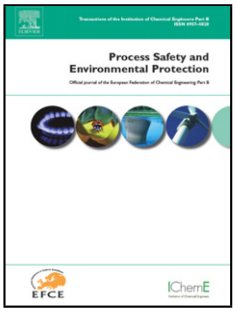

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Statistical optimization of electrochemical oxidation of ethylene glycol using response surface methodology

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Research highlights

- Electrochemical oxidation of EG was performed using BDD as working anode.
- Optimization of operating conditions was carried out using RSM approach.
- A maximum COD and TOC removal (91 ± 2.2 % and 80 ± 4 %, respectively) were recorded.
- Current and treatment time contributed with respectively 49 % and 43 % in the COD removal.
- The residual COD was below the legislation standards set by the province of Quebec.

Abstract

Large amounts of ethylene glycol (EG) based antifreeze liquids are daily discharge into the receiving waters. The chemical oxygen demand (COD) detected in most of the lakes and rivers close to the discharge points exceeded 100 000 mg O_2/L. With such an amount, biological and chemical processes are inefficient to completely remove EG. In order to efficiently remove EG, electrochemical oxidation (ECO) of EG was carried out. Niobium Boron Doped Diamond (Nb/BDD) was used as anode whereas carbon felt was used as cathode. Different operating parameters including current intensity, treatment time, electrolyte concentration and pollutant concentration were tested. The application of 0.077A/cm^2 of current density during 120 min in the presence of 7.0 g/L of Na_2SO_4 allowed 89.6 ± 0.2 % of COD removal with 490 mg O_2/L of residual COD. This result was far below the legislation standard set by the province of Quebec that allows the discharge of 800 mg O_2/L of COD. The efficiency of ECO process was attributed to both direct and indirect oxidation that generate strong oxidizing species (OH°, $S_2O_8^{2-}$, H_2O_2, etc.) capable of oxidizing organic matters on the surface of the anode and in the bulk of the solution.

Keywords

Ethylene glycol; electrochemical oxidation; Factorial; Central Composite design.

Nomenclature

ECO	Electrochemical oxidation
EG	Ethylene Glycol
COD	Chemical Oxygen Demand
TOC	Total organic carbon
Nb/BDD	Niobium Boron Doped Diamond
RSM	Response surface methodology
FD	Factorial design
CCD	Central composite design
ANOVA	ANalysis Of VAriance

1. Introduction

Ethylene glycol (EG) is a dihydroxy alcohol that is well known for its relatively high boiling point (197.6°C) and freezing point well below zero (-13°C) (Kim and Hoffmann, 2008). Owing to these properties, EG could be used in heat exchangers as cooling fluid, in airports as deicer liquid, in pharmaceutical industry as surface active agents, in plastic industries as plasticizers and in resin manufacturing purposes (Orecki et al., 2006; Staples et al., 2001). In 2001, 83 kt of EG were produced in Canada to be used as cooling and antifreeze liquids (EC, 2001). Consequently, large amounts of EG ranging between 1000 and 25 000 mg/L have been detected in wastewaters with a possibility of exceeding 250 000 mg/L in some cases (Araña et al., 2012). Once discharged into lakes, aquatic organisms could be exposed to high concentrations of EG reaching 19 000 mg/L. With such concentrations, the chemical oxygen demand (COD) and the total organic carbon (TOC) increase considerably, thereby causing several environmental damages to the living organisms (brain damage, nervous system damage, etc.) (Louhichi et al., 2008). In order to protect aquatic and terrestrial organisms from EG toxicity effects, biological and chemical treatments have been used. However, EG at large concentrations limit the efficiency of biological processes (McGinnis et al., 1999) whereas with chemical processes such as Photo-Fenton, large amounts of sludge could be generated leading to an increase in the treatment cost (Rajeshwar and Ibanez, 1997).

Over the last few years, advanced oxidation processes such as electrochemical oxidation (ECO) have been proposed as an adequate alternative for biological and chemical treatments (Daghrir et al., 2014). In fact, two mechanisms could be distinguished in ECO process: (1) direct oxidation on the surface of the working anode where the oxidation of water molecules generates strong oxidants ($E°(OH^{°}/H_2O)$ = 2.80 V vs.SHE) capable of oxidizing different organic pollutants and (2) indirect oxidation in the bulk of the solution where the same compounds could be oxidized via other mediators (eg.H_2O_2, HClO, $S_2O_8^{2-}$) (Anglada et al., 2009).

The main objective of this current study was to optimize the operating conditions (EG concentration, current intensity, treatment time and electrolyte type) of EG removal using electrochemical oxidation process. Therefore, a factorial design methodology was applied to investigate the effect and interactions of operating parameters on EG removal followed by a central composite design targeting the optimization of the treatment process. The overall process cost was also investigated at the end of this study.

2. Materials and methods

2.1. EG effluent

The EG solution used in this study was an anti-freeze sample provided by Produits Chimiques Magnus Ltd Company (Boucherville, QC, Canada) and used in industrial cooling systems. It was comprised of 530 g/L of ethylene glycol ($C_2H_6O_2$), 0.60 g/L of azole and 8.72 g/L of phosphate (PO_4^{3-}). The EG solution had an initial COD content of more than 100 g/L and a pH around 9.5. Synthetic EG effluents having different concentrations (2.5 to 3.5 g/L) were prepared using distilled water. 7g/L of salt (Na_2SO_4 or NaCl) was added to increase the electrical conductivity. The choice of such EG and electrolyte concentrations was based on previous study conducted by Jardak et al. (2016). Mixing and stirring time of 5 min was required to completely dissolve sodium salt.

