Electro–oxidation of industrial wastewater containing 1,4-dioxane in the presence of different salts

H. Barndõk, D. Hermosilla*, L. Cortijo, E. Torres, Á. Blanco

Department of Chemical Engineering, Universidad Complutense de Madrid, Avda. Complutense, s/n, 28040 Madrid. E-mail addresses (in order of appearance): hbarndok@quim.ucm.es, dhermosilla@quim.ucm.es, lcortijo@quim.ucm.es, cetorres@quim.ucm.es, ablanco@quim.ucm.es

* Corresponding author:
Daphne Hermosilla
Tel.: +34 91 394 4645; fax: +34 91 394 4243.
E-mail address: dhermosilla@quim.ucm.es

Abstract

The treatment of 1,4-dioxane solution by electrochemical oxidation on boron-doped diamond was studied using a central composite design and the response surface methodology to investigate the use of SO_4^{2-} and HCO_3^- as supporting electrolytes considering the applied electric current, initial COD value, and treatment time. Two industrial effluents containing bicarbonate alkalinity, one just carrying 1,4-dioxane (S1), and another one including 1,4-dioxane and 2-methyl-1,3-dioxolane (S2), were treated under optimized conditions, and subsequently subjected to biodegradability assays with *Pseudomonas putida* culture. Electro-oxidation was compared with ozone oxidation (O_3) and its combination with hydrogen peroxide (O_3/H_2O_2). Regarding the experimental design, the optimal compromise for maximum COD removal at minimum energy consumption was shown at the maximum tested concentrations of SO_4^{2-} and HCO_3^- (41.6 and 32.8 $mEq\cdot L^{-1}$, respectively), and the maximum selected initial COD (750 $mg\cdot L^{-1}$), applying a current density of 11.9 $mA\cdot cm^{-2}$ for 3.8 hours. Up to a 98% of the COD was removed in the electro–oxidation treatment of S1 effluent using 114 kWh per kg of removed COD; and about a 91% of the COD from S2 wastewater applying 49 kWh per kg of removed COD. The optimal biodegradability enhancement was achieved after 1 h of electro-oxidation treatment. In comparison with O_3 and O_3/H_2O_2 alternatives, electrochemical oxidation achieved the fastest degradation rate per oxidant consumption unit; as well as it also resulted to be the most economical treatment in terms of kWh consumption and price per unit of removed COD.

Keywords: electro-oxidation; 1,4-dioxane; boron doped diamond; biodegradability; *Pseudomonas putida*; central composite design; surface response methodology

1. Introduction

1,4-dioxane is widely used as an industrial solvent and it is also a common by-product of several chemical processes. Therefore, its occurrence in industrial effluents is an emerging issue that may contribute to a continuous xenobiotic contamination of groundwater and drinking water if it is not removed previously. In fact, there is a growing concern about the occurrence of 1,4-dioxane in water because of its impact on human health. 1,4-dioxane is known to cause liver damage and kidney failure; and it has been reported to potentially promote cancer based on the evidence of carcinogenicity tests in animals, resulting classified as a Group 2B (probable) human carcinogen (Adams *et al*. 1994; Choi *et al*. 2010; ECB 2002; USEPA 2010; Zenker *et al*. 2003).

Owing to its high water solubility and resistance to biodegradation, conventional wastewater treatment processes are generally inefficient for 1,4-dioxane removal (Zenker *et al*. 2003); although some modified biological processes have been reported viable for degrading 1,4-dioxane at a low initial concentration and at very long residence time (Han *et al*. 2012; Shen *et al*. 2008; Zenker *et al*. 2004).

Advanced oxidation processes (AOPs) are currently recognized as effective for the removal of biorefractory organic substances (Balcioglu *et al*. 2003; Coleman *et al*. 2007; Comninellis *et al*. 2008). The degradation of 1,4-dioxane has actually been carried out by several combinations of AOPs, namely: sonochemical decomposition enhanced by ferrous ion (Beckett and Hua 2003), photochemical degradation enhanced by H_2O_2 (Maurino *et al*. 1997; Stefan and Bolton 1998), ozonation combined with H_2O_2 (Adams *et al*. 1994; Barndõk *et al*. 2013), photocatalysis combined with electro-oxidation (Yanagida *et al*. 2008), and electro-oxidation (Choi *et al*. 2010).

The main advantage of electro-oxidation over other AOPs is that this treatment does not require the presence of additional oxidants, like hydrogen peroxide (H_2O_2).

Particularly, boron doped diamond (BDD) is considered the most efficient electrode material for anodic oxidation due to its significant chemical and electrochemical stability, good conductivity, and very high current efficiency, resulting in increased rates of effluent mineralization; since during the treatment by BDD electrodes, most degradation is expected to occur via reaction with the OH· radicals that are generated on the anode without requiring the use of additional oxidizing agents (Comninellis *et al.* 2008; Rodrigo *et al.* 2010; Vasudevan and Oturan 2013).

On the other hand, electrolysis requires the presence of electrical conductivity. Therefore, the presence of different salts in the water matrix is an important factor to be considered. Various supporting electrolytes have been evaluated for the degradation of recalcitrant organics in synthetic solution, and sulphate has often been reported to be the most effective regarding degradation improvement (Cañizares *et al.* 2009a; Murugananthan *et al.* 2010; Velegraki *et al.* 2010).

However, the presence of diverse salts and bicarbonate alkalinity in industrial wastewater are often inevitable and non-optional. The use of bicarbonate as a supporting electrolyte has generally been overlooked most likely due to its radical scavenging effect, which has been reported to occur in many AOPs (Beckett and Hua 2003). For example, Adams *et al.* (1994) reported that both, the presence of bicarbonate and the competition by 2-methyl-1,3-dioxolane (MDO), increase the required dose of O_3/H_2O_2 for the oxidation of 1,4-dioxane in synthetic water. However, this has not been confirmed in industrial effluents yet. Although 1,4-dioxane is usually referred to as a contaminant of industrial wastewater, the studies on its degradation by AOPs (Beckett and Hua 2003; Choi *et al.* 2010; Barndõk *et al.* 2013; Maurino *et al.* 1997; Stefan and Bolton 1998; Yanagida *et al.* 2008) have almost all been performed using synthetic solutions; besides the particular exception of Fenton reaction. In this case, a considerably slower rate of organic carbon removal (11% of TOC in 10 h) was observed (Klecka and Gonsior 1986).

The electrochemical treatment of industrial wastewater contaminated by 1,4-dioxane and its by-products, (e.g. MDO; ECB 2002) in an effluent where the presence of HCO_3^- could theoretically provide the necessary conductivity for electrolysis has not been reported yet. Therefore, the treatment of 1,4-dioxane by electrochemical oxidation on BDD electrodes was studied by a central composite design and using response surface methodology in order to assess the use of SO_4^{2-} and HCO_3^- as supporting electrolytes considering different levels for the applied electric current, initial COD, and treatment time. The treatment of industrial effluents in the presence of bicarbonate alkalinity was studied under optimized conditions, and electrochemically treated industrial samples were subsequently subjected to biodegradability assay by *Pseudomonas putida*. The cost analysis of this treatment, and a comparison with other AOPs (O_3 oxidation and O_3 combined with H_2O_2), were also carried out.

2. Materials and methods

2.1. Materials

Treatment optimization was carried out using a synthetic solution of 1,4-dioxane. This solution was prepared prior to experiments with ultra-pure deionized water containing the electrolyte salts that were previously added. The final study performing electro-oxidation under optimized conditions and biodegradability assessment were performed using industrial effluent samples out-flowing biological treatment that were supplied by a particular factory. Two industrial samples were treated (Table 1), both in the presence of bicarbonate alkalinity: one just containing 1,4-dioxane (S1); and the other one carrying both 1,4-dioxane and MDO (S2).

All used chemicals were of analytical grade. 1,4-dioxane (99.8%) was provided by Sigma-Aldrich® Chemie GmbH (Steinheim, Germany). The supporting electrolytes that were used for electrochemical treatment were sodium sulphate (Na_2SO_4, 99.0%) and sodium hydrogen carbonate ($NaHCO_3$, 99.7%), supplied by PANREAC S.A. (Barcelona, Spain).

Pseudomonas putida CECT 324 came from the Spanish Type Culture Collection (Colección Española de Cultivos Tipo, Valencia, Spain). Cultures were grown at pH=7 in 1 $g \cdot L^{-1}$ of beef extract, 1 $g \cdot L^{-1}$ of yeast extract, 5 $g \cdot L^{-1}$ of peptone, and 5 $g \cdot L^{-1}$ of NaCl; and kept at -80 ºC in a cryogenic solution (glycerol 87%). The mineral solution added to the culture medium in the biodegradability assays was made of 0.5 $g \cdot L^{-1}$ of NH_4Cl, 0.5 $g \cdot L^{-1}$ of K_2HPO_4, 0.5 $g \cdot L^{-1}$ of KH_2PO_4, 0.5 $g \cdot L^{-1}$ of $MgSO_4 \cdot 7H_2O$, and 10 $ml \cdot L^{-1}$ of trace minerals solution providing a final concentration of 0.6 $mg \cdot L^{-1}$ of $FeSO_4 \cdot 7H_2O$, 0.2 $mg \cdot L^{-1}$ of $CoCl_2$, 0.2 $mg \cdot L^{-1}$ of $MnSO_4 \cdot H_2O$, and 0.2 $mg \cdot L^{-1}$ of $CuSO_4 \cdot 5H_2O$.

2.2. Analytical methods

Chemical oxygen demand (COD) was measured, according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2005), by the colorimetric method at 600 nm using an Aquamate-spectrophotometer (Thermos Scientific AQA 091801, Waltham, USA). Total organic carbon (TOC) was measured using a TOC/TN analyzer multi N/C® 3100 (Analytik Jena AG, Jena, Germany) with catalytic oxidation on cerium oxide at 850ºC. The quantitative determination of 1,4-dioxane and MDO was done by gas−liquid chromatography (GLC) on 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 analysed 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 programme: 80°C to 240°C after a 9 min initial hold and at a 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 internal standard, and the software *GC-ChemStation Rev.B.04.02 (96)* from Agilent.

2.3. Electrochemical treatment

Electrochemical treatment was performed at ambient temperature (25 ºC) in an undivided rectangular electrolytic flow-cell (methacrylate, 10x7x15 cm^3) in a batch recirculation mode. Commercial BDD electrodes of 100 cm^2 (Metakem GmbH, Usingen, Germany) were used as both, anode and cathode, arranged parallel to each other at a distance of 2.4 cm. Experiments were carried out under galvanostatic conditions using AMEL potentiostat/galvanostat 7050 (AMEL Instruments, Milano, Italy) as power supply. The working solution (total volume of 1.5 L) was recirculated at a constant flow rate of 0.5 $L·min^{-1}$ by a peristaltic pump (Masterflex® Console Drive, Cole-Parmer Instrument Company, Illinois, USA). Electrodes were fed with ordinary grade air (passed through polycarbonate filters) at a 4.5 $L·min^{-1}$ rate to facilitate mass transfer in the reactor. Na_2SO_4 and $NaHCO_3$ were added as supporting electrolytes at different concentrations. The pH of the solution was not controlled, and it increased from 8.0-8.5 up to 9.0-9.5 during the process. All the experiments were performed for 5 hours.

