioxane from water because of this inherent high aqueous solubility and its low vapor pressure [3,4]. Moreover, it has been addressed that the chemical oxidation of 1,4-dioxane by chlorine could lead to the formation of even more toxic compounds [1]. In conclusion, traditional treatments have not been shown as effective degrading this substance. Only distillation technology has efficiently been proved to separate 1,4-dioxane from the solution due to its high volatility; but its use has a very high associated cost, particularly at very low concentration levels [1,3,4].

Advanced oxidation processes (AOPs) may represent a feasible treatment alternative for 1,4-dioxane [4] because they can be applied at a lower economical cost just transforming this persistent compound into simpler more biodegradable compounds that might be further degraded by traditional biological treatment [5]. Particularly, Fenton method is one of the most commonly used AOPs. It is based on the electron transfer between hydrogen peroxide and ferrous ion, which acts as a homogenous catalyst, yielding hydroxyl radicals ($OH\cdot$) that are able to degrade a wide range of organic compounds [6]. In general, the Fenton process is usually very efficient, and it even implies a lower economical cost than the application of others AOPs [7]. Regardless a high chemical oxygen demand (COD) removal efficiency could be achieved and a relative overall environmental friendliness, a Fenton treatment of wastewater is limited by the final production of iron sludge, which requires ultimate disposal [8], and the optimal pH range of application, which is usually set at acid values (pH≈3) [9,10].

There are very few limited studies considering the treatment of 1,4-dioxane by Fenton's reagent [1,3,11]. Although all these essays have assessed the improved elimination of 1,4-dioxane and COD from wastewater, an increased biodegradability of the final solution, and the reduced consumption of reagents; a comprehensive process optimization has not been addressed yet. In fact, the identification of which by-products are formed along the degradation of 1,4-dioxane by Fenton has not been addressed to date. Some authors have previously reported the removal of 1,4-dioxane and other by-products that are formed along its treatment, but the production of other chemical species along the reaction has not really been assessed in full yet [1,11,12]. Only Stefan and Bolton [13] have previously proposed a degradation mechanism for 1,4-dioxane treating this chemical by UV/H_2O_2 and taking periodical samples that were analyzed by gas chromatography (GC), solid phase microextraction (SPME), gas chromatography/mass spectrometry (GC/MS), ion chromatography (IC), and high-performance liquid chromatography (HPLC), in order to identify intermediate chemical species and by-products. The advantage of monitoring similar processes using Fourier transform infrared spectroscopy (FTIR) has previously been addressed identifying the compounds that are appearing and disappearing in the solution along the reaction sampling aliquots at preselected time intervals [14, 15].

Therefore, the main objectives of this research are: (1) optimizing conventional Fenton method as a promising alternative for the treatment of 1,4-dioxane; and (2) developing an FTIR-based methodology enabling the on-line control of the use of reagents, and the production of intermediates and by-product along the degradation of 1,4-dioxane.

2. Material and methods

2.1. Materials and analytical methods

All used chemicals were of analytical grade and supplied by PANREAC S.A. (Barcelona, Spain) or Sigma-Aldrich (Highland, USA).The solutions were prepared in deionized water and kept in the dark until use. All the analyses were made according to the standard methods for the examination of water and wastewaters [16]. COD was measured by the colorimetric method at 600 nm using an Aquamate-spectrophotometer (Thermo Scientific AQA 091801, Waltham, USA). Hydrogen peroxide concentration was analyzed by the titanium sulphate spectrophotometric method [17].

In order to confirm FTIR results, 1,4-dioxane and ethylene glycol were identified and quantified along the reaction by gas-liquid chromatography (GLC) using a 7980A instrument (Agilent Technologies Inc., Palo Alto, CA) 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, 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 the following temperature program: 80 °C to 240 °Cat a 15 $°C·min^{-1}$ ramp rate after a 9 min initial hold. Peaks were identified on the basis of sample coincidence to relative retention times of commercial standards. Quantification was performed according to peak areas that were corrected by response factors that were calculated for each compound using 1-butanol (250 $mg·L^{-1}$) as internal standard, and *GC-ChemStation Rev.B.04.02 (96)* software from Agilent.

Formic, oxalic, acetic, glycolic, and methoxyacetic acids were also complementarily identified and quantified by ion chromatography (IC) using a Dionex DX-500 device (Thermo Scientific, Sunnyvale, CA) equipped with a conductivity detector. A 40 to 60 mM NaOH gradient was used as the eluent for measurement keeping the flow at 1.5 $L\cdot min^{-1}$. The injection loop was 75 μL. An AS11HC Ion Pac ionic resin column was used aided with a previous Anion Trap Column (ATC3) and a AG11-HC guard column. Peaks were identified and quantified on the basis of sample coincidence to relative retention times and standard concentrations of commercial standards.

2.2. FTIR analytical equipment

Mettler-Toledo ReactIR iC10 (Columbia, USA) is a Fourier transform infrared (FTIR) spectrometer that measures chemical species as they react over a period of time. It uses a Mercury Cadmium Telluride (MCT) detector that is cooled by liquid nitrogen. Measurements are optically taken using a diamond tipped probe with a 1 meter fiber optic conduit. The system should be purged (using instrument grade air, nitrogen or other suitable inert gas) in order to prevent water vapour from collecting inside the optics, which might otherwise obscure spectral data.

Data acquisition in the absorbance scale was taken from 2000 to 750 cm^{-1} with an 8 cm^{-1} nominal resolution; and 256 scans were co-added for each spectrum. A background on pure water was carried out just before performing each spectral record under the same resolution and scanning conditions that were used for the trials. Real-time component analyses were run using ConcIRT software (Mettler-Toledo, Columbia, USA), which calculates associated component spectra, and relative concentration profiles.

2.3. Experimental procedure

Experiments were performed in a 500 mL glass reactor placed on a magnetic mixing device. Temperature was adjusted to the desired value (25 ºC) using a water heater and circulator. pH was monitored along the process, and adjusted to the desired value (± 0.1) using 1 $mol \cdot L^{-1}$ sodium hydroxide, or 1 $mol \cdot L^{-1}$ sulphuric acid, as required. Considering 1,4-dioxane is degraded to ethylene glycol at a very slow rate at acid pH values, whereas it is ionized and keeps a stable structure under basic ones, pH adjustment was carried out after adding dioxane (247.8 $mg \cdot L^{-1}$; initial COD=450 $mgO_2 \cdot L^{-1}$) when performing trials under acid conditions, and before its incorporation to the solution otherwise. After temperature and initial pH adjustment, ferrous sulphate was added to the solution at the ferrous ion concentration specified in the experimental design described next to optimize treatment results. Hydrogen peroxide (30% w/v) was then added in batch mode until the designed concentration was also reached. Treatments were run until all the added H_2O_2 was totally consumed, so maximum COD removal was achieved for a set of reaction variables values.

Aliquots of the treated solution were periodically sampled with a syringe along the trials. These samples were adjusted to $pH \approx 9.0$ adding 40% sodium hydroxide (NaOH), and then centrifuged during 15 min at 2000 rpm. COD and H_2O_2 concentrations were measured in the collected supernatant. H_2O_2 concentration values were used to correct COD values according to Hermosilla et al. [18].

Initial reaction conditions and concentrations of reagents chosen to perform on-line FTIR control experiments were determined after optimizing the Fenton treatment of 1,4-dioxane. In general, the experimental procedure used for FTIR trials was the same, despite the concentration of 1,4-dioxane was 0.07 $mol \cdot L^{-1}$, and the addition of hydrogen peroxide was carried out in continuous mode (8.8 mmol $H_2O_2 \cdot min^{-1}$ to a total 100 mL of reaction solution) because it allows to understand better the reaction process; besides it has previously shown better results than batch mode in this particular process [18, 19].

The main compounds that actual scientific literature proposes to be considered in the degradation route of 1,4-dioxane by oxidation are: ethylene glycol diformate, glycolic acid, glyoxylic acid, methoxiacetic acid, formic acid, acetic acid and oxalic acid [1,3,11,13, 20]. Their reference spectra were first experimentally collected by FTIR (Figure 1). Despite the likeness of these compounds, the proper interpretation of mixture spectra (recorded during Fenton processes) have been successfully carried out with the help of the mathematical algorithms integrated in ConcIRT software, and comparing spectra of pure solutions with those obtained along the process. Water spectra were subtracted from the obtained on-line spectra in all experimental runs.