2.2. Electrolytic reactor set up

The electrolytic cell used was made of Plexiglas material with a dimension of 17 cm (depth) × 5cm (width) × 15cm (length). It was comprised of one anode and one cathode with an inter-electrode gap of 1 cm. The anode had a solid surface area of 65 cm^2 and a void surface area of $45cm^2$. The circular anode (12 cm of diameter × 0.1 cm thick) was made of niobium coated with boron doped diamond (Nb/BDD) whereas the cathode was a carbon felt having a surface area of $127cm^2$.The electrodes were vertically installed on a perforated Plexiglas plate at 2 cm from the bottom of the cell.

All experiments were carried out in a closed loop as shown in Fig1. The loop consisted of 2.0 L of a Plexiglas tank (1), a peristaltic recycling pump (2) and the electrolytic cell (3). During the treatment, the solution in the electrolytic cell was recirculated through the pump. A recycle flow rate of 170 ml/min was maintained using the peristaltic recycling pump (Master flex, Model 77200-50, USA). A current intensity ranging between 3.0 and 6.0 A was imposed during 60 to 120 min of treatment time. The current intensity was delivered by means of DC power supply Xantrex XFR 40-70 (Aca Tmetrix, Mississauga, Ontario, Canada). All experiments were carried out at room temperature (25 ± 0.1 °C) with a total volume of 1.0 L.

2.3. Experimental design

Four different operating parameters including EG concentration (X_1), current intensity (X_2), treatment time (X_3) and electrolyte type (X_4) were chosen as the most important parameters in the electrochemical oxidation of EG. In order to optimize these parameters, a response surface methodology (RSM) has been considered. RSM is a collection of mathematical and statistical methods for modeling, optimizing, and analyzing a treatment process in which the response can be influenced by several variables (Daghrir et al., 2012). Both factorial design (FD) and central composite design (CCD) are the most widely used design in experimental design methodology. The objective of FD is to determine the main interactions and effects of the selected factors on the target responses whereas CCD allows the optimization of the treatment process.

In this case of study, the number of factors was set to 4 (X_1, X_2, X_3, and X_4) and responses to 2 (COD and TOC removal). The FD matrix was comprised of 16 experiments ($2^k= 2^4$, k is the number of factors) where each factor was fixed to two different levels (-1) and (+1), as illustrated in Table 1. The CCD matrix, on the other hand, was comprised of FD matrix (16 experiments) with 24 additional assays. Based on the categorical factor (electrolyte type), six assays were run at the center of the domain whereas the other six were axial assays (with $\alpha = \pm 1.68$).

2.4. Analytical details

The pH was determined using a pH-meter (Fisher Acumet model 915) equipped with a double junction Cole-Palmer electrode with Ag/AgCl reference cell. The conductivity was also measured using a conductivity meter (Oakton Model 510). During this study, the Chemical Oxygen Demand (COD) was determined using the method prescribed by the Ministry of Sustainable Development, Environment and Parks, Quebec (Analysis method – AM. 315-DCO 1.0). The reading was realized using a spectrophotometer (λ = 600nm). Total organic carbon (TOC) was also investigated using a Shimadzu TOC 5000A analyzer. The identification and quantification of EG by products was performed using high pressure liquid chromatography (HPLC).

2.7. Economic aspect

During electrochemical treatment, different chemical reagents such as sodium sulfate Na_2SO_4 and sodium hydroxide NaOH were used. A unit cost of 0.1$/kg for Na_2SO_4 and 3.84$/kg for NaOH were considered. The energy consumed was estimated at a cost of 0.06$CAN/KWh, which corresponds to the cost fixed by the province of Quebec (Canada). The total cost was evaluated in terms of CAN dollars spent per cubic meter of treated solution ($\$CAN/m^3$).

3. Results and discussions

3.1. Effect of operating parameters on EG removal using FD methodology

The effect of different variables including pollutant concentration (X_1), current intensity (X_2), treatment time (X_3) and electrolyte type (X_4) on EG removal was investigated using FD methodology. Each factor was fixed to two different levels (minimum) and (maximum) normalized as (-1) and (+1). The experimental region and the coded values are represented in Table 1. The factorial matrix obtained was comprised of 16 assays in which two responses (COD and TOC removal) were investigated. The results are summarized in Table 2 using 7g/L of salt (Na_2SO_4 or NaCl). Based on these results; it was possible to determine the effect (b) of each factor (X) as well as the effect of their interactions (X_i X_j) on the response (Y). This was well illustrated in the following polynomial model (Eq.1):

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_4 X_4 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 + b_{14} X_1 X_4 + b_{24} X_2 X_4 + b_{34} X_3 X_4 \quad (1)$$

Where Y is the experimental response (for COD or TOC removal); b_0 represents the average value of the responses of the 16 assays; X_i the coded variable (-1 or +1); b_i represents the principal effect of each factor «i» on the response and b_{ij} represents the interaction effect between factor «i» and factor «j» on the response (Y). The coefficients of the model were calculated using the half-difference between the arithmetic average of the response values when the associated coded variable is at a level (+1) and the arithmetic average of the response values when the associated coded variable is at level (-1). Design-Expert Program Software (Design Expert 7, Stat-Ease Inc., Minneapolis) was used to calculate the coefficient of the polynomial model. Since two different responses (COD and TOC removal) were considered, two mathematical models could be deduced:

$$Y_1 = 62.54 - 4.81\, X_1 + 12.44\, X_2 + 11.74\, X_3 \qquad (2)$$

$$Y_2 = 48.11 - 9.8\, X_1 + 15.65\, X_2 + 16.03\, X_3 - 7.76\, X_4 \qquad (3)$$

Where X_i vary between (+1) and (-1), Y_1 is the COD removal percentage and Y_2 is the TOC removal percentage.