2.4. Experimental design

Central composite design and response surface methodology were applied to optimize the treatment of 1,4-dioxane in synthetic solution. Four factors were initially chosen to evaluate the influence of operating parameters on the efficiency of electro-oxidation: the concentrations (mEq·L^{-1}) of the supporting electrolytes, sulphate (X_1) and bicarbonate (X_2); the initial COD of the solution (X_3, mg·L^{-1}); and the applied current density (X_4, mA·cm^{-2}).

A total of 31 experiments were carried out, including a 2^4 full factorial design, augmented by 8 axial points, 4 replications at the centre point, and 3 extra points chosen for a better definition of the extremes. The levels for the independent variables (Table 2) were chosen considering the local sulphate limit for effluent discharge to the municipal treatment ($[SO_4^{2-}]_{lim}$=1000 mg·L^{-1}=20.8 mEq·L^{-1} , in Madrid), the actual alkalinity and COD of the real industrial effluent ($[HCO_3^-]$=900-1000 mg·L^{-1}=14.8-16.4 mEq· L^{-1}; COD_{S1}=450-500 mg·L^{-1}≈250 mg·L^{-1} of 1,4-dioxane in S1 effluent), and preliminary experiments changing the applied current, which were performed prior to the current study taking into account the example of Choi *et al.* (2010).

The studied responses were: Y_1= COD removal (%); Y_2=amount of removed COD (ΔCOD, kgCOD$_{removed}$·m^{-3}); Y_3=total current efficiency (TCE); and Y_4, energy consumption (EC, kWh·kgCOD$_{removed}^{-1}$) Particularly, TCE and EC were calculated by Equation 1 and 2 (Montilla *et al.* 2002; Panizza *et al.* 2001):

$$TCE = 4FV \cdot \left(\frac{COD_0 - COD_t}{I \cdot t} \right), \qquad \text{(Eq. 1)}$$

where COD_0 and COD_t (mol O_2·m^{-3}) are the values of initial COD and the COD at treatment time t, respectively. I (A) is the applied current intensity, F (C/mol) is the Faraday constant, and V (m^3) is the volume of the sample solution.

$$EC = \frac{(\text{t}\cdot\text{I}\cdot\text{U/V})\cdot 10^{-3}}{(COD_0 - COD_t)\cdot 10^{-6}}, \qquad \text{(Eq. 2)}$$

where COD_0 and COD_t (mol $O_2\cdot m^{-3}$), I (A), and V (L) are the same variables as in Eq. 1;and U (V) is average cell voltage.

All the resulting responses (Y_1-Y_4) were obtained for 1, 2, 3, 4 and 5 h of the electrochemical process (complete number of process responses = 4·5 = 20). Finally, to reduce the number of responses (20) and to obtain 4 comprehensive regression models, reaction time was added to the list of factors as a fifth independent variable X_5 (h). Therefore, the final experimental design resulted five times bigger in terms of the total number of experimental points became 31·5=155. This magnification of the design is described schematically in Table 3 along with the complete set of the results for COD removal (Y_1).

Regression analyses were carried out using the following quadratic model:

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i=1}^{k}\sum_{j=1}^{k} b_{ij} X_i X_j , \qquad \text{(Eq. 3)}$$

where Y is the process response, and $X_i \ldots X_k$ (k=5) are the above considered independent variables.

Experimental data were analyzed using both Systat 13 (SYSTAT Software Inc., Chicago, USA) and Minitab 16 (Minitab Inc., State College, USA).

2.5. Biodegradability assays using Pseudomonas putida

Electrochemically treated industrial effluents samples were subsequently subjected to biodegradability assays with *Pseudomonas putida* cultures. The bacterial stock described in the methodology was previously melted at room temperature and cleaned twice with saline solution by centrifuging at 10000 rpm for 5 min, removing the baseline medium, and substituting it with a 0.9% NaCl solution in order to remove the baseline COD provided by the organic growth medium and the glycerol solution. The sample pH was adjusted to 7.0 adding 1N HCl . A culture medium sample made up of 40 mL of sample and 10 mL of the mineral solution described above, was inoculated with 200 µL of cleaned bacterial stock and incubated at 30 ºC for 100 hours inside 250-mL Erlenmeyer flasks placed on a rotary platform. Assays were passed through 0.20-µm syringe filters (Minisart SRP 15, Sartorius Stedim Biotech, GmbH Germany) and analyzed for COD, TOC, and 1,4-dioxane and MDO contents; taking into account the dilution ratio resulting from the addition of the mineral solution.

3. Results and discussion

3.1. Optimization of the electrochemical treatment of 1,4-dioxane in synthetic solution by experimental design.

The complete set of experimental results for COD removal, ΔCOD, TCE and EC are presented in Table 4. The quadratic models for the responses Y_1, Y_2, Y_3 and Y_4, based on these results, resulted all highly significant according to the high F and low p values resulting from the performed analysis of variance (ANOVA): $F(Y_1)=129.53$ ($p<0.0001$) for COD removal, $F(Y_2)=133.23$ ($p<0.0001$) for ΔCOD, $F(Y_3)=134.39$ ($p<0.0001$) for TCE, and $F(Y_4)=213.45$ ($p<0.0001$) for EC. The constants (b values of Eq. 3, where X_1, X_2, X_3, X_4 and X_5 are the coded independent variables) for the obtained second order regression models for these four process responses are shown in Table 5. When plotting the experimental results against the values calculated by these quadratic models, the model prediction accuracy in terms of R^2 of the linear regression was 95.08% for COD removal, 95.21% for ΔCOD, 95.25% for TCE, and 96.96% for EC. These regression coefficients, along with the predicted and adjusted R^2 (R^2_{pred} and R^2_{adj}), are also included in Table 5.

Figs. 1 and 2 report 3D response surfaces of each model as a function of two influential process parameters, while keeping constant the other 3 process variables at their designed middle level (X_i=0; [SO_4^{2-}]=20.8 mEq·L^{-1}, [HCO_3^-]=16.4 mEq·L^{-1}, and [COD]$_0$=450 mg·L^{-1} for Fig. 1; and [SO_4^{2-}]=20.8 mEq·L^{-1}, [HCO_3^-]=16.4 mEq·L^{-1}, and time=3 h for Fig. 2). Reaction time was the most important factor increasing COD removal (Fig. 1a), which agrees to the standardized effect estimates of each model component, and model analyses performed by ANOVA. The percentage contribution based on the portion of the sums of squares in ANOVA (Dopar *et al*. 2011; Yetilmezsoy *et al*. 2009) was 55.7 and 37.3 % for time (X_5) in the models of COD removal and ΔCOD, respectively. Up to the 100% COD removal could be achieved in 5 hours of electro-oxidation (≈130 kWh/kgCOD$_{removed}$$^{-1}$); whereas about the 85% of the COD was already removed in 3 h (≈85 kWh/kgCOD$_{removed}$$^{-1}$). Applied current density (*j*) also had an important positive influence on COD removal. The percentage contribution of *j* to COD removal and ΔCOD in the models was 23.8 and 26.6 %, respectively. However, the surface curvature reached a plateau around 12 mA·cm^{-2}, showing that a further increase in *j* does not bring along a significant COD removal increase.

The response surface for TCE (Fig. 1.b) shows an opposite tendency, that is, electric current efficiency was highest at the lowest applied current density and at the shortest reaction time. As COD decreases in time, more current excess was gradually provided for its oxidation. This current did not further contribute to the degradation of such a low initial COD because the process was limited by mass transportation instead (Montilla *et al*. 2002; Panizza *et al*. 2001). For instance, TCE dropped from about 0.75 at 1 hour of treatment to approximately 0.4 after 5 h when using *j*=12 mA·cm^{-2}.

Although the percentage of COD removal was greater when performing the process using a lower initial COD, the actual amount of COD removed in terms of kg per sample volume (Fig. 2a), and therefore TCE and EC as well (Fig. 2b), resulted greater when adding a higher initial COD value. The percentage contributions of COD_0 to explain the models for ΔCOD, TCE and EC were 15.1, 35.0, and 18.6%, respectively. As shown in Fig. 2a, ≈0.13 $kg \cdot m^{-3}$ (nearly a 90 %) of the COD was removed in 3 hours of electro-oxidation at 12 $mA \cdot cm^{-2}$ when the initial COD was 150 $mg \cdot L^{-1}$; whereas much greater amount of COD (≈0.55 $kg \cdot m^{-3}$) was removed under the same conditions when COD_0 was 750 $mg \cdot L^{-1}$. The same pattern was shown for EC (Fig. 2b). Under the same reaction conditions, ≈190 kWh was consumed per 1 kg of COD removed when COD_0 was 150 $mg \cdot L^{-1}$; whereas much less EC (≈50 $kWh \cdot kgCOD_{removed}^{-1}$) was consumed when 750 $mg \cdot L^{-1}$ of COD_0 were used. However, the positive effect of *j* in increasing COD removal and ΔCOD was minimal at low initial COD values, which means that nearly the same result could be achieved using 2 $mA \cdot cm^{-2}$. Therefore, EC could substantially be reduced.

Regarding the effect of the supporting electrolyte, no radical scavenging effect in terms of a negative influence on COD removal was found for either SO_4^{2-} or HCO_3^-. On the contrary, the presence of both salts rather enhanced the process. While HCO_3^- was slightly more influential than SO_4^{2-} in increasing COD removal (and ΔCOD), their positive effect (significance in terms of $p \leq 0.05$) was rather small in the studied concentration range (Fig. 3a). The percentage contribution of SO_4^{2-} and HCO_3^- to the COD removal (Y_1) model was 0.7% and 1.6%, respectively. On the other hand, both salts were important factors to be considered for decreasing the consumption of kWh, meaning that their principal effect simply laid on providing the necessary conductivity for electrolysis. Neither the scavenging effect of bicarbonate, nor the additional oxidative effect of sulphate, played an important role in the oxidation process. As presented in Fig. 3b, SO_4^{2-} had a slightly greater effect on EC than HCO_3^- (percentage contributions based on the sums of squares were 7.3% and 5.3%, respectively), since the first one provides somewhat higher conductivity to the solution. However, differences were small, addressing that the natural bicarbonate alkalinity of certain wastewater may serve as a good electrolyte for performing electrochemical oxidation; just as good as SO_4^{2-} salts may be. To illustrate the discussion above, Fig. 4 shows the optimization plot for a maximum COD removal, ΔCOD and TCE at a minimum EC. The optimal compromise is reached in the presence of the maximum concentrations of both electrolytes (41.6 $mEq\cdot L^{-1}$ of SO_4^{2-} and 32.8 $mEq\cdot L^{-1}$ of HCO_3^-) when the maximum initial COD, of 750 $mg\cdot L^{-1}$ was used and a current density of 11.9 $mA\cdot cm^{-2}$ was applied for 3.8 hours.