2.4. Experimental design

Response surface methodology (RSM) was used to optimize the Fenton treatment of 1,4-dioxane statistically assessing the significance of the effects of the considered individual factors, and the interactions between them, that influence the process [21, 22]. In addition, Pareto charting was used to highlight the most important factors that influenced the treatment efficiency. In short, this methodology allows determining optimum operation conditions for the system, as well as the region in which the operating specifications are satisfied [22]. Experimental design, regressions, response surfaces, and Pareto charts, were run by Systat 13 software (SYSTAT Software Inc., Chicago, USA).

pH, temperature, the concentrations of reagents, and reaction time, are the main factors that may influence the Fenton treatment of an organic compound. Among them, temperature has previously been reported not to affect much between 25 to 45 ºC, and reaction time is really dependent on the concentrations of reagents [18]. Therefore, experiments were designed to optimize pH, hydrogen peroxide and ferrous ion concentrations. Based upon previously reported results for optimizing Fenton treatment of organics [23], RSM was actually performed considering pH values of 2.8, 5.0 and 7.2; and H_2O_2 concentration dependent ratios of $[H_2O_2]_0/COD_0$ = 1.063, 2.125 and 4.250; and $[H_2O_2]_0/[Fe^{2+}]_0$ molar ratios of 1.0, 5.0 and 10.0.

In short, RSM regression analysis was performed according to a full factorial design (N=27) using the following quadratic model:

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i=1}^{k}\sum_{j=1}^{k} b_{ij} X_i X_j$$

Where Y (COD removal) is the process response dependent variable; X_i are the considered independent variables ($X_1 = [H_2O_2]_0/COD_0$; $X_2 = [H_2O_2]_0/[Fe^{2+}]_0$; X_3 = pH); and b_i, b_{ii} and b_{ij} are the corresponding regression coefficients.

3. Results and discussion

3.1. Optimization of the conventional Fenton treatment of 1,4-dioxane

pH is one of the most important factors influencing the final result of a Fenton process because it mainly controls the speciation of iron and the stability of hydrogen peroxide [24, 25]. In short, iron precipitation as $Fe(OH)_3$ is avoided under acid conditions because the solubility of iron increases [26] and, as a consequence, the efficiency of the process also increases. In addition, hydrogen peroxide decomposition is also impeded under acid environments, favoring its stabilization [27]; as well as the scavenger function of inorganic carbon is also prevented because it should mainly have already been removed. Nonetheless, further significance may be found in the case of the Fenton treatment of 1,4-dioxane because of the structural changes this compound shows in relation to the pH value of the solution.

The resulting estimations of the regression coefficients of the quadratic model used to optimize the Fenton treatment of 1,4-dioxane by RSM (Figure 2) are shown in Table 1. Whether a positive value of one of these coefficients indicates a positive relation of the associated factor to COD reduction; negative coefficients mean a lower COD removal would be achieved at a higher value the related factor. In particular, the negative coefficient related to the pH factor means that higher COD reductions were achieved working at lower pH values (Figure 2); as well as higher doses of H_2O_2 (a higher $[H_2O_2]_0/COD_0$ ratio, actually) increased the difference between the reduction of the COD that was achieved working at those designed lower and higher pH values. In fact, the effect of pH was slight at the designed lower dose value of H_2O_2 (less than 10%).

The optimum pH value for performing the Fenton treatment of 1,4-dioxane resulted 2.8, as it has previously been also reported, although the effect of pH was not as relevant as it has been addressed before [18, 28]. The highest influence of pH was exerted at a ratio of $[H_2O_2]_0/COD_0=4.250$, obtaining a good COD removal result (≈55%) when the process was performed at pH=7.2 if it is compared to the optimized result at pH = 2.8 (COD removal≈65%; Figure 2). This shorter difference in the efficiency of the process being performed at both pH values was probably the result of the structural changes that are promoted in the molecule of 1,4-dioxane when the pH value changes from acid to basic. In fact, the ionization of 1,4-dioxane under basic reaction conditions favors its reaction with hydroxyl radicals. As a result, the use of chemicals for controlling the pH may be partially counterbalanced as the main drawback for the implementation of Fenton process at industrial scale [29].

In general, the optimization of chemical reagents use is an important issue for the industrial application of Fenton processes due to its related high economical cost. A higher COD removal was achieved when a higher ratio of $[H_2O_2]$ was used in relation to the initial COD value of the solution (Figure 2) because as more hydrogen peroxide is available, the generation of hydroxyl radical is also higher; although an excessive amount of H_2O_2 may scavenge hydroxyl radicals reducing the efficiency of the treatment [18]. In fact, this ratio between the used H_2O_2 concentration and the initial value of the COD in the solution was addressed to show the highest influence on the reduction of the COD (Figure 3). As a consequence, COD removal losses derived from not performing the process under such a low optimum pH value did not result so important when the optimum amount of H_2O_2 is added to the solution (Figure 2). In addition, the molar rate between reagents ($[H_2O_2]_0/[Fe^{2+}]_0$) resulted the second most important parameter influencing process efficiency. Its associated negative coefficient in the resulting RSM model (Table 1) implies that COD removal was enhanced when this ratio between reagents was lower. Therefore, considering certain amount of H_2O_2 is added to perform treatment, the higher tested related supply of Fe^{2+} yielded the higher removal of COD.

In summary, the best tested reaction conditions achieved a 65% COD removal (pH = 2.8, $[H_2O_2]_0/COD_0 = 4.250$ and $[H_2O_2]_0/[Fe^{2+}]_0 = 1$). The COD remaining in the solution after this optimum treatment was characterized by the high content of volatile fatty acids (72.5 $mg \cdot L^{-1}$), which represents a high increase of biodegradability in the final solution. Therefore, the oxidative degradation of 1,4-dioxane at least resulted in the final persistence of more biodegradable organic acids, which is in agreement with previous results reporting an almost total destruction of 1,4-dioxane and a progressive decrease of the pH of the solution due to the formation of organic acids [1]. In addition, a poor elimination of the DOC further supported the degradation of 1,4-dioxane into more biodegradable products rather than to CO_2, which is also in agreement with previous related results [11].

In addition, more feasible industrial treatment conditions were chosen to perform further trials exploring the potential biodegradability enhancement of wastewater containing dioxane, namely: pH=2.8, $[H_2O_2]_0/COD_0=2.125$ and $[H_2O_2]_0/[Fe^{2+}]_0=5$. Higher doses of the reagents involve a proportional increase in the costs of chemicals and disposing iron sludge. Therefore, optimum reaction values resulting from RSM modeling are not really justified for real applications. As a result, a 43% COD removal was achieved performing the Fenton treatment of 1,4-dioxane under these reaction conditions; as well as the final presence of volatile fatty acids reached 58 $mg \cdot L^{-1}$, which also means a significant increase of the biodegradability of the final solution.

3.2. On-line FTIR monitoring of the degradation of 1,4-dioxane by Fenton oxidation

Concentration profiles of the main compounds that were generated in the solution along the Fenton oxidation of 1,4-dioxane (Figure 4) were obtained monitoring the process with an on-line FTIR probe. The ConcIRT software identified the compounds that were being on-line detected by FTIR comparing them to the previously obtained reference FTIR spectra of these compounds (Figure 1). Initially, FTIR spectra did not show any change after the addition of a low concentration of H_2SO_4 at the studied wavenumber spectral region; as well as it was shown that the degradation of 1,4-dioxane into ethylene glycol under acid reaction conditions resulted too slow to be detected at the beginning of the reaction (Figure 5). In fact, the absence of ethylene glycol at this point was also checked by chromatographic analysis before the addition of Fenton's reagent, after which certain very early changes can be noticed in the spectra. The dissolution of ferrous sulphate heptahydrate reported a peak at about 1100 cm^{-1}, which surely represents sulphate ion [30]. The evolution of iron content cannot be followed separately.