In order to evaluate the significance of these models, Analysis Of Variance (ANOVA) was performed by the design expert software. It was found that the correlation coefficient (R^2) of the proposed models were 0.93 and 0.92 for COD removal and TOC removal, respectively. According to Joglekar and May (1987), a correlation coefficient that exceeds 0.8 indicates that the models are acceptable with a good correlation between predicted and experimental values. Consequently, the models presented in Eq.2 and Eq.3 are significant and predicted-experimental values are well correlated.

Based on the results summarized in Eq.2, the COD removal (Y_1) was positively influenced by the current intensity (X_2) and the treatment time (X_3) showing the highest effects (b_2= +12.44 and b_3= +11.74). In other terms, an increase in one or both of these factors enhances the COD removal efficiency, leading to a better performance of the ECO process. According to Daghrir et al. (2014), the simultaneous increase of the COD removal with the current intensity could be explained by the higher generation of hydroxyl radicals (OH°) on the BDD surface, the persulfate ions ($S_2O_8^{2-}$) in the bulk of the solution and the hydrogen peroxide (H_2O_2) on the carbon felt surface. Likewise, the longer the treatment time is the better the oxidant production will be, leading to a higher COD removal.

The increase in EG concentration (X_1), on the other hand, reduces considerably the COD removal efficiency (b_1= - 4.81), as demonstrated in Eq.2. Such an effect could be due to the fact that the calculation of COD removal is in percentage which explains that with the increase of EG concentration, the removal of COD decreases in term of percentage. However in term of mass balance, the quantity of COD removed from solution increased from 3225 mg to 4053 mg when the initial EG concentration passed from 2500 mg/L to 5000 mg/L, probably due the higher mass transfer of pollutant. On the other hand, the electrolyte type (X_4) showed no significance at all and its effect was automatically eliminated by the design expert software in order to improve the model.

The same observation could be deduced for the TOC removal (Y_2), where current intensity and treatment time show the same positive effects on the target response (b_2= +15.65 and b_3= +16.03).

Further investigations were also conducted by plotting Pareto charts for all selected factors. Pareto charts allow the hierarchical arrangement of both influencing factors and interactions based on their effects, as shown in SM1. It is well known that the effects situated above the dotted line (t-value limit) are statistically significant and should be taken into account in the study (Han et al., 2006). Consequently, current intensity (X_2) and treatment time (X_3) influenced significantly the COD removal with the predominance of the current intensity (X_2) (SM2). For the TOC removal, the current intensity (X_2) and the treatment time (X_3) had almost the same significant effect on the response whereas electrolyte type (X_4) was the least influent factor in both cases (SM1).

In order to seek more information, the contribution of each significant factor in COD and TOC removal was evaluated using the following equation (Eq.4):

$$P_i = \left(\frac{bi^2}{\Sigma bi^2}\right) * 100 \qquad (4)$$

Where b_i represents the estimation of the principal effects of the factor «i». The results are summarized in Fig 2 and Fig 3.

It was found that the current intensity (X_2) and the treatment time (X_3) were the major contributors in the COD removal with 49 % and 43 %, respectively (Fig.2). The same trend was observed with TOC removal where X_2 and X_3 contributed with 39 % and 37 %, respectively (Fig.3). EG concentration (X_1), on the other hand, showed an extremely low contribution in both cases (between 7.0 and 9.0%).

Overall, FD methodology has been used as an effective tool for determining the effects and interactions of the different factors on EG removal by ECO process. However, such a method is not sufficient to optimize the treatment process. Therefore, a more sophisticated method known as central composite design (CCD) methodology has been carried out in the second part of this study.

3.2. Optimization of EG removal using central composite design methodology

As stated earlier, four different operating parameters (EG concentration (X_1), Current intensity (X_2), treatment time (X_3) and electrolyte type (X_4)) were chosen as key factors in the ECO of EG. In order to be optimized, a CCD methodology was carried out. The CCD matrix was comprised of 40 assays including the FD matrix (16 assays). Based on the categorical factor (Electrolyte type), the CCD matrix was divided into two. For each electrolyte (NaCl or Na_2SO_4), six assays were replicated in the center whereas the other six were axial assays ($\alpha = \pm 1.41$). The results are summarized in Table 3 and Table 4.

In order to investigate these results, a second order model relating dependent variables and independent ones was expressed as follows (Eq.5) (Amalraj Appavoo et al., 2014):

$$\mathrm{Y} = \mathrm{b_0} + \Sigma\, \mathrm{b_i} * \mathrm{X_i} + \Sigma \mathrm{b_{ii}} * \mathrm{X_i^2} + \Sigma\Sigma\, \mathrm{b_{ij}} \mathrm{X_i} * \mathrm{X_j} + \mathrm{e_i} \qquad (5)$$

where Y refers to the response, b_0 is the constant, b_i, b_{ii} and b_{ij} represent the linear, quadratic and interactive effects, respectively, of the input factors X_i and X_j (i =1, 2, 3 and 4; j= 1, 2, 3 and 4), and “e” represents the residual term. All of the coded variables (X) were calculated using Eq.6:

$$\mathrm{X_i} = \frac{\mathrm{U_i} - \mathrm{U_{i0}}}{\Delta \mathrm{U_i}} \qquad (6)$$

Where $\mathrm{U_i} = (\frac{\mathrm{U_{imax}} + \mathrm{U_{imin}}}{2})$ is the value of $\mathrm{U_i}$ at the center; $\Delta\mathrm{U_{i0}} = (\frac{\mathrm{U_{imax}} - \mathrm{U_{imin}}}{2})$ is the value of variable change step and $U_{i\ max}$ and $U_{i\ min}$ are respectively the maximum and the minimum values of the effective variable U_i.