3.2 Treatment of industrial wastewater containing 1,4-dioxane

3.2.1. Electrochemical degradation of industrial effluents.

Considering the results of the just reported experimental design, the electrochemical treatment of industrial effluents was carried out applying a current density of 12 $mA\cdot cm^{-2}$, in the presence of the initial bicarbonate alkalinity of the effluent (16.4 $mEq\cdot L^{-1}$), and using 20.8 $mEq\cdot L^{-1}$ of SO_4^{2-} as a supporting electrolyte, which is a concentration that still meets discharge limitation in force. As shown in Fig. 5, up to a 98% COD removal was achieved for S1 effluent after 5 h of treatment using 114 $kWh\cdot kgCOD_{removed}^{-1}$; and about a 91% of the COD was removed from S2 effluent using 49 $kWh\cdot kgCOD_{removed}^{-1}$ (≈60 $kWh\cdot m^{-3}$ were used in both cases). The results for the electrochemical oxidation of the S1 effluent (just containing 1,4-dioxane) resulted in a good correlation to the values predicted by the models resulting from the experimental design performed for a synthetic solution of 1,4-dioxane. After a 4 h treatment, which matches the treatment time recommended by the model optimizer, the following results were achieved: COD removal=93% (predicted: 96%), ΔCOD=0.48 kgCOD·m^{-3} (predicted: 0.50 kgCOD·m^{-3}), TCE=0.48 (predicted: 0.55), and EC=93 kWh·kgCOD$_{\text{removed}}^{-1}$ (predicted: 92 kWh·kgCOD$_{\text{removed}}^{-1}$). In fact, very good regression coefficients were achieved ($R^2_{COD\%}$=99.01%; $R^2_{\Delta COD}$=99.21%; R^2_{TCE}=99.27%; and R^2_{EC}=98.95%) when plotting the experimental results using industrial effluent against the model predictions reported using synthetic dioxane solution.

Fig. 6 illustrates the evolution of the biodegradability of S1 and S2 effluents along with the degradation of COD, TOC, and 1,4-dioxane and MDO contents during their electrochemical treatment. A nearly complete mineralization was achieved in the electrochemical treatment of S1, whereas an almost 90% of the TOC was removed from S2. The major part of 1,4-dioxane (about an 85% in both S1 and S2 effluents), as well as almost all MDO from S2 (≈90% removal) was degraded in 2 hours of electro-oxidation treatment (using ≈ 21 kWh·m^{-3} for both effluents). 1,4-dioxane removal was independent of the presence of MDO, following a similar trend in both effluents (Figs 6a and 6b). The degradation of dioxane was greater at the beginning of the experiment, and started slacking off in time as its concentration diminished. About a 60, 85 and 90% of the compound was degraded in 1, 2 and 3 hours of treatment, respectively. The removal of MDO from S2 (Fig 6b) otherwise appeared to be independent of its concentration, showing a linear degradation in time: about the 45 and a 90% removals were achieved after 1 and 2 hours of the process, respectively; and no MDO was detected after 3 h of electro-oxidation treatment.

The initial biodegradability of S1 effluent (5% of the initial COD) was significantly increased by the electrochemical process. After 1 hour of electro-oxidation treatment, the biodegradable part of the residual COD was 19%. A further treatment time did not lead to a further increase of the biodegradability of the solution, meaning either that the intermediates produced afterwards resulted less biodegradable, or that the remaining part of the organic matter was already too diluted for feeding bacteria. On the other hand, the biodegradability of S2 was initially higher (26% of the COD), which means that MDO is more susceptible to biodegradation. In fact, more than a 50% of the initial MDO content in S2 effluent was removed by the biological treatment with *Pseudomonas Putida*, whilst a negligible amount of 1,4-dioxane was degraded. As a result, the biodegradability of S2 effluent remained similar after a 1 h of electro-oxidation treatment (27% of the COD). However, considering overall results, almost a 50% of the COD, along with an 85% of the content of MDO, and 75% of 1,4-dioxane were removed by the combined process treatment of S2 effluent. If the starting solution for biodegradation was the resulting solution of a 2 h of electro-oxidation process, the biodegradability of S2 effluent decreased, meaning that the resulting intermediate products were less biodegradable. Considering these results, if electro-oxidation is to be used as a pre-treatment for such industrial effluents prior to a biological process, the optimal time for the advanced oxidation step with the current reactor design would be approximately of 1 hour applying a current density of 12 $mA \cdot cm^{-2}$ (≈ 10 $kWh \cdot m^{-3}$). However, further research should be conducted to monitor the evolution of biodegradability determined by several methods, and using a shorter time interval, in order to determine the precise optimal time for an electrochemical pre-treatment.

3.2.2. Comparing electro-oxidation with O_3 and O_3/H_2O_2 oxidation processes.

Regarding the economic assessment and feasibility of the electrochemical treatment compared with other AOPs, the results of the current study were compared with a previous work devoted to the treatment of the same effluents S1 and S2 by O_3 and O_3 combined with H_2O_2 oxidation processes (Hermosilla *et al*. 2011). To compare several

AOPs that use different oxidative agents, the so-called Oxygen-equivalent Chemical-oxidation Capacity (OCC) parameter was used, as proposed by Cañizares *et al*. (2009b) to quantify the amount of oxidant that were added to wastewater in comparable units (Equations 4 to 6):

$$OCC_{EO}\left(kgO_2m^{-3}\right)=Q\left(\frac{kAh}{m^3}\right)\frac{1kmol^{-}}{96487kAs^{-}}\frac{3600s}{1h}\frac{1kmolO_2}{4kmol^{-}}\frac{32kgO_2}{kmolO_2}=0.298Q\left(\frac{kAh}{m^3}\right) \qquad \text{(Eq. 4)}$$

$$OCC_{O_3}\left(kgO_2m^{-3}\right)=\left[O_3\right]\left(\frac{kgO_3}{m^3}\right)\frac{1kmolO_3}{48kgO_3}\frac{6kmol^{-}}{1kmolO_3}\frac{1kmolO_2}{4kmol^{-}}\frac{32kgO_2}{kmolO_2}=1.000\left[O_3\right]\left(\frac{kgO_3}{m^3}\right) \text{(Eq. 5)}$$

$$OCC_{H_2O_2}\left(kgO_2m^{-3}\right)=\left[H_2O_2\right]\left(\frac{kgH_2O_2}{m^3}\right)\frac{1kmolH_2O_2}{34kgH_2O_2}\frac{2kmol^{-}}{1kmolO_2}\frac{1kmolO_2}{4kmol^{-}}\frac{32kgO_2}{kmolO_2}=$$

$$=0.471\left[H_2O_2\right]\left(\frac{kgH_2O_2}{m^3}\right) \qquad \text{(Eq. 6)}$$

Figs. 7a and 7b show the evolution of COD in both effluents (S1 and S2) along the application of all three different AOPs as a function of treatment time and OCC, respectively. It can be checked that the electrochemical treatment produced a faster degradation compared with ozonation; whereas O_3 oxidation combined with H_2O_2 addressed a much faster kinetics along the first process hour (Fig. 7a), but also an almost ineffective degradation during the following treatment time, which implies that the faster oxidation was mainly caused by the presence of H_2O_2, which was consumed in about one hour. Fig. 7b however demonstrates that the elevated amount of H_2O_2 required for the higher organic load present in the S2 effluent significantly increased the OCC for the O_3/H_2O_2 process, and that the fastest degradation per consumed oxidant was really produced by the electro-oxidation process.

The enhancements of biodegradability by both electro-oxidation and O_3 processes were also compared performing bioassays with *Pseudomonas putida* (Fig. 8). The biological treatment was applied to the industrial effluent S1; and two other effluents with the same COD (50% of the initial COD) remaining after applying either electro-oxidation or O_3 pre-treatments to S1. The initial wastewater containing dioxane had not enough biodegradability to be treated by *Pseudomonas putida*, so COD remained constant after this biodegradation trial. After an electro-oxidation or O_3 pre-treatment, a further 25% of the remaining COD was degraded by *Pseudomonas putida* in 48 h, and about a 45% after 120 h in both cases. This indicates that the degradation of 1,4-dioxane is most likely to follow a similar pathway along both AOPs, achieving a similar biodegradability if the same COD amount was previously removed. However, as COD reduction resulted faster for the electrochemical pre-treatment (Fig. 7), this similar level of biodegradability was also achieved faster than in the ozonation process.

In addition, the treatment cost per unit of removed COD was estimated considering the price of industrial electric power in Spain (0.12 EUR/kWh; Eurostat 2012), and the wholesale price of industrial grade H_2O_2 and Na_2SO_4 (0.61 and 0.09 EUR/kg, respectively; ISIC 2012). Electricity consumption was estimated considering the average consumption of a typical industrial O_3 generator (8 kWh per 1 kg of O_3 rich gas; i.e. 8% of O_3 in oxygen), an additional energy consumption for refrigerating the O_3 generator (approx. 30%), and the additional consumption of an Adamant PP1000industrial power supply per applied kWh to the process (an extra 5% from the grid). Results shown in Table 6 indicates that electrochemical oxidation was the most economical alternative in terms of consumed kWh and the price per amount of removed COD; whereas O_3 oxidation may be rendered unfeasible due to its high treatment cost and slow oxidation kinetics. O_3/H_2O_2 treatment may result competitive to electro-oxidation when optimizing treatment time to consume all H_2O_2; but an electro-oxidation/H_2O_2 combination might be considered instead.

4. Conclusions

In the electrochemical treatment of synthetic 1,4-dioxane solution, the optimal compromise for achieving a maximum COD removal at a maximum current efficiency and producing the minimum energy consumption was reached using the designed highest concentrations of SO_4^{2-} (41.6 $mEq·L^{-1}$) , HCO_3^- (32.8 $mEq·L^{-1}$),and initial COD (750 $mg·L^{-1}$); and applying a current density of 11.9 $mA·cm^{-2}$ for 3.8 hours. The regression models resulting from the experimental design for the electro-oxidation treatment of a 1,4-dioxane synthetic solution accurately predicted the posterior electro-oxidation treatment of an industrial sample just containing 1,4-dioxane (S1): $R^2_{COD\%}$=99.01%; $R^2_{\Delta COD}$=99.21%; R^2_{TCE}=99.27%; and R^2_{EC}=98.95%.