1,4-dioxane and $FeSO_4 \cdot 7H_2O$ were already present in the solution before any H_2O_2 was added. A red-brown colour appeared just after hydrogen peroxide was incorporated, denoting iron oxidation from pale-green ferrous ion to red-orange ferric one. A final intense orange color remained in the solution during almost all the process. When 8.8 mmol of H_2O_2 were already added to the reaction medium, ethylene glycol began to increase its presence, as well as glycolic acid and oxalate anion; whereas 1,4-dioxane began to decrease (Figure 5). After 35 mmol of H_2O_2 were fully added, glycolic acid and oxalate anion reached a maximum of absorbance and began to decrease their presence thereafter. On the other hand, the presence of formic acid was newly detected at this point, and increased much its content until reaching a constant value at the end of the reaction. Thereafter, the reaction evolved until the complete reduction of 1,4-dioxane just when all the H_2O_2 dosage (70.5 mmol) was added. In addition, the profile of ethylene glycol showed a slightly decreasing tendency at the same time that glycolic acid and oxalate anion increased their presence at a similar linear pace, denoting certain relationship between both trends towards the end of the process.

Chromatographic analyses confirmed the presence of all these compounds at the same moments of the reaction and the full removal of 1,4-dioxane at the end of the Fenton treatment. Therefore, the same process evolution shown in Figure 5 was confirmed by the performed chromatographic determinations at singular reaction moments. Particularly, IC analyses indicated that, whether glycolic acid was produced in a small quantity, the presence of oxalate was very high. This might have been the result of a fast degradation of glycolic acid into oxalic acid, which may actually be the main responsible of the detected trend.

The pH-dependence of oxalic acid caused the appearance of the corresponding oxalate anion [31]. Some other peaks appeared along the reaction indicating the presence of other possible intermediates that the ConcIRT software could not identify, such as ethylene glycol diformate and methoxyacetic acid (Figure 6). Complementarily, the chromatographic analyses detected the production of a low concentration of methoxyacetic acid and a negligible amount of acetic acid; whereas ethylene glycol was actually found along the reaction, which pointed out that the pathway of degradation mainly progressed through the formation of ethylene glycol diformate.

As a consequence, a mechanism for the degradation pathway that was followed along the Fenton treatment of 1,4-dioxane may be proposed based on a radical reaction mechanism (Schemes 1-3). First, hydroxyl radicals that were generated by the reaction between Fe^{+2} and H_2O_2, attacked 1,4-dioxane molecules to form 1,4-dioxanyl radical. Thereafter, this reaction proceeded until 1,4-dioxan-α-oxyl radical was obtained by the reaction of 1,4-dioxanyl radical with available dissolved oxygen (Scheme 1), first resulting in the formation of the peroxyl radical that next underwent termination reactions to generate the tetroxide precursor of 1,4-dioxan-α-oxyl radical, which was finally produced releasing oxygen [2,3,13]. Thereafter, 1,4-dioxan-α-oxyl radical progressed splitting the C-C bond, which was stabilized by ring opening. This linear peroxyl radical evolved then reacting with oxygen to produce a linear tetroxide that may undergo two further reactions: (1) the electrocyclic process of this linear tetroxide, which finally yields ethylene glycol diformate [2,13]; or (2) the decomposition in two alkoxyl radicals and oxygen, followed by β-fragmentation and H abstraction, finally producing ethylene glycol monoformate [13] (Scheme 1).

Stephan and Bolton [13] also proposed an alternative degradation pathway from 1,4-dioxan-α-oxyl radical consisting on the formation of methoxyacetic acid, and finally resulting in the formation of acetic acid. Although some peaks that were recorded along the reaction could be assigned to methoxyacetic acid (Figure 6), and chromatographic analyses showed this by-product was somewhat produced, the almost completely absence of acetic acid along the reaction actually denotes that this degradation alternative was not significantly followed in comparison to the degradation pathway through ethylene glycol. Nevertheless, Beckett and Hua [2] reported that the degradation of methoxyacetic acid may also result in the generation of glycolic acid and formic acid.

Finally, ethylene glycol mono- and diformate may have progressed by acid hydrolysis to yield ethylene glycol and formic acid as by-products [32] (Scheme 2). Whereas ethylene glycol may be degraded to glycolic acid, and then evolve to oxalic acid by deformilation [33]; oxalic acid itself really shows up as oxalate anion under the acidic pH values predominating in the solution (Scheme 3).

In summary, during the oxidation of 1,4-dioxane, several by-products were produced as the consequence of the ring opening of 1,4-dioxane molecules, namely: ethylene glycol, glycolic acid, oxalate anion and formic acid. As a result, all 1,4-dioxane was removed, resulting in the appearance of more biodegradable by-products, which may allow a further biological treatment stage when necessary. An 80% total COD removal was finally achieved during these trials thanks to the previously identified optimum reaction conditions for this treatment and the further selection of a continuous addition mode for H_2O_2 during the process, which has previously been reported to address a similar treatment efficiency enhancement [18, 19].

4. Conclusions

The treatment of 1,4 dioxane by Fenton's reagent achieved the total removal of this compound from wastewater, as well as 80% COD reduction efficiency under the best tested treatment conditions. In addition, wastewater biodegradability may be further enhanced, which has been addressed by a significant high presence of volatile fatty acids at the end of the reaction. Therefore, although the total mineralization of 1,4-dioxane was not achieved, final persisting by-products were highly biodegradable; thus allowing further conventional treatment if final disposal requirements make it necessary.

FTIR technique allowed the identification of the main compounds involved in the degradation of 1,4-dioxane by conventional Fenton treatment, as well as the control of the behavior of the target compound, denoting its presence and evolution along the reaction. This methodology also allowed addressing a new degradation mechanism, monitoring the formation of by-products, and optimizing the process identifying the presence of biodegradable compounds that may easily be treated by conventional biological technologies, which may furthermore represent a saving in the overall treatment cost.

ACKNOWLEDGMENTS

This research was developed in the frame of the projects “AQUAFIT4USE” (211534), and “E4WATER” (280756), both funded by the European Union; and “OXIPAPEL” (CIT-310000-2008-15), funded by the Ministry of Science and Innovation of Spain.

REFERENCES

[1] P. Ghosh, A.N. Samanta, S. Ray, Oxidation kinetics of degradation of 1,4-dioxane in aqueous solution by H_2O_2/Fe(II) system, J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng. 45 (2010) 395-399.

[2] M.A. Beckett, I. Hua, Enhanced sonochemical decomposition of 1,4-dioxane by ferrous iron, Water Res. 37 (2003) 2372-2376.

[3] H.S. Kim, B.H. Kwon, S.J. Yoa, I.K. Kim, Degradation of 1,4-Dioxane by Photo-Fenton Processes, J. Chem. Eng. of Jpn. 41, 8 (2008) 829-835.

[4] M.H. So, J.S. Han, T.H. Han, J.W. Seo, C.G. Kim, Decomposition of 1,4-dioxane by photo-Fenton oxidation coupled with activated sludge in a polyester manufacturing process, Water Sci. Technol. 59, 5 (2009) 1003-1009.

[5] J.H. Suh, M. Mohseni, A study on the relationship between biodegradability enhancement and oxidation of 1,4-dioxane using ozone and hydrogen peroxide, Water Res. 38 (2004) 2596-2604.

[6] F. Harber, J.J. Weiss, The catalytic decomposition of Hydrogen Peroxide by iron salts, J. Amer. Chem. Soc. 45 (1934) 338-351.

[7] C.P. Huang, C. Dong, Z. Tang, Advanced chemical oxidation: its present role and potential future in hazardous waste treatment, Waste Manag. 13 (1993) 361-377.

[8] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Crit. Rev. Environ. Sci. Technol. 36 (2006) 1-84.

[9] D. Hermosilla, M. Cortijo, C.P. Huang, The role of iron on the degradation and mineralization of organic compounds using conventional Fenton and photo-Fenton processes, Chem. Eng. J. 155 (2009) 637-646.

[10] R.F.F. Pontes, J.E.F. Moraes, A. Machulek Jr., J.M. Pinto, A mechanistic kinetic model for phenol degradation by the Fenton process, J. Hazard. Mater. 176 (2010) 402-413.