In this case of study, two different responses (COD and TOC removal) were considered. Therefore, two quadratic models could be deduced (Eq.7 and Eq.8 respectively):

$$\mathrm{Y_1} = 64.7 - 4.37\,\mathrm{X_1} + 12.77\,\mathrm{X_2} + 12.78\,\mathrm{X_3} + 4.1\,\mathrm{X_4} + 2.93\,\mathrm{X_1X_2} - 0.96\,\mathrm{X_1X_3} - 0.56\,\mathrm{X_1X_3} - 0.56\,\mathrm{X_1X_4} - 3.11\,\mathrm{X_2X_3} - 0.92\,\mathrm{X_2X_4} + 2\,\mathrm{X_3X_4} - 1.91\,\mathrm{X_1^2} + 0.27\,\mathrm{X_2^2} - 2.15\,\mathrm{X_3^2} \tag{7}$$

$$\mathrm{Y_2} = 61.09 - 9.16\,\mathrm{X_1} + 15.05\,\mathrm{X_2} + 15.69\,\mathrm{X_3} + 4.66\,\mathrm{X_4} + 3.08\,\mathrm{X_1X_2} - 1.69\,\mathrm{X_1X_3} - 1.1\,\mathrm{X_1X_4} + 2.62\,\mathrm{X_2X_3} - 0.17\,\mathrm{X_2X_4} + 1.56\,\mathrm{X_3X_4} - 4.92\,\mathrm{X_1^2} - 4.11\,\mathrm{X_2^2} - 1.08\,\mathrm{X_3^2} \tag{8}$$

Where X_i varies between -1.41 and +1.41; Y_1 is the COD removal and Y_2 is the TOC removal..

Based on these models, two different hypothesis (H_0 and H_1) were defined. The first hypothesis (H_0) considered the models to be insignificant whereas the second one (H_1) considered the models to be significant. In order to accept or to reject H_0, an ANOVA test was carried out, as presented in SM2.

In fact, the acceptance or the rejection of H_0 strongly depends on the F value (F) that should be compared to the critical F value (Fc) obtained from fisher Table (95 % of confidential level). According to the results summarized in SM2, F values (16.53 for COD and 16.66 for TOC) were highly superior to Fc ($F_{c\ (0.05,4,35)}$ = 2.64 for COD and $F_{c\ (0.05,13,26)}$ = 2.12 for TOC). Consequently, H_0 was rejected and both of the proposed models were significant. This was also confirmed by comparing Pr > F with α value (α =0.05). According to Muhamad et al. (2013), Pr> F should be inferior to α in order for the models to be accepted, which was well achieved in this test. Furthermore, the correlation coefficient R^2 of both of the models

(R^2 = 0.89) was higher than 0.8, thus indicating a good correlation between the predicted values and the experimental ones, as documented in Fig 4a and 4b.

Once the proposed models were accepted, the optimization of the operating parameters was possible by considering the following criteria: (1) The treatment cost should be minimized by minimizing the current intensity and the treatment time, and (2) The COD removal as well as the TOC removal should exceed 84 % in order to respect the legislation standards. Taking into account these criteria, a single solution was proposed by the Design-Expert, as shown in Table 4. Theoretically, applying 5.3 A of current intensity during 110 min of treatment time in the presence of 2 500 mg/L of EG and 7 g/L of Na_2SO_4 allows the removal of 87.5 % and 89 % of COD and TOC, respectively. A triplicate assays were then carried out in order to confirm these results. It was found that experimental results for COD (91 ± 2.2 %) and TOC removal (80 ± 4 %) were close to the theoretical ones. Consequently, the operating conditions proposed in Table 4 ([EG] = 2 500 mg/L, I= 5.3 A, t= 110 min and [Na_2SO_4] = 7g/L) were finally defined as the optimal operating parameters allowing a maximum EG degradation (91 ± 2.2 % of COD removal) and mineralization (80 ± 4 % of TOC removal) while maintaining a minimum cost. To seek more information, the kinetic of EG degradation under optimal operating conditions was carried out, as presented in Fig 5. According to these results, the electrochemical oxidation of EG followed a first order kinetic, thus indicating that the degradation rate of EG was subjected to pollutant concentration control (mass transfer control). The kinetic constant k was estimated to 0.02 min^{-1} while the half-life reaction time $t_{1/2}$ was around 34.6 min.

3.3. Oxidation mechanism of EG during ECO process

As stated earlier, the electrochemical oxidation of EG could be realized on the surface of the working anode (BDD) via OH° or in the bulk of the solution via other mediators ($S_2O8_2^-$, H_2O_2, etc.). Consequently, different by-products such as Glycol aldehyde, Glycolic acid, Glyoxylic acid, oxalic acid and formic acid could be generated during the degradation process. According to Dietrick McGinnis et al. (2001), the oxidation of EG by OH° radicals produced oxalic and formic acid as final by-products. Further oxidation of formic acid generated CO_2 and H_2O, as presented in Fig 6.

In order to confirm the generation of oxalic and formic acid during the ECO of EG under optimal conditions (I= 5.3 A, t=110 min, [EG] = 2 500 mg/L, [Na_2SO_4] = 7g/L), a liquid chromatography analysis was carried out for 8 different treatment time (0, 10, 20, 40, 60, 90 and 110 min). The overall results are summarized in Table 5.

It was found that the appearance of oxalic and formic acid in the treated solution took more than 10 min. This could be explained by the insufficient of oxidants concentration (OH°, $S_2O8_2^-$, H_2O_2) capable of oxidizing EG in the beginning of the treatment. As long as the treatment proceeded, the concentration of oxalic and formic acid reached its maximum with respectively 46 mg/L (t=90 min) and 189 mg/L (t=60 min). It is worth underlining that the amount of formic acid produced was much higher than the oxalic acid. According to Fig 5, one molecule of oxalic acid could be oxidized to two molecules of formic acid, thus doubling the concentration of this latter. In parallel, EG molecules could be also oxidized directly to formic acid rather than passing through different forms of by-products as illustrated by Wang et al. (2009). With the existing of both degradation scenarios, the concentration of formic acid will be much higher than the concentration of oxalic acid which was well confirmed in Table 5.