In the treatment of industrial effluents with bicarbonate alkalinity, up to a 98% of the COD was removed in the electro–oxidation of the effluent just containing 1,4-dioxane (S1) consuming 114 $kWh·kgCOD_{removed}^{-1}$; and a 91% COD removal was achieved for the effluent containing both dioxane and MDO (S2), but resulting in the consumption of 49 $kWh·kgCOD_{removed}^{-1}$. Complementarily, the almost total mineralization of effluent S1, and about a 90% TOC removal in effluent S2, were achieved. In addition, the major part of 1,4-dioxane (≈85%) was already degraded in both industrial effluents after 2 hours of electro-oxidation treatment (≈21 $kWh·m^{-3}$).

The highest biodegradability enhancement was achieved in approximately 1 h of electro-oxidation at 12 $mA·cm^{-2}$ (≈10 $kWh·m^{-3}$) for both effluents. The biodegradability of the wastewater containing dioxane and MDO (S2) was originally higher precisely due to the content of MDO, which was more susceptible to biodegradation.

In comparison with O_3 and O_3/H_2O_2, the fastest degradation per consumed oxidant was achieved by electro-oxidation. This treatment also resulted the cheapest one in terms of consumed kWh and the price per the amount of removed COD. Namely, energy consumption and the average price of the process to reach a 90% COD removal were 90 and 50 $kWh \cdot kgCOD_{removed}^{-1}$, and 11 and 6 $EUR \cdot kgCOD_{removed}^{-1}$, for S1 and S2 effluents, respectively.

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Table 1. Characteristics of the industrial effluents.

	S1	**S2**
Main contaminants	1,4-dioxane	1,4-dioxane + MDO
[COD], $mgO_2 \cdot L^{-1}$	450-500	1320-1400
[HCO_3^-], $mg \cdot L^{-1}$	900-1000	900-1000
Conductivity, $\mu S \cdot cm^{-1}$	1900-2100	1900-2100
pH	8.7-9.0	7.8-8.1

Table 2. Levels of the independent variables of the experimental design.

	-2	-1	0	+1	+2
X_1: [SO_4^{2-}], *mEq·L⁻¹*	0	10.4	20.8	31.2	41.6
X_2: [HCO_3^-], *mEq·L⁻¹*	0	8.2	16.4	24.6	32.8
X_3: [COD_0, *mg·L⁻¹*	150	300	450	600	750
X_4: j, *mA·cm⁻²*	2	6	10	14	18
X_5: time, *h*	1	2	3	4	5

Table 3. Experimental design and schematic addition of time as the fifth factor: example of response Y_1 (COD removal, %) at five different treatment time intervals.

						Y_1, COD removal (%)				
	X_1	X_2	X_3	X_4	X_5	*1*	*2*	*3*	*4*	*5 (h)*
28 points of CCD:					↓					
1	-1	-1	-1	-1		30.8	59.8	79.0	89.2	95.6
1_1	-1	-1	-1	-1	-2					
1_2	-1	-1	-1	-1	-1					
1_3	-1	-1	-1	-1	0					
1_4	-1	-1	-1	-1	1					
1_5	-1	-1	-1	-1	2					
……										
2	-1	-1	-1	1		40.6	70.6	86.9	92.8	95.2
3	-1	-1	1	-1		8.8	20.2	34.2	47.1	59.9
4	-1	-1	1	1		34.0	64.0	82.0	92.3	97.0
5	-1	1	-1	-1		28.5	54.3	74.9	86.9	92.9
6	-1	1	-1	1		30.4	55.0	72.1	82.2	90.8
7	-1	1	1	-1		19.5	41.4	63.5	82.1	93.7
8	-1	1	1	1		36.6	70.0	88.4	95.7	99.1
9	1	-1	-1	-1		31.8	60.6	79.8	89.3	94.0
10	1	-1	-1	1		44.4	73.4	86.3	95.2	98.1
11	1	-1	1	-1		17.4	34.2	47.1	55.5	66.4
12	1	-1	1	1		42.6	73.1	91.5	97.0	98.3
13	1	1	-1	-1		25.4	52.8	70.1	83.8	91.6
14	1	1	-1	1		38.5	66.8	86.5	94.2	97.9
15	1	1	1	-1		21.8	44.3	65.5	84.0	94.8
16	1	1	1	1		46.8	80.4	94.7	98.3	100.0
17	-2	0	0	0		34.6	62.2	82.0	94.4	99.4
18	2	0	0	0		34.6	64.5	82.2	94.8	99.4
19	0	-2	0	0		31.8	59.1	72.0	81.5	90.2
20	0	2	0	0		35.1	63.3	81.3	92.9	98.7
21	0	0	-2	0		34.7	53.8	71.5	76.1	81.2
22	0	0	2	0		23.5	48.0	67.2	78.8	87.9
23	0	0	0	-2		10.5	19.5	28.7	38.5	47.9
24	0	0	0	2		48.1	78.1	87.4	95.3	99.3
25	0	0	0	0		37.8	65.9	84.9	91.4	93.7
26	0	0	0	0		31.8	56.3	76.5	90.2	95.3
27	0	0	0	0		32.6	57.3	76.2	87.8	93.9
28	0	0	0	0		37.2	63.8	77.5	88.1	95.2
3 extra points:										
29	2	2	2	2		46.6	77.9	93.4	97.8	100.0
30	-2	2	2	-2		6.4	13.5	18.4	26.9	33.6
31	2	2	2	-2		8.0	14.9	21.4	28.0	33.8
Total number of design points: N = 31 · 5 = **155**										

Table 4. Complete set of experimental results in terms of COD removal (Y_1), amount of COD removed (ΔCOD, Y_2), total current efficiency (TCE, Y_3); and energy consumption (EC, Y_4) for the electrochemical treatment of 1,4-dioxane.

	Y_1	Y_2	Y_3	Y_4		Y_1	Y_2	Y_3	Y_4		Y_1	Y_2	Y_3	Y_4		Y_1	Y_2	Y_3	Y_4
1	30.8	0.10	0.68	60.0	**40**	99.1	0.60	0.42	117.7	**79**	98.3	0.60	0.53	67.5	**118**	87.4	0.40	0.36	151.3
2	59.8	0.19	0.67	60.6	**41**	31.8	0.10	0.72	34.8	**80**	100.0	0.62	0.43	79.3	**119**	95.3	0.44	0.30	185.5
3	79.0	0.25	0.53	75.1	**42**	60.6	0.18	0.72	35.4	**81**	34.6	0.17	0.80	74.5	**120**	99.3	0.45	0.24	228.6
4	89.2	0.29	0.51	94.4	**43**	79.8	0.24	0.62	41.3	**82**	62.2	0.30	0.72	81.6	**121**	37.8	0.17	0.83	43.2
5	95.6	0.31	0.49	109.3	**44**	89.3	0.27	0.52	51.5	**83**	82.0	0.39	0.61	105.0	**122**	65.9	0.30	0.71	50.8
6	40.6	0.13	0.46	140.3	**45**	94.0	0.29	0.44	63.1	**84**	94.4	0.45	0.51	128.1	**123**	84.9	0.39	0.61	60.3
7	70.6	0.23	0.39	168.7	**46**	44.4	0.15	0.53	78.7	**85**	99.4	0.48	0.46	150.1	**124**	91.4	0.42	0.49	76.4
8	86.9	0.28	0.32	205.4	**47**	73.4	0.24	0.43	97.3	**86**	34.6	0.16	0.81	34.2	**125**	93.7	0.43	0.40	94.7
9	92.8	0.30	0.26	251.1	**48**	86.3	0.29	0.33	128.7	**87**	64.5	0.30	0.74	37.7	**126**	31.8	0.14	0.74	47.5
10	95.2	0.31	0.22	301.7	**49**	95.2	0.32	0.31	161.4	**88**	82.2	0.38	0.64	44.7	**127**	56.3	0.26	0.64	55.5
11	8.8	0.05	0.72	57.2	**50**	98.1	0.33	0.22	199.8	**89**	94.8	0.44	0.53	54.8	**128**	76.5	0.35	0.57	63.8
12	20.2	0.13	0.73	54.6	**51**	17.4	0.11	0.70	40.5	**90**	99.4	0.46	0.45	67.0	**129**	90.2	0.41	0.50	75.6
13	34.2	0.21	0.71	55.1	**52**	34.2	0.21	0.71	39.8	**91**	31.8	0.14	0.63	71.1	**130**	95.3	0.43	0.42	92.1
14	47.1	0.29	0.70	62.8	**53**	47.1	0.29	0.69	39.9	**92**	59.1	0.27	0.59	75.7	**131**	32.6	0.15	0.76	47.7
15	59.9	0.37	0.67	63.3	**54**	55.5	0.34	0.69	40.0	**93**	72.0	0.33	0.48	94.5	**132**	57.3	0.26	0.65	56.1
16	34.0	0.21	0.76	83.6	**55**	66.4	0.41	0.63	44.4	**94**	81.5	0.37	0.41	112.0	**133**	76.2	0.35	0.57	66.1
17	64.0	0.39	0.70	90.4	**56**	42.6	0.26	0.92	40.9	**95**	90.2	0.41	0.37	129.7	**134**	87.8	0.40	0.49	80.1
18	82.0	0.50	0.59	109.5	**57**	73.1	0.44	0.80	48.0	**96**	35.1	0.16	0.82	34.6	**135**	93.9	0.43	0.41	97.0
19	92.3	0.56	0.47	134.9	**58**	91.5	0.56	0.65	59.7	**97**	63.3	0.29	0.73	39.8	**136**	37.2	0.17	0.89	40.1
20	97.0	0.59	0.41	164.6	**59**	97.0	0.59	0.52	76.9	**98**	81.3	0.37	0.62	48.6	**137**	63.8	0.30	0.75	48.1
21	28.5	0.09	0.75	37.8	**60**	98.3	0.60	0.42	97.2	**99**	92.9	0.43	0.52	59.3	**138**	77.5	0.36	0.60	61.7
22	54.3	0.17	0.71	40.7	**61**	25.4	0.08	0.68	34.3	**100**	98.7	0.46	0.44	72.0	**139**	88.1	0.41	0.50	75.9
23	74.9	0.24	0.64	46.7	**62**	52.8	0.16	0.69	33.9	**101**	34.7	0.06	0.33	127.1	**140**	95.2	0.45	0.43	90.9
24	86.9	0.27	0.55	56.3	**63**	70.1	0.22	0.63	37.6	**102**	53.8	0.10	0.26	143.2	**141**	46.6	0.35	0.97	37.4