[11] E. Khan, W. Wirojanagud, N. Sermsai, Effects of iron type in Fenton reaction on mineralization and biodegradability enhancement of hazardous organic compounds, J. Hazard. Mater. 161 (2009) 1024-1034.

[12] H.S. Son, J.K. Im, K.D. Zoh, A Fenton-like degradation mechanism for 1,4-dioxane using zero-valent iron (Fe0) and UV light, Water Res. 43 (2009) 1457-1463.

[13] M.I. Stefan, J.R. Bolton, Mechanism of the Degradation of 1,4-Dioxane in Dilute Aqueous Solution Using the UV/Hydrogen Peroxide Process, Environ. Sci. Technol. 32 (1998) 1588-1595.

[14] V. Guzsvány, L. Rajic, B. Jovic, D. Orcic, J. Csanádi, S. Lazic, B. Abramovic, Spectroscopic monitoring of photocatalytic degradation of the insecticide acetamiprid and its degradation product 6-chloronicotinic acid on TiO_2, J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng. 47 (2012) 1919-1929.

[15] V. Guzsvány, M. Kádár, Z. Papp, L. Bjelica, F. Gaál, K. Tóth, Monitoring of Photocatalytic Degradation of Selected Neonicotinoid Insecticides by Cathodic Voltammetry with a Bismuth Film Electrode, Electroanalysis 20 (2008) 291 – 300.

[16] APHA, AWWA, WPCF (Eds.), Standard methods for the examination of water and wastewater, Washington DC, 2005.

[17] H. Pobiner, Determination of hydroperoxides in hydrocarbon by conversion to hydrogen peroxide and measurement by titanium complexing, Anal. Chem. 33 (1961) 1423-1428.

[18] D. Hermosilla, M. Cortijo, C.P. Huang, Optimizing the treatment of landfill leachate by conventional Fenton and photo-Fenton processes, Sci. Total Environ. 407 (2009) 3473-3481.

[19] J.A. Zazo, J.A. Casas, A.F. Mohedano, M.A. Gilarranz, J.J. Rodríguez, Chemical Pathway and Kinetics of Phenol Oxidation by Fenton's Reagent, Environ, Sci. Technol. 39 (2005) 9295-9302.

[20] C.G. Kim, H.J. Seo, B.R. Lee, Decomposition of 1,4-Dioxane by Advanced Oxidation and Biochemical Process, J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng. 41 (2006) 599-611.

[21] R.L. Mason, R.F. Gunst, J.L. Hess, (Eds.), Statistical design and analysis of experiments, eight applications to engineering and science, 2nd ed., Wiley: New York, 2003.

[22] Y. Wu, S. Zhou, F. Qin, X. Ye, K. Zheng, Modeling physical and oxidative removal properties of Fenton process for treatment of landfill leachate using response surface methodology (RSM), J. Hazard. Mater. 180 (2010) 456-465.

[23] D. Hermosilla, N. Merayo, R. Ordoñez, A. Blanco, Optimization of conventional Fenton and ultraviolet-assisted oxidation processes for the treatment of reverse osmosis retentate from a paper mill, Waste Manage. 32 (2012) 1236-1243.

[24] H. Gulsen, M. Turan, Treatment of sanitary landfill leachate using a combined anaerobic fluidized bed reactor and Fenton's oxidation, Environ. Eng. Sci. 21 (2004) 627-636.

[25] H. Zhang, H.J. Choi, C.P. Huang, Optimization of Fenton process for the treatment of landfill leachate, J. Hazard. Mater. 125 (2005) 166-174.

[26] J. Kiwi, C. Pulgarin, P. Peringer, M. Gratzel, Beneficial-effects of homogeneous photo-Fenton pretreatment upon the biodegradation of anthraquinone sulfonate in waste-water treatment, Appl. Catal. B 3 (1993) 85-99.

[27] C. Pulgarin, J. Kiwi, Overview on photocatalytic and electrocatalytic pretreatment of industrial non-biodegradable pollutants and pesticides, Chimia 50 (1996) 50-55.

[28] Y.W. Kang, K. Hwang, Effects of reaction conditions on the oxidation efficiency in the Fenton process, Water Res. 34 (2000) 2786-2790.

[29] D. Hermosilla, N. Merayo, R. Ordoñez, A. Blanco, Optimization of conventional Fenton and ultraviolet-assisted oxidation processes for the treatment of reverse osmosis retentate from a paper mill, Waste Manage. 32 (2012) 1236-1243.

[30] R.T.S.M. Lakshmi, M.K. Vyas, A.S. Brar, I.K. Varma, Synthesis and characterization of sulphonated PEES copolymers by NMR spectroscopy, Eur. Polym. J. 42 (2006) 1423-1432.

[31] N. Merayo, D. Hermosilla, C. Negro, A. Blanco, On-line FTIR as a novel tool to monitor Fenton processes behaviour, Chem. Eng. J. 232 (2013) 519-526.

[32] K.P.C. Vollhardt, N.E. Schore, Organic Chemistry: Structure and Function, 6th Ed., W.H. Freeman and Co., Reston (VA), USA, 2011.

[33] V.Maurino, P.Calza, C.Minero, E.Pehzzettl, M.Vincenti, Light assisted 1,4-dioxane degradation, Chemosphere 35 (1997) 2675-2688.

Table 1. Estimated regression coefficients and standard errors for quadratic model used in RSM analysis.

	Coefficient	Standard error
Constant	39.509	3.851
pH (X1)	-5.489	1.671
$[H_2O_2]_0/COD_0$ (X2)	11.503	1.656
$[H_2O_2]_0/[Fe^{2+}]_0$ (X3)	-6.046	1.669
$X1^2$	4.000	2.866
$X2^2$	-2.625	3.283
$X3^2$	-4.550	2.908
X1·X2	-2.679	1.990
X2·X3	0.083	1.986
X1·X3	3.836	2.022

Figure captions

Figure 1. Reference spectra for the main chemicals that are expected to be found along the Fenton oxidation treatment of 1,4-dioxane.

Figure 2. Response surface and contour plot for the reduction of the COD resulting in the Fenton treatment of 1,4-dioxane (247.8 mg·L^{-1}) being performed at different pH and reagents concentrations values (T = 25ºC).

Figure 3. Pareto chart including the degree of influence of each considered factor in the Fenton treatment of 1,4-dioxane.

Figure 4. Evolution of FTIR spectra within the 2000-750 cm^{-1} region along the Fenton treatment of 1,4-dioxane. *Reaction conditions*: [1,4-dioxane]=70 mmol, pH=2.8±0.2, $[H_2O_2]_0/[Fe^{2+}]_0=5$.

Figure 5. FTIR-absorbance profiles of the main identified by-products that are produced during the Fenton oxidation of 1,4-dioxane. *Reaction conditions*: [1,4-dioxane]=70 mmol, pH=2.8±0.2, $[H_2O_2]_0/[Fe^{2+}]_0=5$.

Figure 6. FTIR-absorbance profiles representing the evolution of representative peaks along the degradation of 1,4-dioxane by Fenton's reagent within the spectral region of 2000-750 cm^{-1} (989 cm^{-1}: ethylene glycol and methoxyacetic acid; 1631 cm^{-1}: glycolic acid, oxalate anion, and oxalic acid; 1581 cm^{-1}: oxalate anion; 1380 cm^{-1}: 1,4-dioxane, ethylene glycol diformate, and formic

acid; 1715 cm^{-1}: ethylene glycol diformate, methoxyacetic acid, and formic acid).*Reaction conditions*: [1,4-dioxane]=70 mmol, pH=2.8±0.2, $[H_2O_2]_0/[Fe^{2+}]_0=5$.

Scheme 1. Degradation mechanism generating ethylene glycol mono- and diformate from 1,4-dioxane

Scheme 2. Degradation route for the acidic hydrolysis of ethylene glycol diformate into ethylene glycol and formic acid.

Scheme 3. Degradation route producing glycolic and oxalic acid from ethylene glycol.