Starting from 60 min of treatment time, 37 % of formic acid was mineralized to CO_2 and H_2O leading to a residual concentration of 119 mg/L at the end of the treatment. Based on the literature, formic acid is a recalcitrant by-product that could resist to its oxidation by hydroxyl radicals (Tong et al., 2010).

4. Conclusion

This study investigated the treatment of EG solution in batch recirculation mode using electrochemical oxidation process. A boron doped diamond electrode was used as working anode while carbon felt was used as working cathode. An experimental design methodology based on factorial design (FD) and central composite design (CCD) was carried out in order to optimize the treatment process. Four different operating parameters including EG concentration, current intensity, treatment time and electrolyte type were chosen for the study. FD was applied to determine the effect of these operating parameters on EG removal. The results showed that both of the current intensity and the treatment time were the most influent parameters in the ECO of EG. In fact, current intensity and treatment time contributed respectively with 49 % and 43 % in the COD removal while they contributed respectively with 39 % and 37 % in the TOC removal. The second most important objective of the study was the optimization of the treatment process using central composite design (CCD) methodology. The best operating conditions obtained while considering the treatment cost and the legislation standards were: 5.3 A of current intensity, 110 min of treatment time, 2 500 mg/L of EG and 7 g/L of Na_2SO_4. Consequently, a maximum COD and TOC removal of respectively 91 ± 2.2 % and 80 ± 4 % were obtained under these operating conditions. During the ECO treatment of EG solution, oxalic acid and formic acid were identified as by-products with a residual concentration of 40 and 119 mg/L, respectively. It was concluded that only 37 % of formic acid was mineralized, indicating that the mineralization of EG was not complete. Therefore, a further increase in the current intensity or/and the treatment time is well recommended for better EG mineralization. In an economic point of view, the ECO of EG under optimal conditions costs 8.35 CAN\$/m^3 while its storage as hazardous substance is estimated to 300 CAN\$/m^3.

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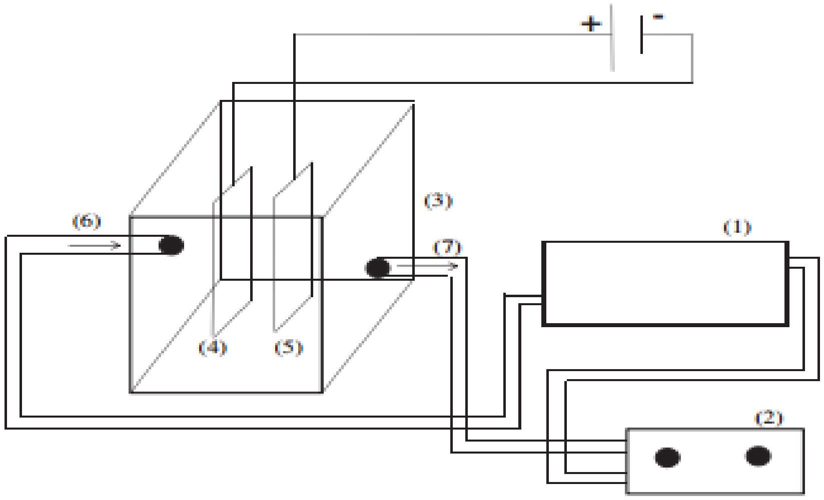

Fig.1 Electrolytic reactor design; Plexiglas tank (1), peristaltic recycling pump (2), electrolytic cell (3), Anode (4), cathode (5), inlet (6), outlet (7).