25	92.9	0.29	0.47	68.1	**64**	83.8	0.26	0.53	45.7	**103**	71.5	0.13	0.24	149.5	**142**	77.9	0.58	0.79	46.0
26	30.4	0.10	0.27	124.6	**65**	91.6	0.28	0.46	53.8	**104**	76.1	0.14	0.20	187.7	**143**	93.4	0.69	0.63	59.2
27	55.0	0.17	0.25	141.5	**66**	38.5	0.12	0.41	86.3	**105**	81.2	0.14	0.17	225.1	**144**	97.8	0.73	0.49	78.7
28	72.1	0.23	0.19	187.5	**67**	66.8	0.21	0.33	105.9	**106**	23.5	0.18	0.93	38.5	**145**	100.0	0.74	0.40	99.8
29	82.2	0.26	0.19	205.2	**68**	86.5	0.27	0.29	122.8	**107**	48.0	0.37	0.93	38.3	**146**	6.4	0.05	1.13	16.0
30	90.8	0.28	0.19	249.6	**69**	94.2	0.29	0.20	166.1	**108**	67.2	0.52	0.85	42.4	**147**	13.5	0.10	1.17	15.4
31	19.5	0.12	1.00	24.3	**70**	97.9	0.31	0.20	188.5	**109**	78.8	0.61	0.74	50.3	**148**	18.4	0.14	1.04	17.5
32	41.4	0.26	1.05	23.5	**71**	21.8	0.13	0.94	24.9	**110**	87.9	0.68	0.65	57.8	**149**	26.9	0.20	1.11	16.6
33	63.5	0.39	1.05	23.6	**72**	44.3	0.26	0.99	23.2	**111**	10.5	0.05	1.12	13.5	**150**	33.6	0.25	1.09	17.2
34	82.1	0.51	0.98	24.9	**73**	65.5	0.39	0.99	23.2	**112**	19.5	0.09	1.09	13.7	**151**	5.0	0.04	0.89	16.0
35	93.7	0.58	0.90	28.1	**74**	84.0	0.50	0.94	24.6	**113**	28.7	0.13	1.00	13.6	**152**	11.0	0.09	1.04	17.0
36	36.6	0.22	0.85	57.4	**75**	94.8	0.57	0.84	28.2	**114**	38.5	0.18	0.96	13.3	**153**	17.0	0.13	0.96	17.0
37	70.0	0.42	0.78	61.3	**76**	46.8	0.29	1.04	32.1	**115**	47.9	0.22	0.97	14.2	**154**	24.0	0.18	0.99	18.0
38	88.4	0.53	0.65	72.9	**77**	80.4	0.49	0.88	39.1	**116**	48.1	0.22	0.61	87.2	**155**	30.0	0.22	0.97	19.0
39	95.7	0.58	0.52	93.8	**78**	94.7	0.58	0.68	52.0	**117**	78.1	0.36	0.49	110.0					

Table 5. Regression coefficients of the quadratic models describing the results (Y_1 = COD removal; Y_2 = amount of removed COD, ΔCOD; Y_3 = total current efficiency, TCE; and Y_4 = energy consumption, EC) for the electrochemical treatment of 1,4-dioxane.

	COD removal, %		**ΔCOD, $kgCOD_{removed} \cdot L^{-1}$**		**TCE**		**EC, $kWh \cdot kgCOD_{removed}^{-1}$**	
	$b(Y_1)$	$SE(Y_1)$	$b(Y_2)$	$SE(Y_2)$	$b(Y_3)$	$SE(Y_3)$	$b(Y_4)$	$SE(Y_4)$
Model	**81.29**	*±1.25*	**0.387**	*±0.007*	**0.642**	*±0.012*	**63.43**	*±2.03*
X_1	**2.67**	*±1.15*	**0.010**	*±0.007*	**0.021**	*±0.011*	**-34.00**	*±1.87*
X_2	**2.82**	*±1.16*	**0.018**	*±0.007*	**0.054**	*±0.011*	**-21.27**	*±1.89*
X_3	**-5.91**	*±1.16*	**0.165**	*±0.007*	**0.281**	*±0.011*	**-54.80**	*±1.89*
X_4	**20.40**	*±1.15*	**0.109**	*±0.007*	**-0.261**	*±0.011*	**76.27**	*±1.87*
X_5	**28.33**	*±0.76*	**0.130**	*±0.004*	**-0.145**	*±0.007*	**29.54**	*±1.23*
X_1^2	**0.65**	*±2.06*	**-0.007**	*±0.012*	**-0.035**	*±0.019*	**9.75**	*±3.33*
X_2^2	**-3.56**	*±2.06*	**-0.038**	*±0.012*	**-0.102**	*±0.019*	**5.73**	*±3.33*
X_3^2	**-11.89**	*±2.06*	**-0.067**	*±0.012*	**-0.132**	*±0.019*	**37.99**	*±3.33*
X_4^2	**-18.85**	*±2.06*	**-0.106**	*±0.012*	**0.053**	*±0.019*	**15.08**	*±3.33*
X_5^2	**-12.55**	*±1.25*	**-0.059**	*±0.007*	**0.003**	*±0.012*	**7.20**	*±2.02*
$X_1 \cdot X_2$	**-2.93**	*±2.39*	**-0.019**	*±0.014*	**0.008**	*±0.023*	**15.48**	*±3.87*
$X_1 \cdot X_3$	**1.49**	*±2.39*	**0.020**	*±0.014*	**0.012**	*±0.023*	**8.93**	*±3.87*
$X_1 \cdot X_4$	**0.78**	*±2.14*	**0.009**	*±0.012*	**0.013**	*±0.020*	**-15.20**	*±3.47*
$X_1 \cdot X_5$	**-1.08**	*±1.39*	**-0.008**	*±0.008*	**-0.033**	*±0.013*	**-7.46**	*±2.26*
$X_2 \cdot X_3$	**14.31**	*±2.60*	**0.064**	*±0.015*	**0.140**	*±0.025*	**-8.93**	*±4.21*
$X_2 \cdot X_4$	**-10.98**	*±2.39*	**-0.049**	*±0.014*	**-0.153**	*±0.023*	**14.01**	*±3.87*
$X_2 \cdot X_5$	**-0.45**	*±1.47*	**-0.010**	*±0.009*	**-0.008**	*±0.014*	**-1.00**	*±2.38*
$X_3 \cdot X_4$	**21.79**	*±2.39*	**0.163**	*±0.014*	**0.136**	*±0.023*	**-57.49**	*±3.87*
$X_3 \cdot X_5$	**-2.27**	*±1.47*	**0.067**	*±0.009*	**-0.024**	*±0.014*	**-16.33**	*±2.38*
$X_4 \cdot X_5$	**1.85**	*±1.39*	**0.017**	*±0.008*	**-0.079**	*±0.013*	**30.41**	*±2.26*
R^2	95.08%		95.21%		95.25%		96.96%	
R^2_{pred}	93.00%		93.11%		93.69%		95.48%	
R^2_{adj}	94.35%		94.50%		94.54%		96.50%	

Table 6. Energetic and economic comparison of the treatment of dioxane (S1) and dioxane+MDO (S2) effluents by electro-oxidation (EO), O_3 and O_3/H_2O_2.

Process	Energetic and economical parameters for varying COD removal % **kgCOD/OCC**[a]			**kWh/kgCOD**			**EUR/kgCOD**		
Treatment of S1									
	50%	*70%*	*90%*	*50%*	*70%*	*90%*	*50%*	*70%*	*90%*
EO[b]	0.9	0.7	0.5	55	63	90	7	8	11
O_3/H_2O_2[c]	0.4	0.5	0.4	69	76	164	14	13	22
O_3[d]	0.3	0.2	0.2	402	474	682	46	55	79
Treatment of S2									
	50%	*70%*	*90%*	*50%*	*70%*	*90%*	*50%*	*70%*	*90%*
EO[b]	1.7	1.4	0.9	30	35	50	4	4	6
O_3/H_2O_2[c]	0.3	0.2	0.1	167	322	1037	25	42	123
O_3[d]	0.5	0.4	0.3	216	268	399	25	31	46

[a] OCC denominates Oxygen-equivalent Chemical-oxidation Capacity, calculated by Equations 4-6 (Cañizares *et al.* 2009b)

[b] $j=12\ mA \cdot cm^{-2}$; $[HCO_3^-]=16.4\ mEq \cdot L^{-1}$; $[SO_4^{2-}]=20.8\ mEq \cdot L^{-1}$

[c] $[H_2O_2]/[COD]=2.215$ ($[H_2O_2]_{S1} \approx 1.00\ kg \cdot m^{-3}$, $[H_2O_2]_{S2} \approx 2.90\ kg \cdot m^{-3}$); average $0.45\ kgO_3 \cdot h^{-1} \cdot m^{-3}$ for S1 and $0.66\ kgO_3 \cdot h^{-1} \cdot m^{-3}$ for S2

[d] average $0.40\ kgO_3 \cdot h^{-1} \cdot m^{-3}$

FIGURE CAPTIONS:

Fig. 1. 3D response surfaces for a) % COD removal, and b) total current efficiency (TCE), built up as a function of the applied current density (*j*) and treatment time. Constant values at X_i=0: [SO_4^{2-}]=20.8 mEq·L^{-1}; [HCO_3^-]=16.4 mEq·L^{-1}, and $[COD]_0$=450 mg·L^{-1}.

Fig. 2. 3D response surfaces for a) the amount of COD removed (ΔCOD), and b) energetic consumption (EC), constructed as a function of the initial COD value and the applied current density. Constant values at X_i=0: [SO_4^{2-}]=20.8 mEq·L^{-1}, [HCO_3^-]=16.4 mEq·L^{-1}, and time=3 h.

Fig. 3. Surface plots for a) % COD removal, and b) energetic consumption (EC), drawn as a function of the concentrations of supporting electrolytes (SO_4^{2-} and HCO_3^-). Constant values at X_i=0: $[COD]_0$=450 mg·L^{-1}, j=10 mA·cm^{-2}, and time=3 h.

Fig. 4. Optimization plot for maximum COD removal (%) and amount of COD removed (ΔCOD) at a maximum total current efficiency (TCE) and a minimum energetic consumption (EC) ("y" stands for the process response at optimal compromise, "d" stands for the desirability of the process response, and "D" for composite desirability).

Fig. 5. COD removal and simultaneous energetic consumption (EC) increase during the electrochemical treatment of industrial effluents S1 and S2 at 12 mA·cm^{-2} in the presence of its inherent initial bicarbonate alkalinity (16.4 mEq·L^{-1}) using 20.8 mEq·L^{-1} of SO_4^{2-} as supporting electrolyte.

Fig. 6. Evolution of effluent biodegradability by *Pseudomonas putida* (100-h bioassays) along with the degradation of COD, TOC, 1,4-dioxane, and MDO during the electrochemical treatment of a) the dioxane containing effluent (S1), and b) the effluent

with dioxane and MDO (S2) at 12 mA·cm^{-2} in the presence of initial bicarbonate alkalinity (16.4 mEq·L^{-1}) using 20.8 mEq·L^{-1} of SO_4^{2-} as supporting electrolyte.