FIGURE 1

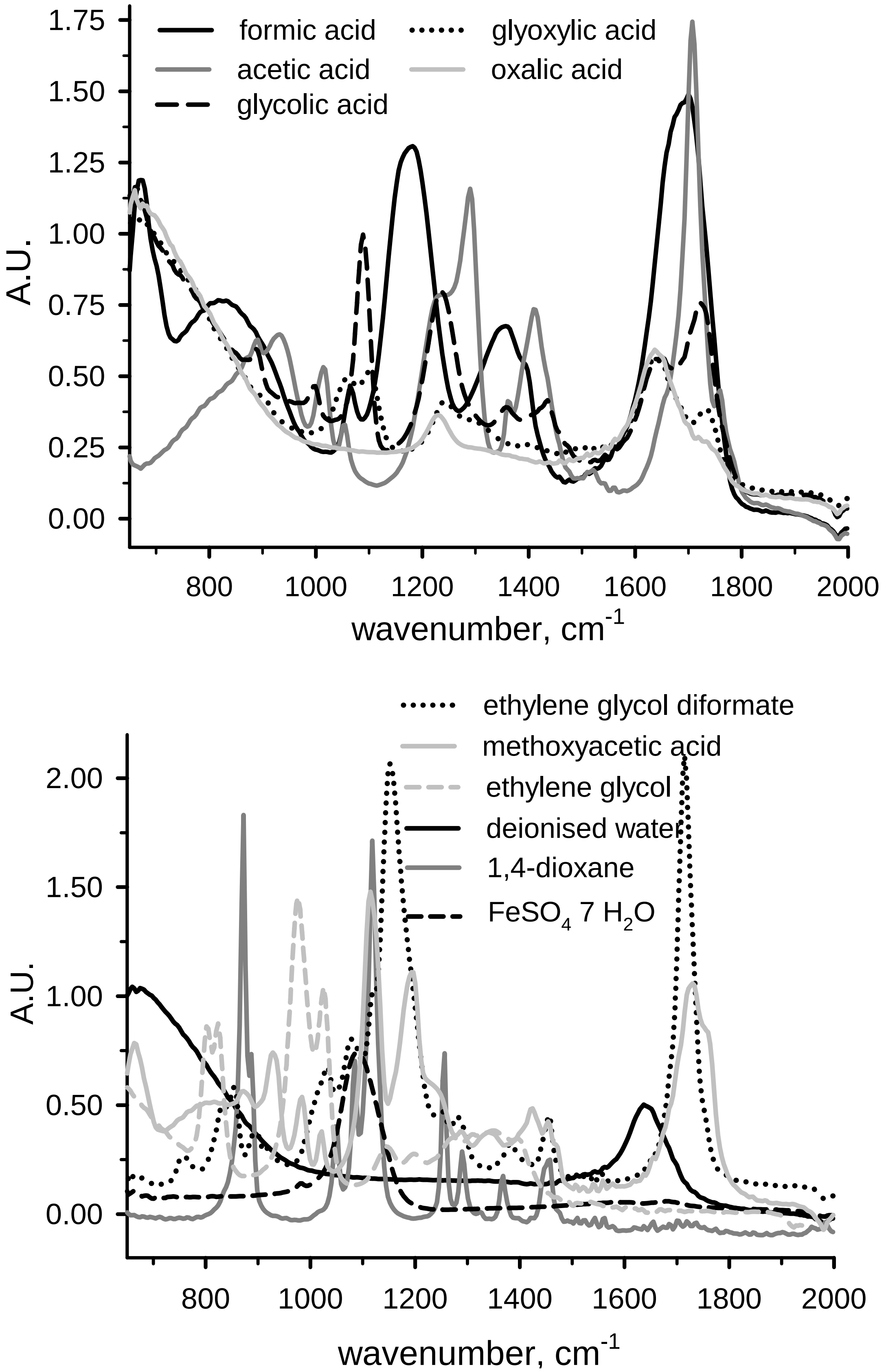

formic acid
acetic acid
glycolic acid
glyoxylic acid
oxalic acid
A.U.
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
800
1000
1200
1400
1600
1800
2000
wavenumber, cm^{-1}
ethylene glycol diformate
methoxyacetic acid
ethylene glycol
deionised water
1,4-dioxane
$FeSO_4$ 7 H_2O
A.U.
2.00
1.50
1.00
0.50
0.00
800
1000
1200
1400
1600
1800
2000
wavenumber, cm^{-1}

FIGURE 2

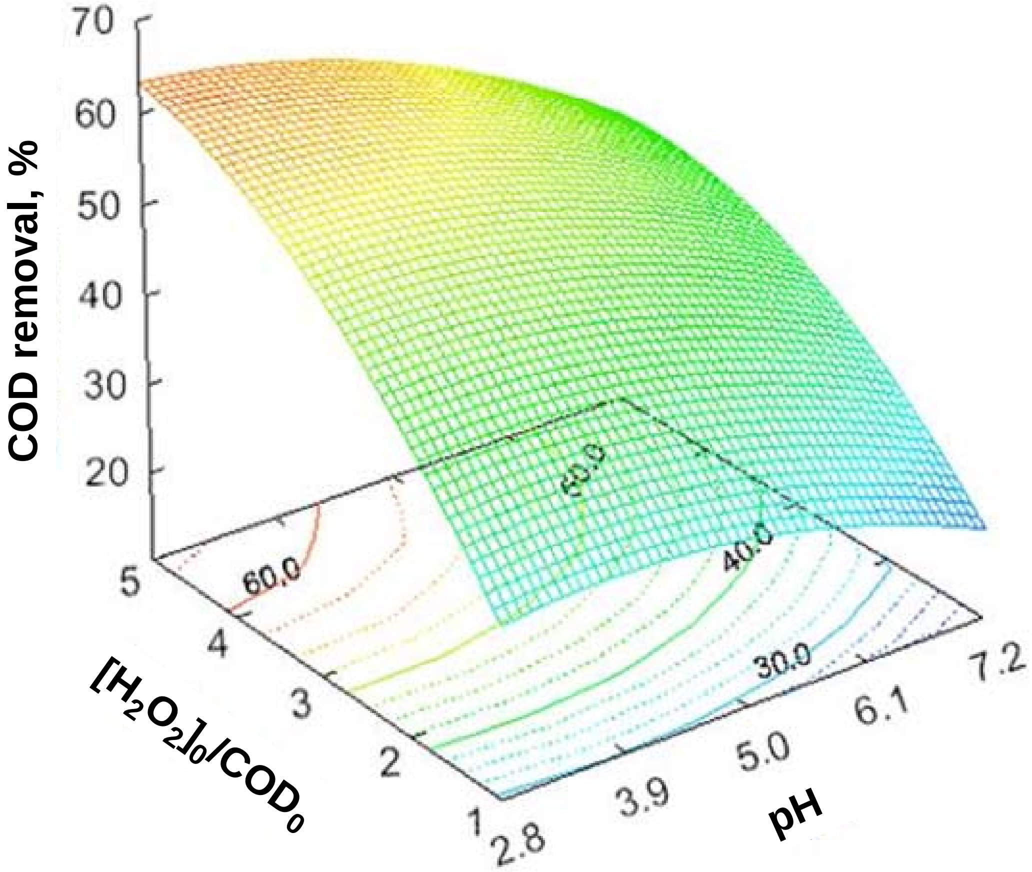

COD removal, %
70
60
50
40
30
20
$[H_2O_2]_0/COD_0$
5
4
3
2
1
pH
2.8
3.9
5.0
6.1
7.2
60.0
50.0
40.0
30.0