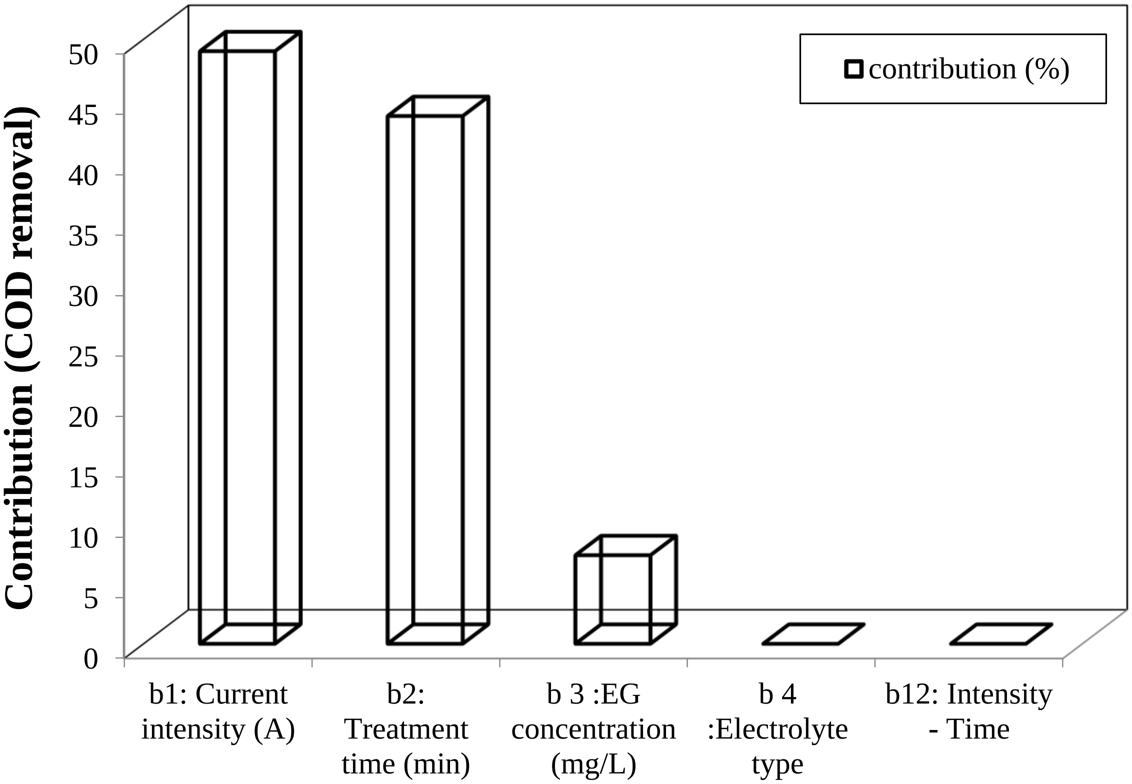

Fig. 2 Contribution of current intensity, treatment time, pollutant concentration, and electrolyte type on COD removal using FD methodology.

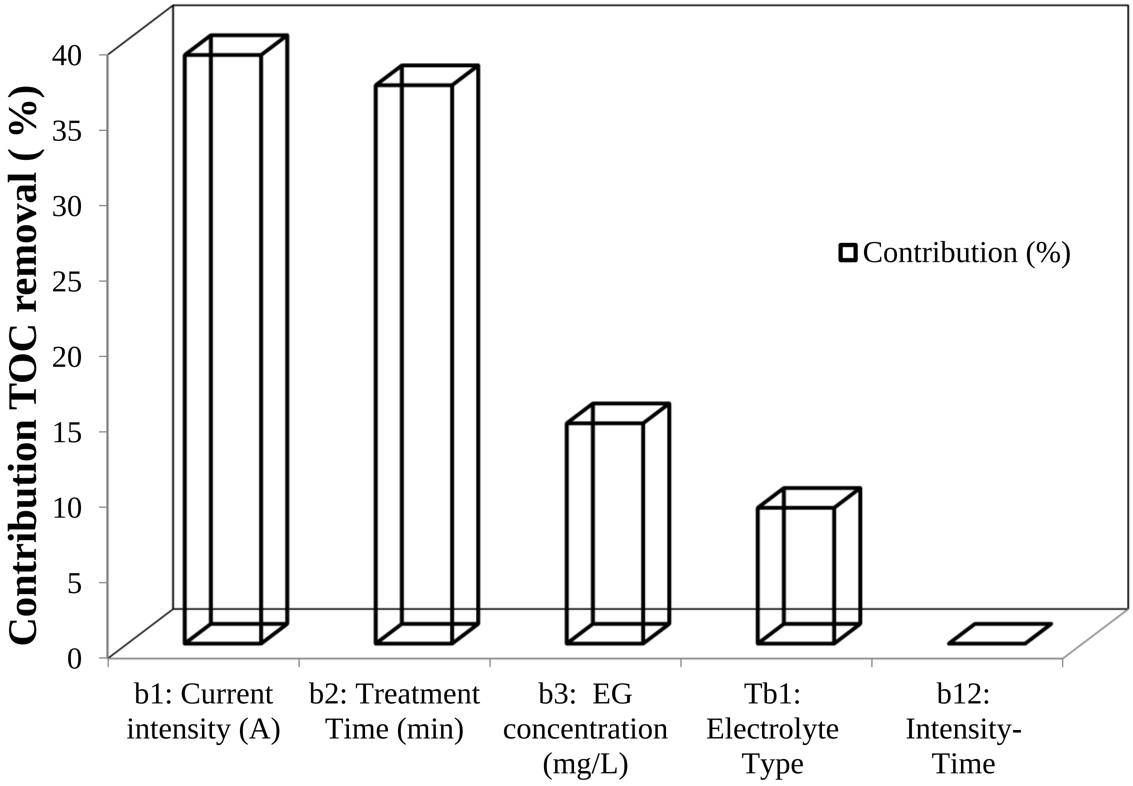

Fig. 3. Contribution of current intensity, treatment time, pollutant concentration, and electrolyte type on TOC removal using FD methodology.