Fig. 7. The evolution of the COD during the treatment of both industrial effluents (S1 and S2) by three different AOPs [electro-oxidation (EO), O_3 and O_3/H_2O_2] as a function of a) treatment time, and b) Oxygen-equivalent Chemical-oxidation Capacity (OCC, calculated by Equations 4-6; Cañizares *et al*. 2009b). Conditions for EO: j=12 mA·cm^{-2}; $[HCO_3^-]$=16.4 mEq·L^{-1} (initial bicarbonate alkalinity); $[SO_4^{2-}]$=20.8 mEq·L^{-1} (supporting electrolyte). Conditions for O_3: average consumption=0.40 kgO_3·h^{-1}·m^{-3}. Conditions for O_3/H_2O_2: $[H_2O_2]/[COD]$=2.215 ($[H_2O_2]_{S1}\approx1.00$ kg·m^{-3}; $[H_2O_2]_{S2}\approx2.90$ kg·m^{-3}); average O_3 consumption was approx. 0.45 kgO_3·h^{-1}·m^{-3} for S1, and 0.66 kgO_3·h^{-1}·m^{-3} for S2.

Fig. 8. Evolution of the COD in the biodegradation tests carried on by *Pseudomonas putida* on the initial industrial effluent containing 1,4-dioxane (S1) and on the same S1 effluent previously treated by electro-oxidation (EO) or O_3 (both performed until a 50% of COD removal was achieved). Conditions for EO: j=12 mA·cm^{-2}; $[HCO_3^-]$=16.4 mEq·L^{-1} (initial bicarbonate alkalinity); $[SO_4^{2-}]$=20.8 mEq·L^{-1} (supporting electrolyte). Conditions for O_3: average consumption=0.40 kgO_3·h^{-1}·m^{-3}.

FIGURE 1

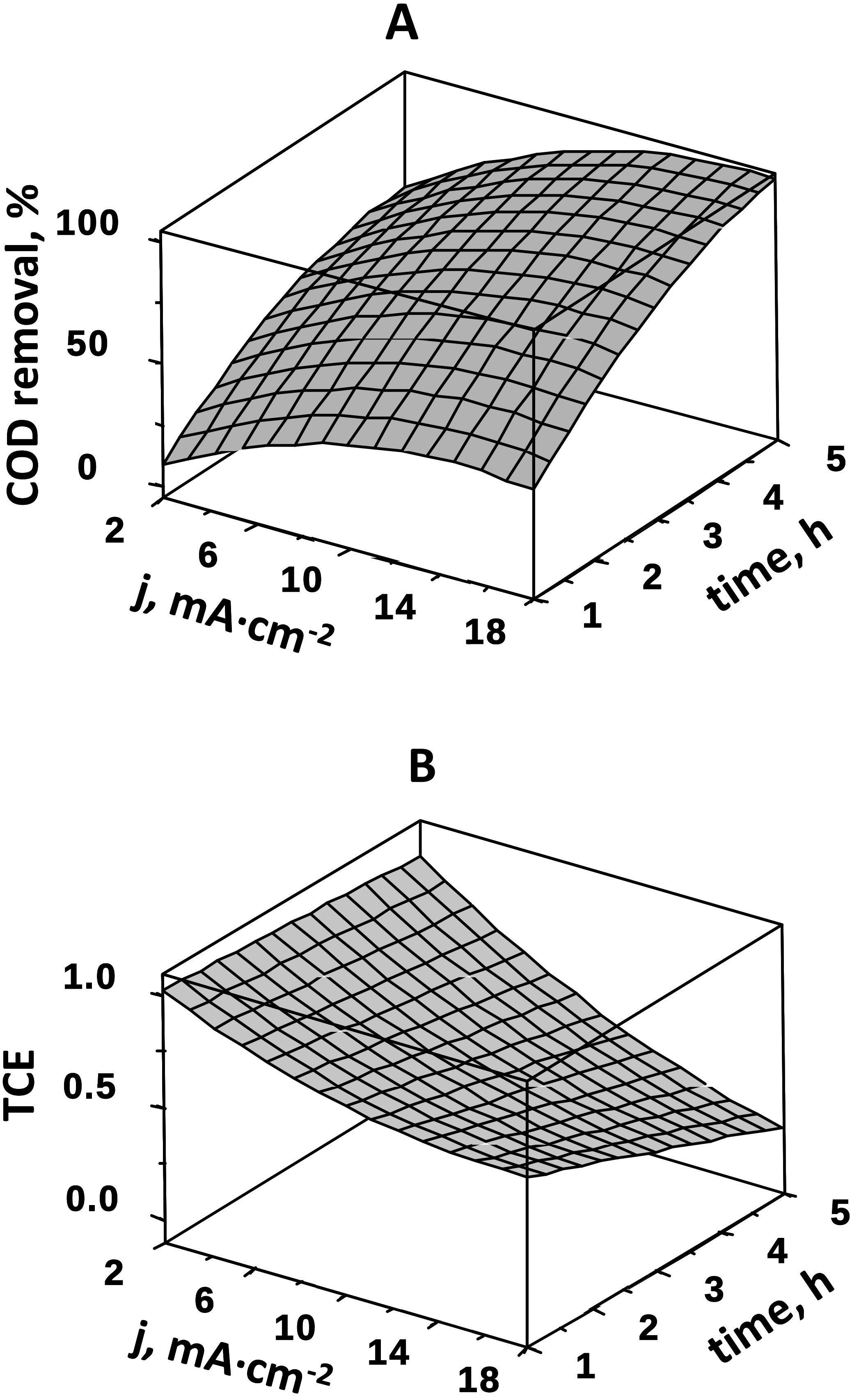

A
COD removal, %
100
50
0
2
6
10
14
18
j, mA·cm-2
1
2
3
4
5
time, h
B
TCE
1.0
0.5
0.0
2
6
10
14
18
j, mA·cm-2
1
2
3
4
5
time, h