FIGURE 3

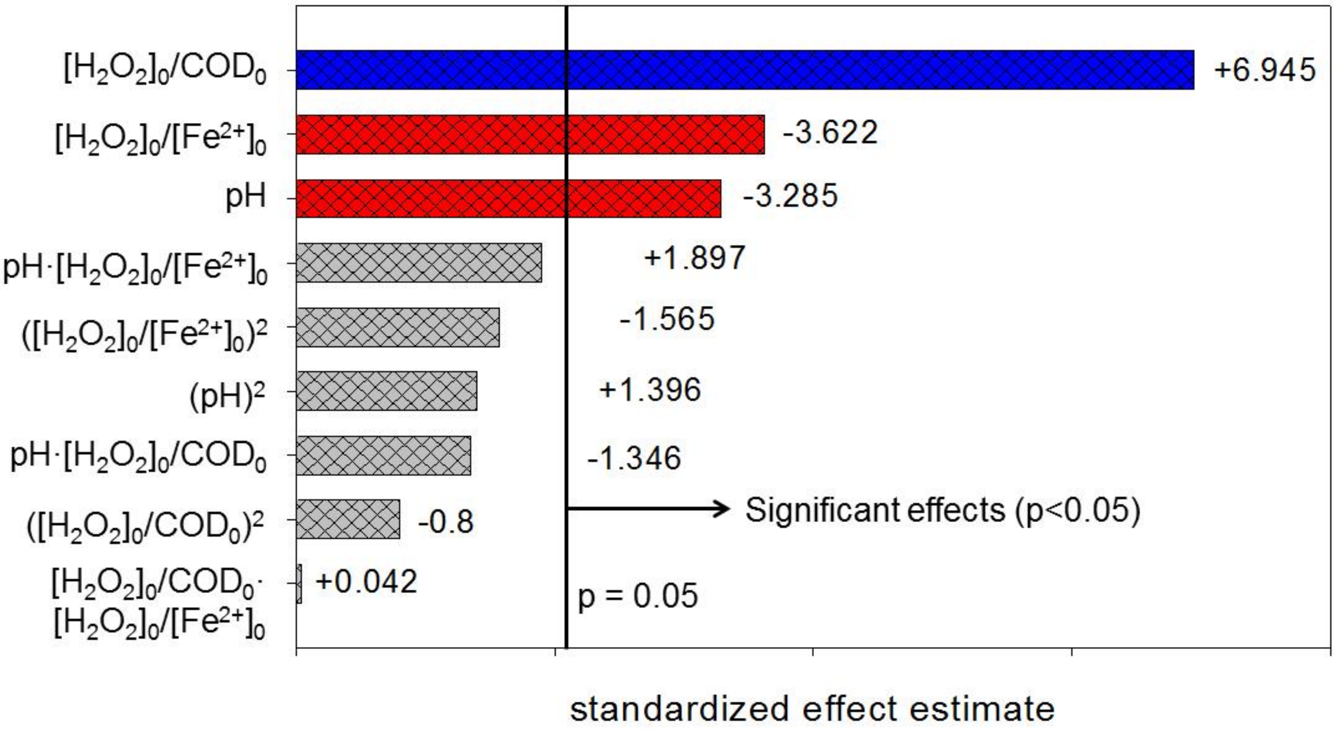

[H2O2]0/COD0
[H2O2]0/[Fe2+]0
pH
pH·[H2O2]0/[Fe2+]0
([H2O2]0/[Fe2+]0)2
(pH)2
pH·[H2O2]0/COD0
([H2O2]0/COD0)2
[H2O2]0/COD0·[H2O2]0/[Fe2+]0
+6.945
-3.622
-3.285
+1.897
-1.565
+1.396
-1.346
-0.8
+0.042
Significant effects (p<0.05)
p = 0.05
standardized effect estimate

FIGURE 4

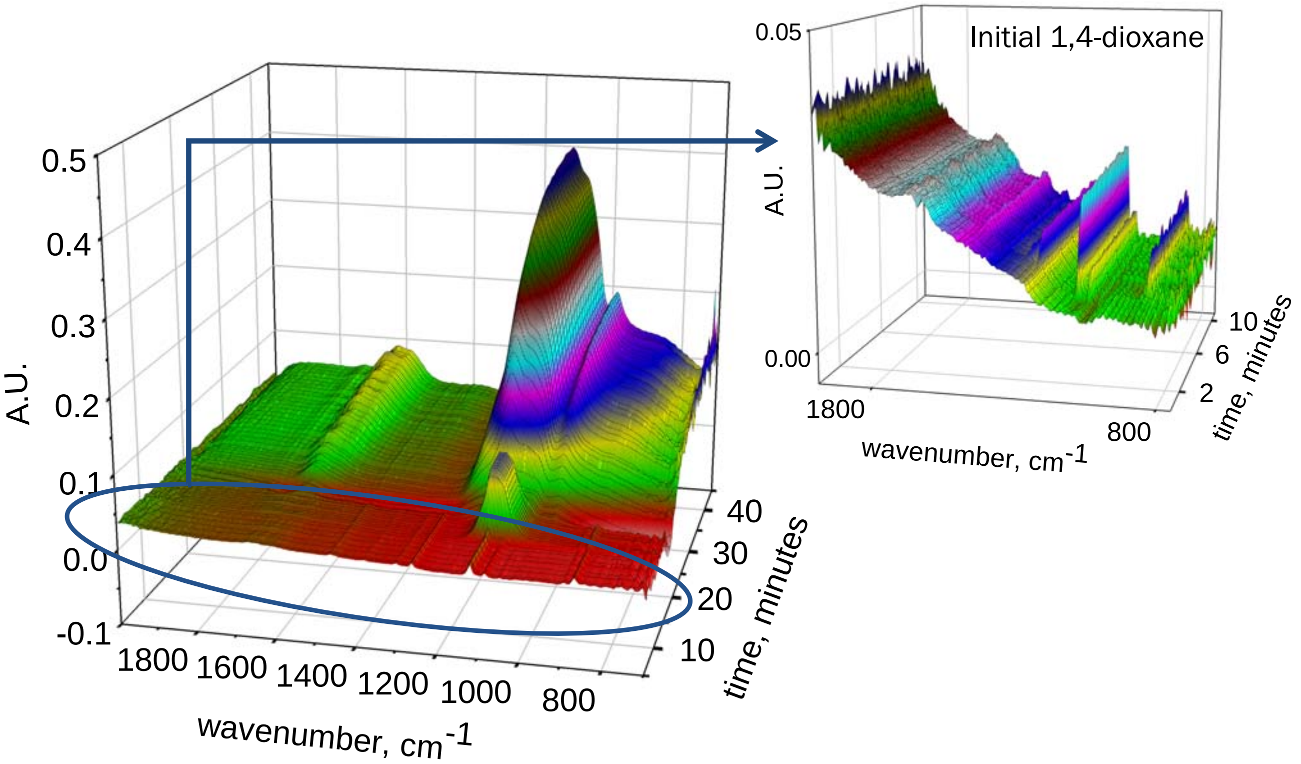

0.5
0.4
0.3
0.2
0.1
0.0
-0.1
A.U.
1800
1600
1400
1200
1000
800
wavenumber, cm^{-1}
40
30
20
10
time, minutes
0.05
Initial 1,4-dioxane
A.U.
0.00
1800
800
wavenumber, cm^{-1}
10
6
2
time, minutes