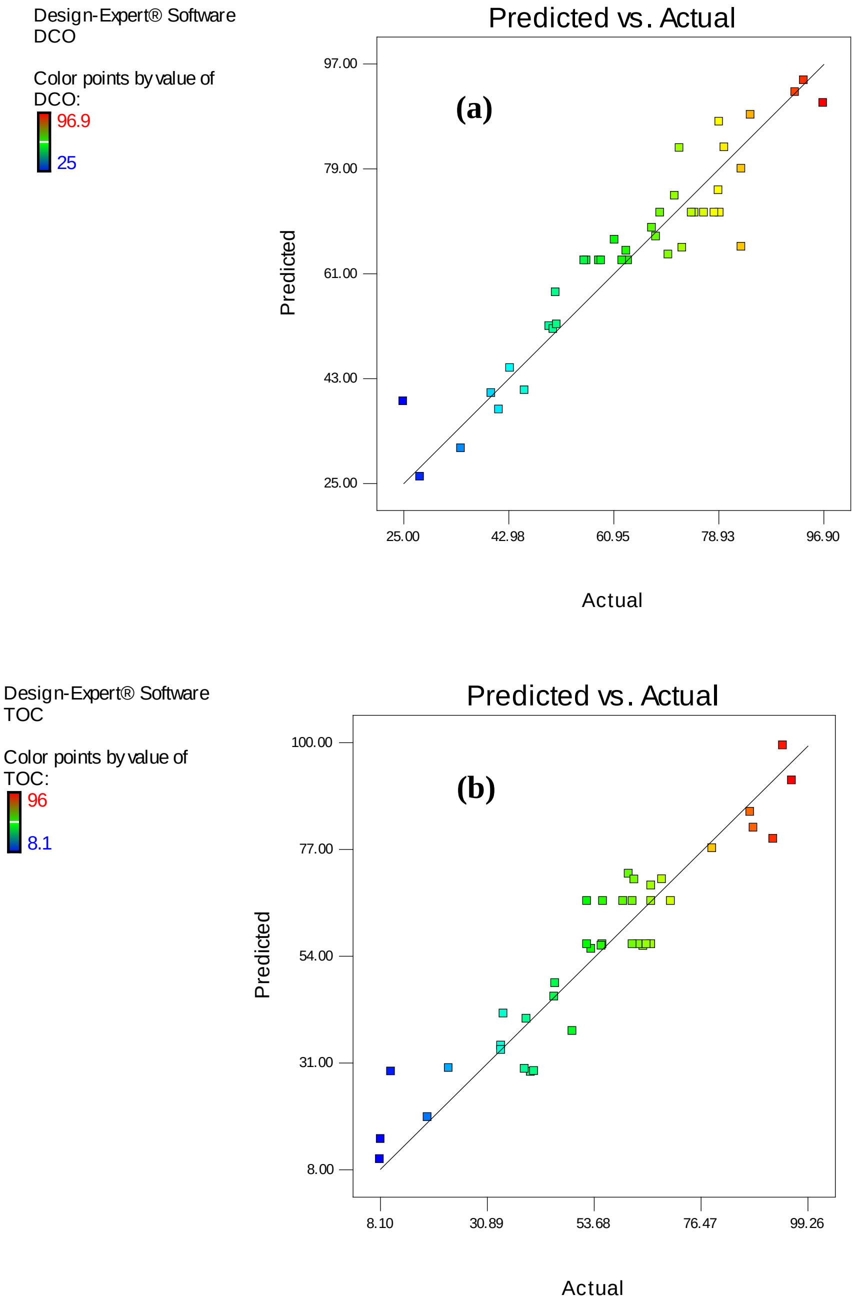

Fig. 4 Comparison between actual and predicted values for (**a**) COD removal and (**b**) TOC removal using CCD methodology.

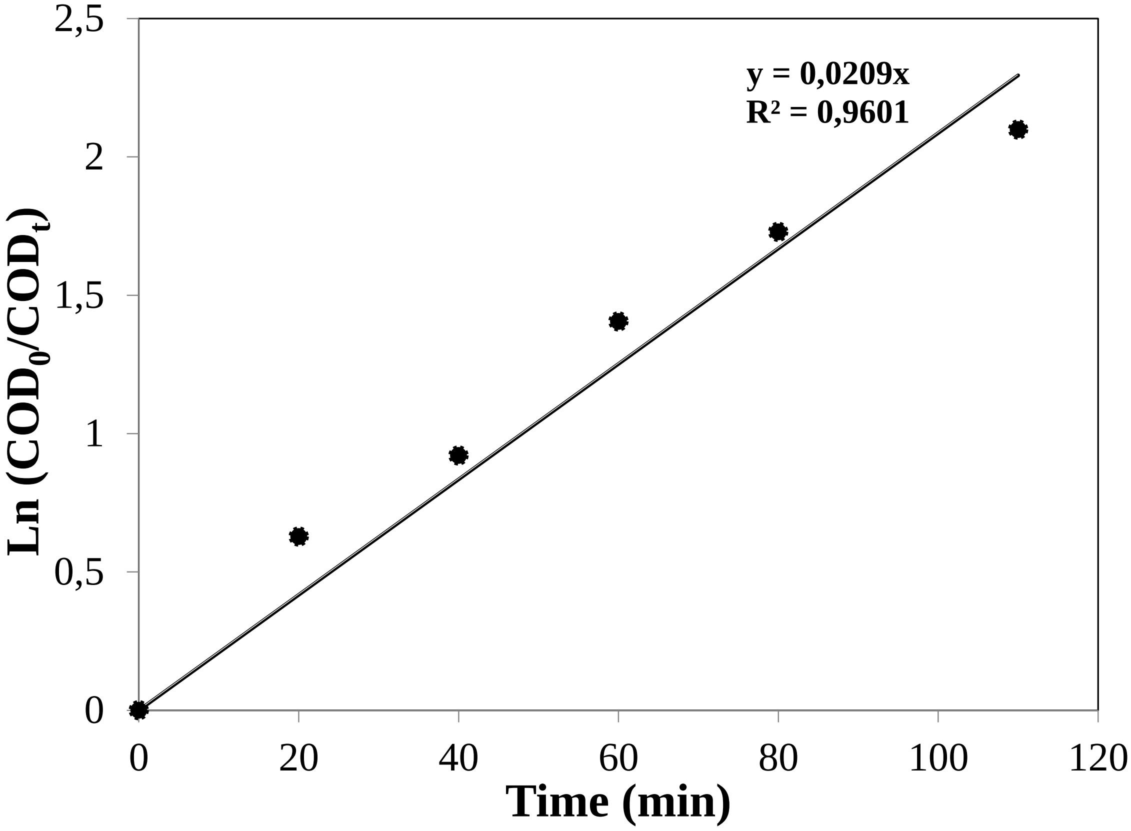

Fig. 5 Kinetic of EG degradation under optimal operating conditions of ECO process (I= 5.3 A, t=110 min, [EG] = 2 500 mg/L, [Na_2SO_4] = 7g/L).