FIGURE 2

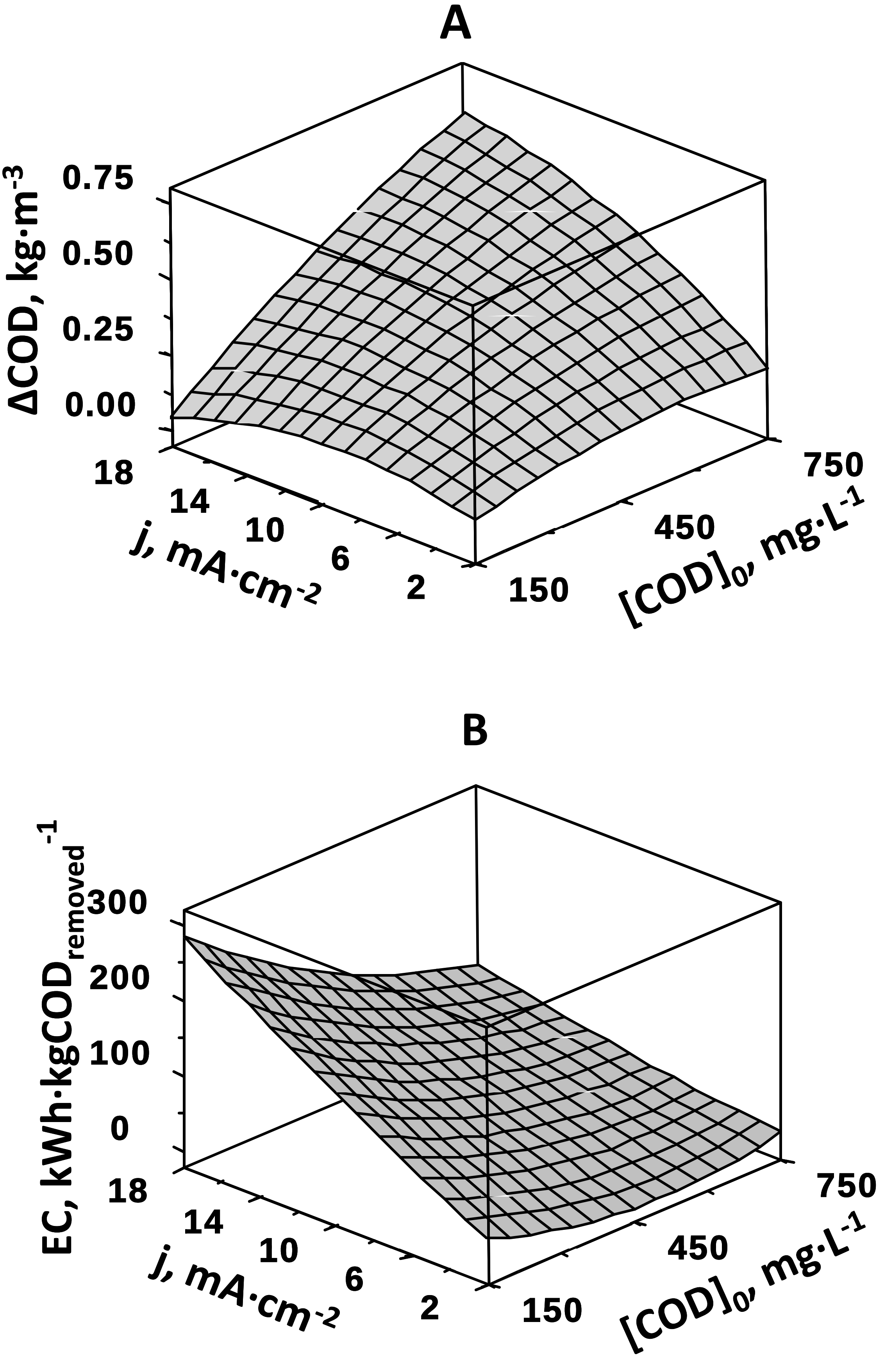
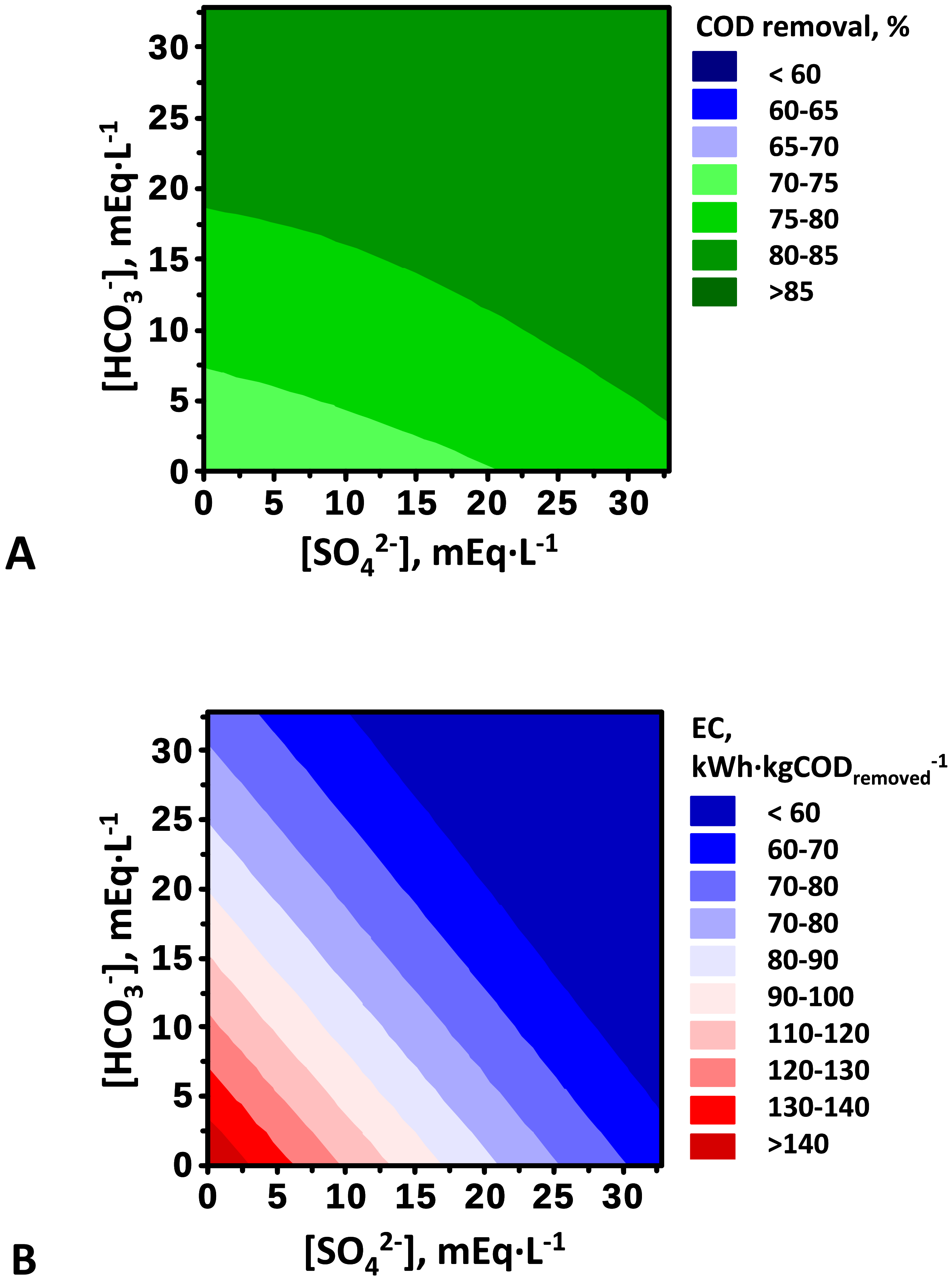
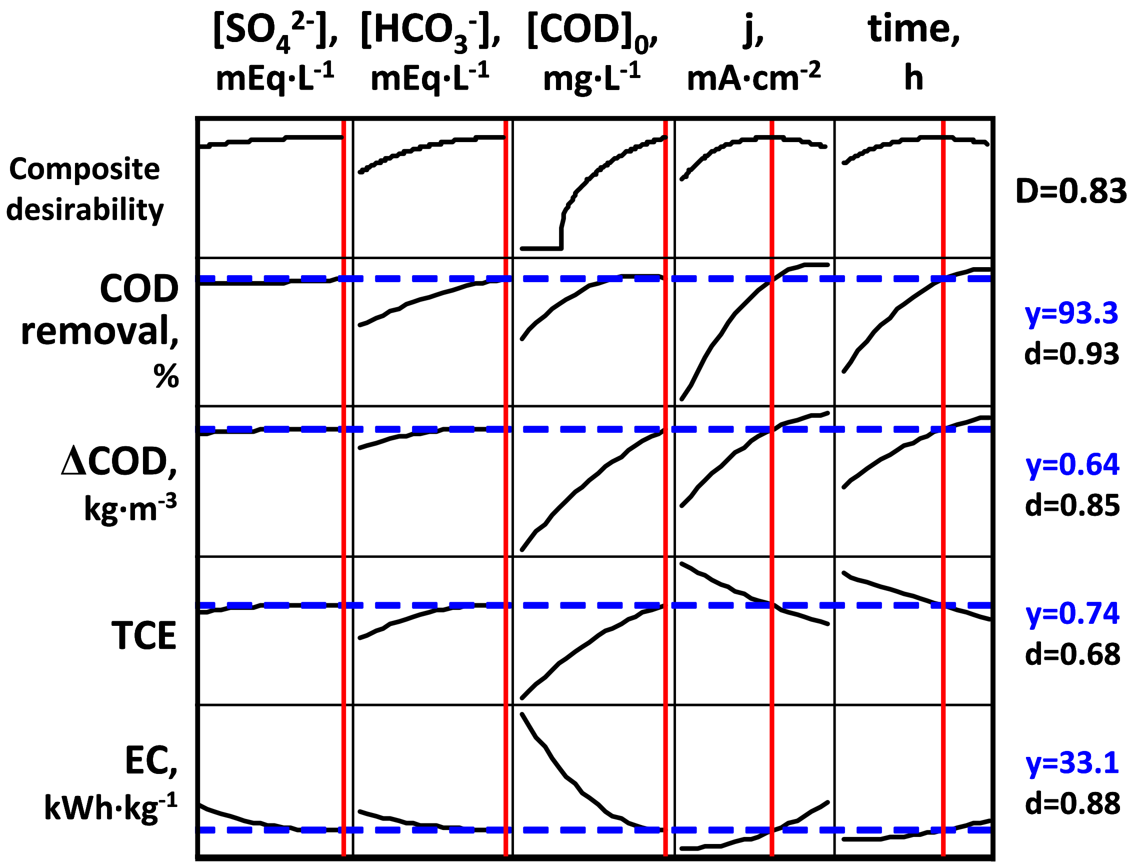

A
ΔCOD, kg·m-3
0.75
0.50
0.25
0.00
18
14
10
6
2
j, mA·cm-2
150
450
750
[COD]0, mg·L-1
B
EC, kWh·kgCODremoved-1
300
200
100
0
18
14
10
6
2
j, mA·cm-2
150
450
750
[COD]0, mg·L-1

FIGURE 3



A
[HCO$_3^-$], mEq·L^{-1}
0
5
10
15
20
25
30
[SO$_4^{2-}$], mEq·L^{-1}
COD removal, %
< 60
60-65
65-70
70-75
75-80
80-85
>85
B
[HCO$_3^-$], mEq·L^{-1}
[SO$_4^{2-}$], mEq·L^{-1}
EC, kWh·kgCOD$_{removed}^{-1}$
< 60
60-70
70-80
70-80
80-90
90-100
110-120
120-130
130-140
>140

FIGURE 4



$[SO_4^{2-}]$, $mEq \cdot L^{-1}$
$[HCO_3^-]$, $mEq \cdot L^{-1}$
$[COD]_0$, $mg \cdot L^{-1}$
j, $mA \cdot cm^{-2}$
time, h
Composite desirability
D=0.83
COD removal, %
y=93.3
d=0.93
ΔCOD, $kg \cdot m^{-3}$
y=0.64
d=0.85
TCE
y=0.74
d=0.68
EC, $kWh \cdot kg^{-1}$
y=33.1
d=0.88

FIGURE 5

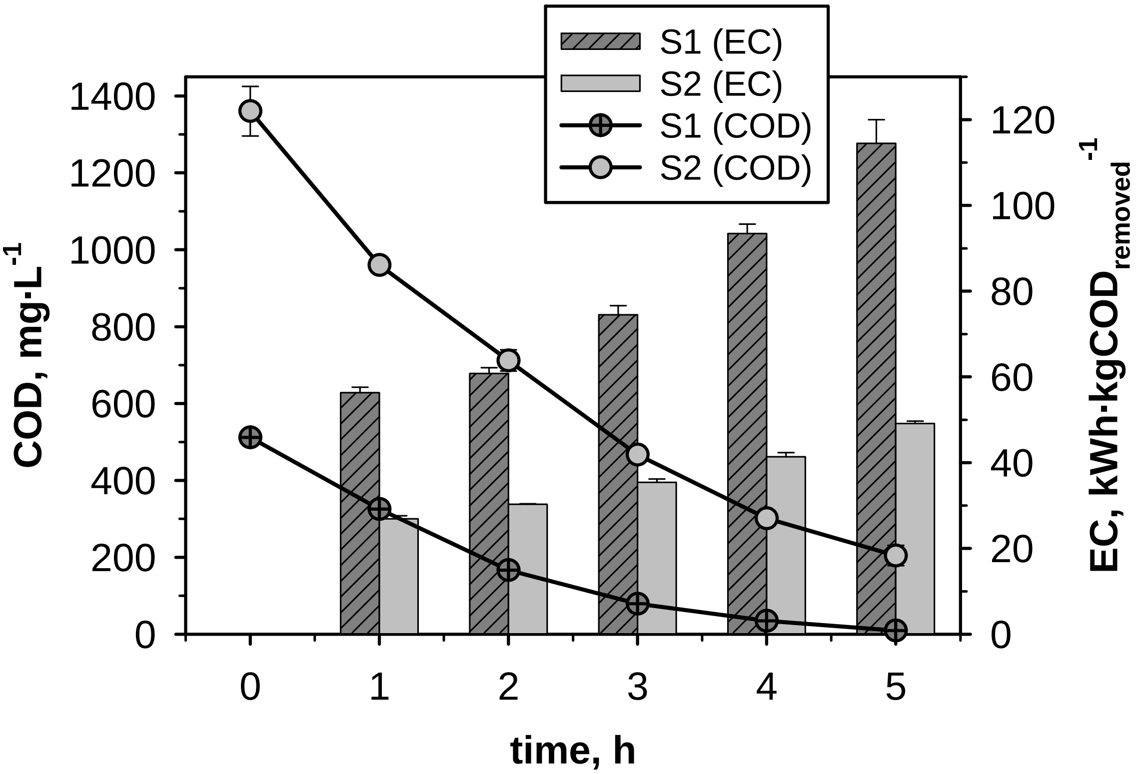

S1 (EC)
S2 (EC)
S1 (COD)
S2 (COD)
COD, mg·L-1
EC, kWh·kgCODremoved-1
time, h
0
1
2
3
4
5
0
200
400
600
800
1000
1200
1400
0
20
40
60
80
100
120