FIGURE 5

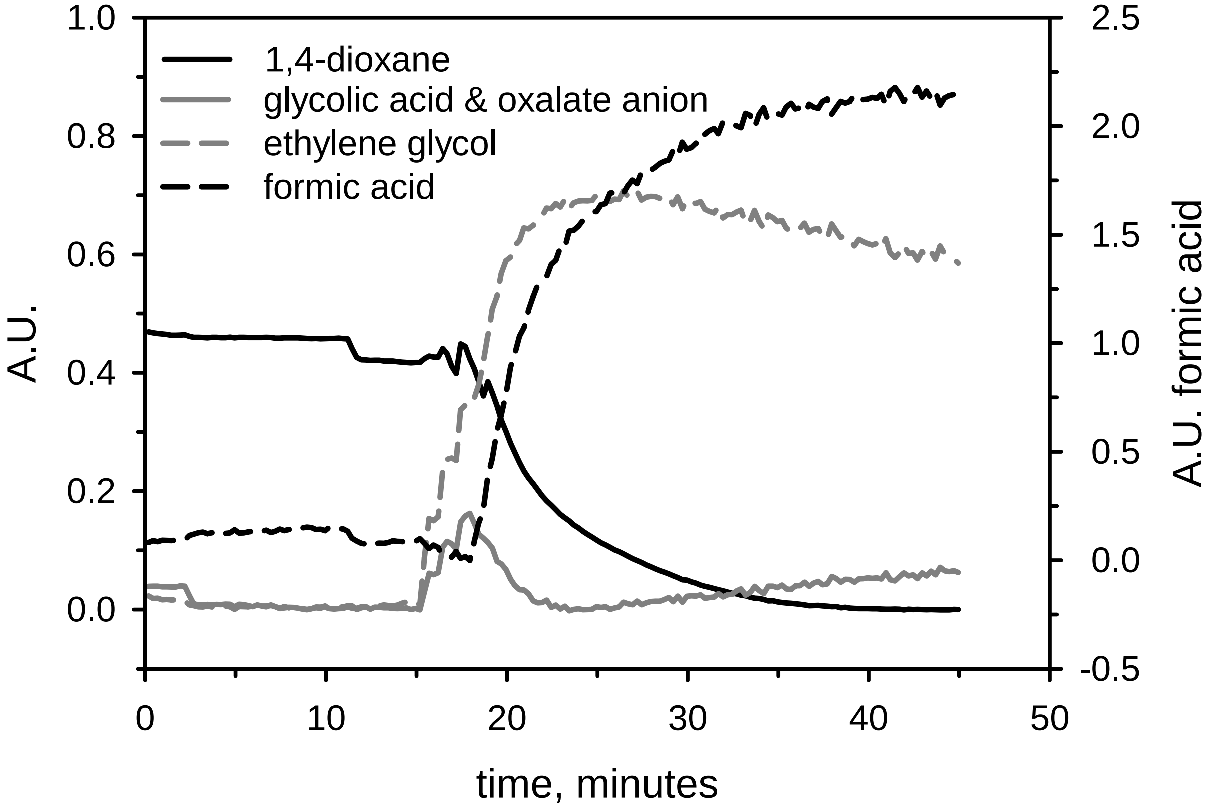
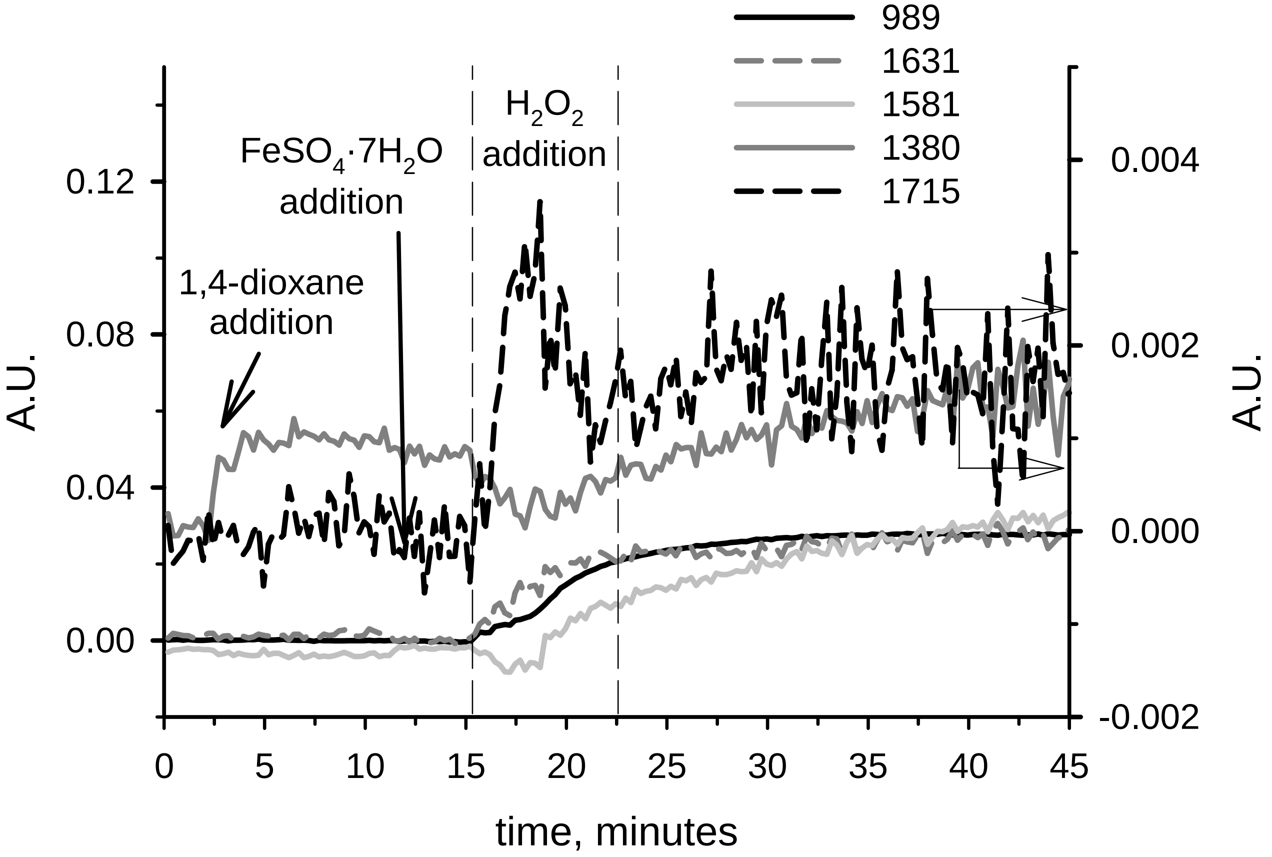
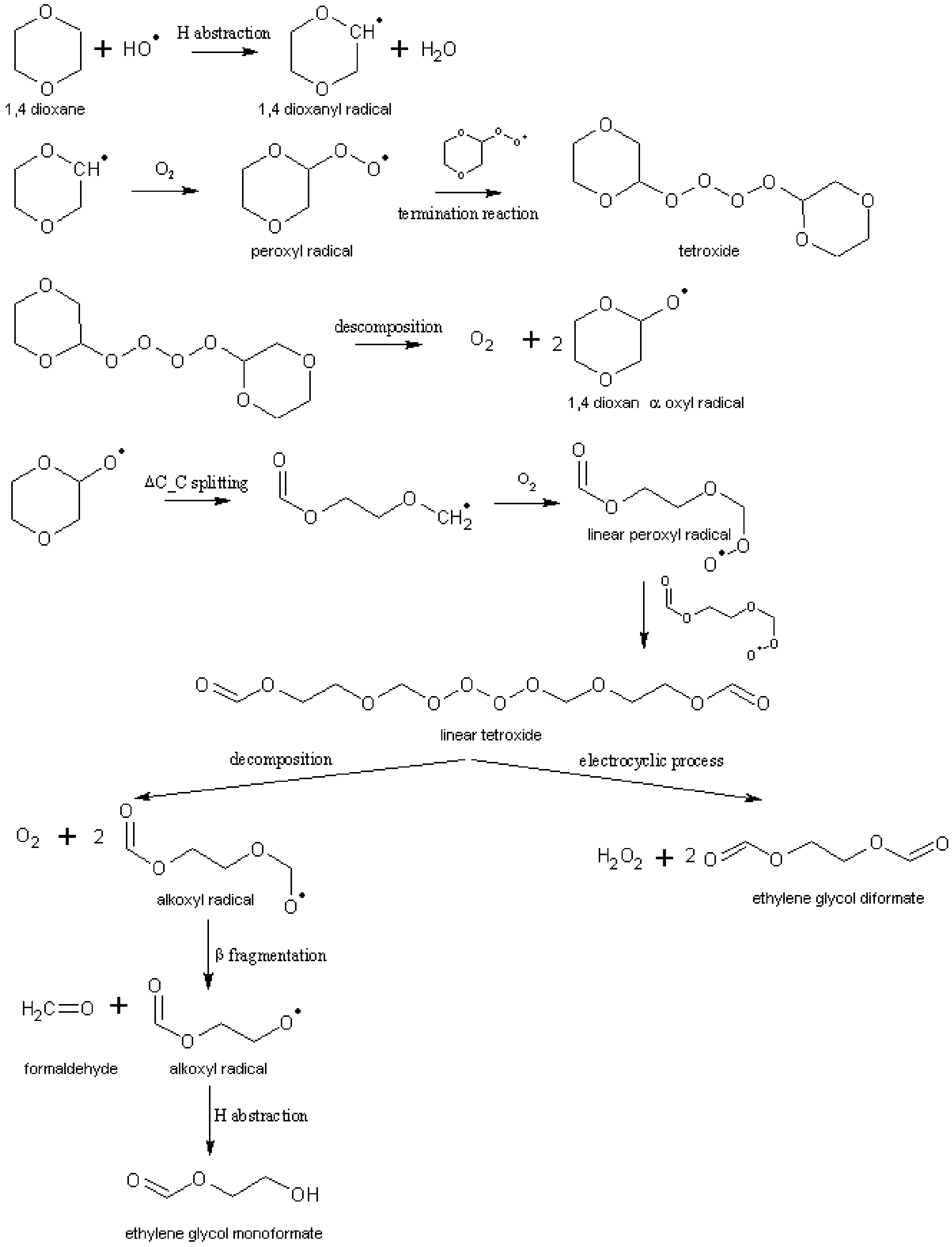

1,4-dioxane
glycolic acid & oxalate anion
ethylene glycol
formic acid
A.U.
1.0
0.8
0.6
0.4
0.2
0.0
A.U. formic acid
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0
10
20
30
40
50
time, minutes

FIGURE 6

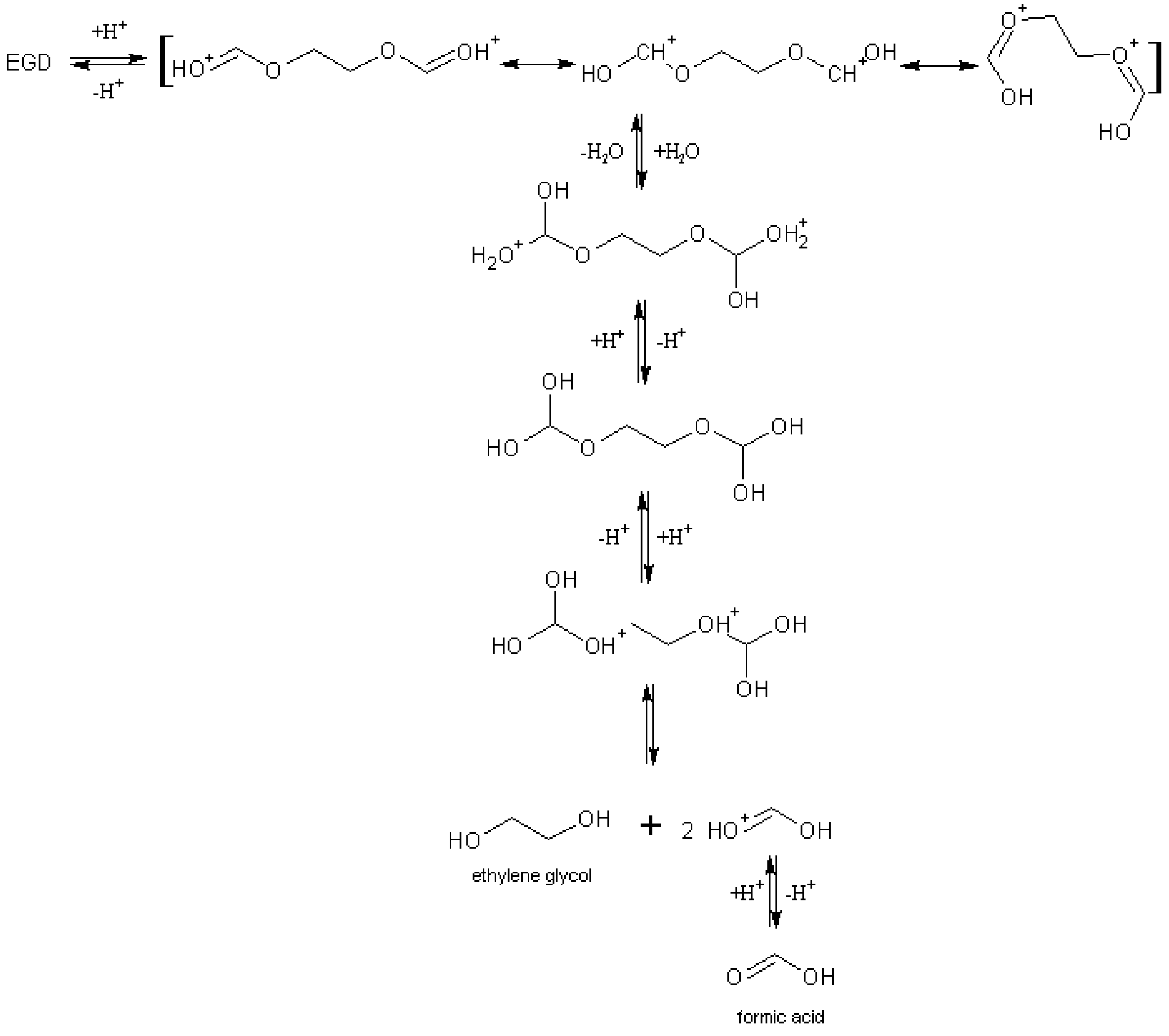


989
1631
1581
1380
1715
1,4-dioxane addition
FeSO4·7H2O addition
H2O2 addition
A.U.
A.U.
time, minutes
0.12
0.08
0.04
0.00
0.004
0.002
0.000
-0.002
0
5
10
15
20
25
30
35
40
45

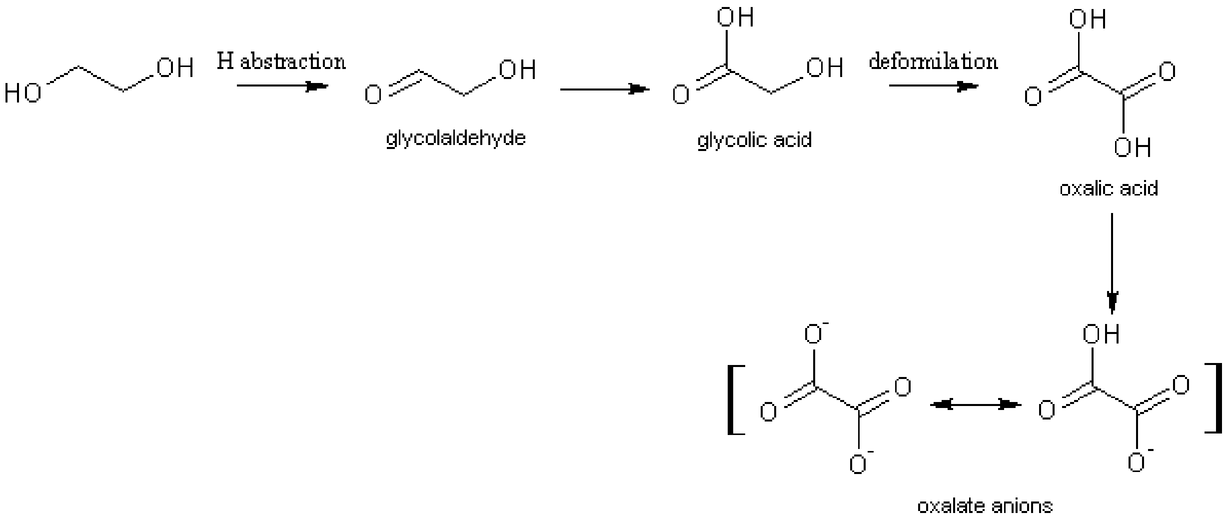
SCHEME 1


H abstraction
1,4 dioxane
1,4 dioxanyl radical
O2
termination reaction
peroxyl radical
tetroxide
descomposition
1,4 dioxan α oxyl radical
ΔC_C splitting
O2
linear peroxyl radical
linear tetroxide
decomposition
electrocyclic process
alkoxyl radical
ethylene glycol diformate
β fragmentation
formaldehyde
alkoxyl radical
H abstraction
ethylene glycol monoformate

SCHEME 2



SCHEME 3


H abstraction
glycolaldehyde
glycolic acid
deformilation
oxalic acid
oxalate anions