FIGURE 6

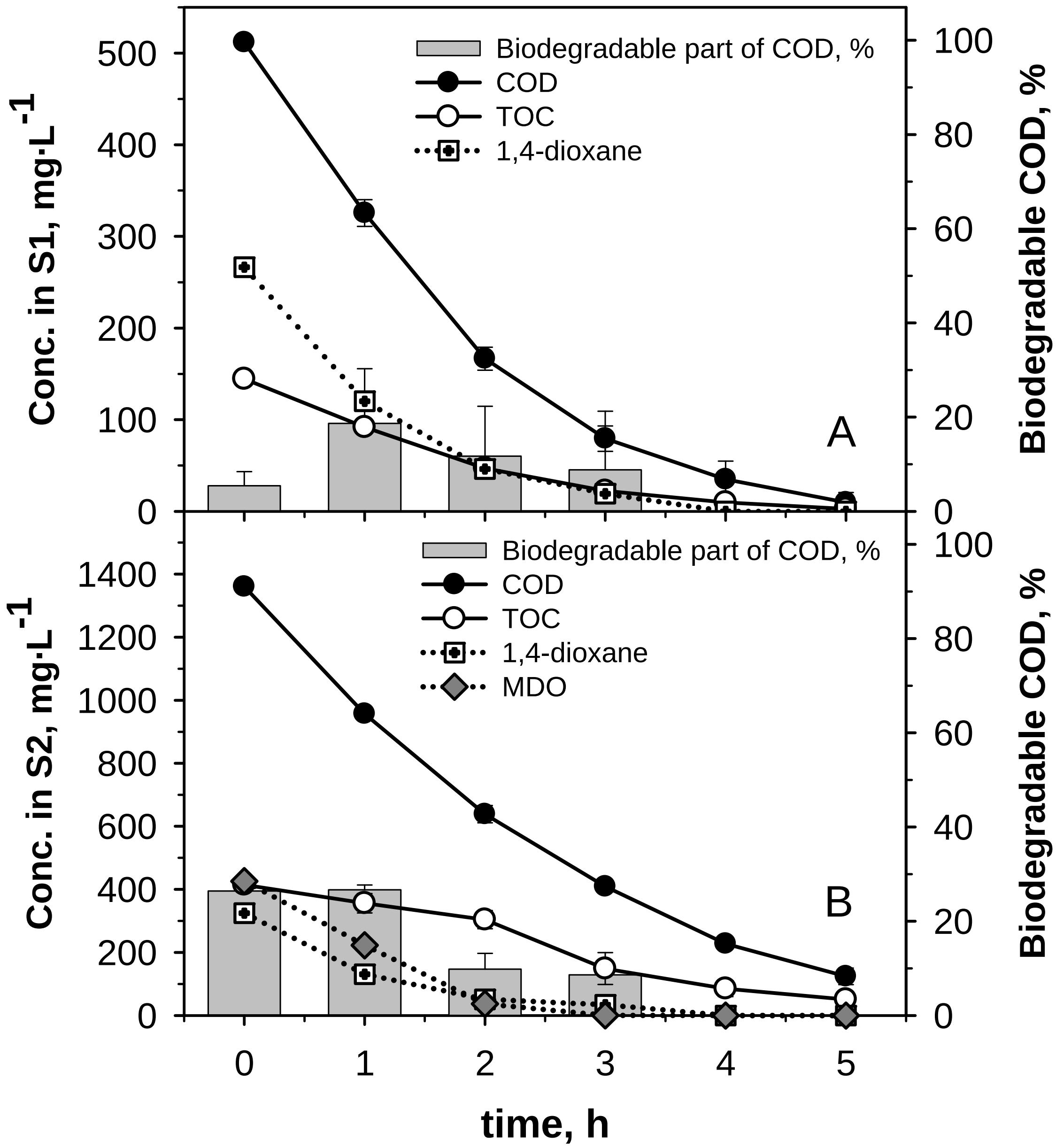

Conc. in S1, mg·L-1
Biodegradable COD, %
Biodegradable part of COD, %
COD
TOC
1,4-dioxane
A
500
400
300
200
100
0
100
80
60
40
20
0
Conc. in S2, mg·L-1
Biodegradable COD, %
Biodegradable part of COD, %
COD
TOC
1,4-dioxane
MDO
B
1400
1200
1000
800
600
400
200
0
100
80
60
40
20
0
0
1
2
3
4
5
time, h

FIGURE 7

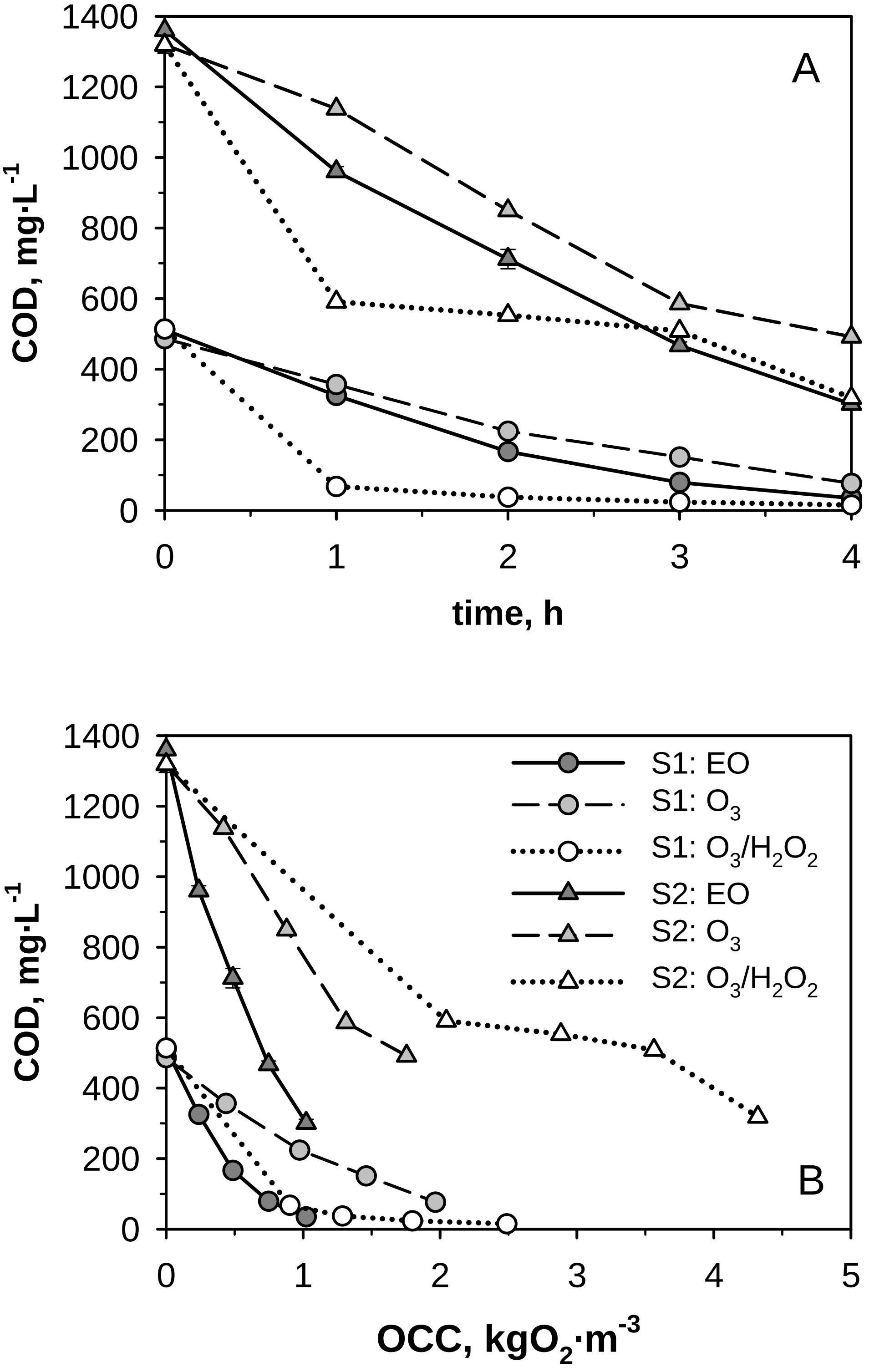
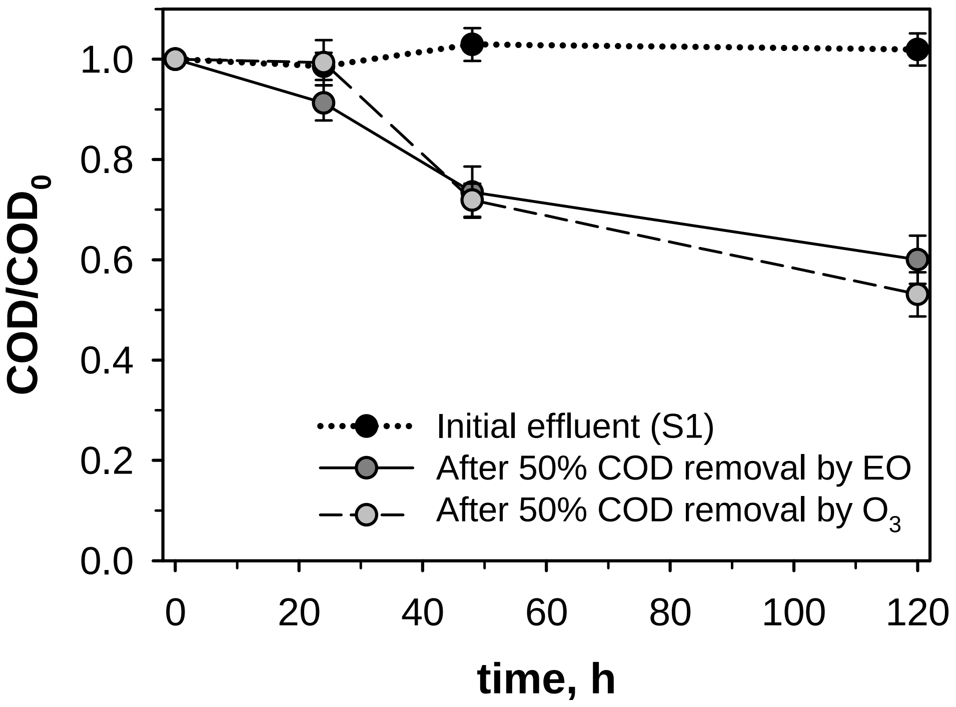

A
COD, mg·L⁻¹
1400
1200
1000
800
600
400
200
0
0
1
2
3
4
time, h
B
COD, mg·L⁻¹
1400
1200
1000
800
600
400
200
0
0
1
2
3
4
5
OCC, kgO₂·m⁻³
S1: EO
S1: O₃
S1: O₃/H₂O₂
S2: EO
S2: O₃
S2: O₃/H₂O₂

FIGURE 8


COD/COD$_0$
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
100
120
time, h
Initial effluent (S1)
After 50% COD removal by EO
After 50% COD removal by O$_3$