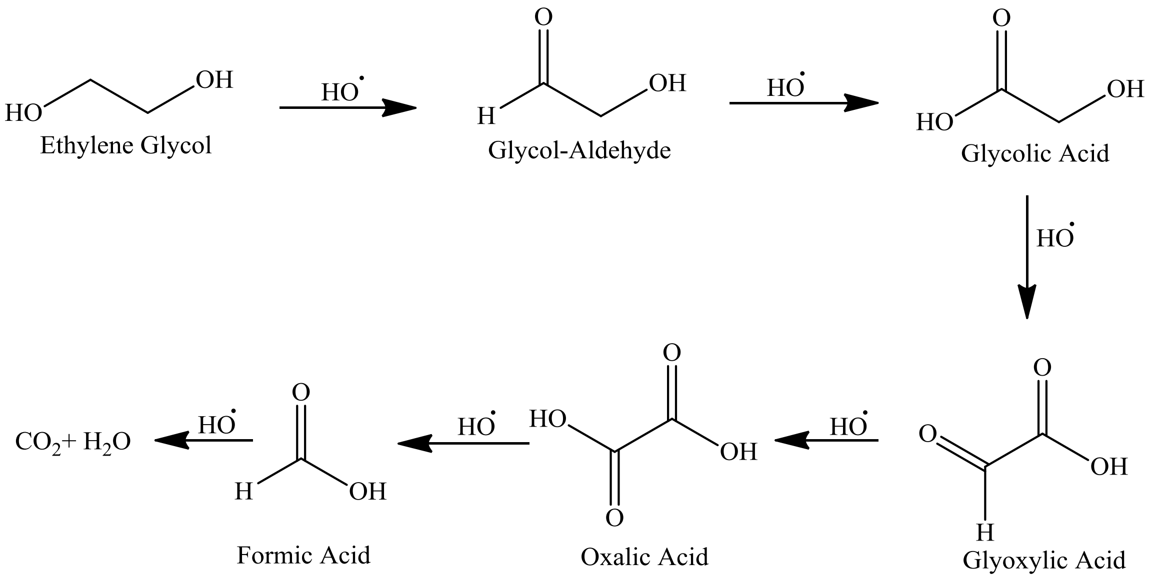

Fig. 6 Proposal oxidation mechanism of EG by OH° radicals.

Tables

Table 1. Experimental range and levels of independent process variables using FD methodology.

Coded variables (X_i)	**Factor (U_i)**	**Experimental Field**		**$U_{i,0}$**	**ΔU_i**
		Min value (-1)	**Max value (+1)**		
X_1	U_1 : Concentration (mg/L)	2 500	3500	3 000	500
X_2	U_2 : Intensity (A)	3	6	4.5	1.5
X_3	U_3 : Time (min)	60	120	90	30
X_4	U_4 : Electrolyte	NaCl	Na_2SO_4	-	-

Table 2. Experimental factorial matrix in the 2^4 design in FD methodology.

Assays	**Experiment Design**				**Experiment Plan**				**Results**	
	X_1	**X_2**	**X_3**	**X_4**	**U_1 (mg/L)**	**U_2 (A)**	**U_3 (min)**	**U_4**	**COD removal (%)**	**TOC removal (%)**
1	-1	-1	-1	-1	2500	3	60	Na_2SO_4	43.3	49.2
2	-1	-1	1	-1	2500	3	120	Na_2SO_4	72.3	68.3
3	-1	1	-1	-1	2500	6	60	Na_2SO_4	67.6	55.4
4	-1	1	1	-1	2500	6	120	Na_2SO_4	93.6	94.1
5	-1	-1	-1	1	2500	3	60	NaCl	41.4	10.5
6	-1	-1	1	1	2500	3	120	NaCl	68.3	53.2
7	-1	1	-1	1	2500	6	60	NaCl	72.8	45.5
8	-1	1	1	1	2500	6	120	NaCl	80.0	87.1
9	1	-1	-1	-1	3500	3	60	Na_2SO_4	35.0	8.3
10	1	-1	1	-1	3500	3	120	Na_2SO_4	63.2	39.4
11	1	1	-1	-1	3500	6	60	Na_2SO_4	61.2	45.3
12	1	1	1	-1	3500	6	120	Na_2SO_4	84.4	87.8
13	1	-1	-1	1	3500	3	60	NaCl	28.0	8.1
14	1	-1	1	1	3500	3	120	NaCl	50.0	22.8
15	1	1	-1	1	3500	6	60	NaCl	57.6	34.5
16	1	1	1	1	3500	6	120	NaCl	83.0	61.2

Table 3. Central composite matrix and experimental results

Assays	Experimental design			Experimental plan			Results	
	X_1	**X_2**	**X_3**	**U_1 (mg/L)**	**U_2 (A)**	**U_3 (min)**	**COD (%)**	**TOC (%)**
NaCl used as supporting electrolyte (**U4**)								
1	0	0	-1.41	3 000	4.5	39.55	25	39.5
2	0	0	0	3 000	4.5	90	56.4	42.5
3	0	0	+1.41	3 000	4.5	140.45	79	79.8
4	0	0	0	3 000	4.5	90	58.9	65.9
5	0	0	0	3 000	4.5	90	58.5	52.3
6	0	0	0	3 000	4.5	90	63.5	82
7	0	0	0	3 000	4.5	90	56	66.6
8	0	0	0	3 000	4.5	90	62	45.8
9	0	-1.41	0	3 000	1.98	90	45.8	18.3
10	0	+1.41	0	3 000	7	90	79.1	62.4
11	+1.4	0	0	3840,9	4.5	90	50.7	40.3
12	- 1.4	0	0	2 159	4.5	90	70.4	64.3
Na_2SO_4 used as supporting electrolyte (U4)								
13	0	0	-1.41	3 000	4.5	39.55	40.1	34.8
14	0	0	0	3 000	4.5	90	79.2	70.2
15	0	0	+1.41	3 000	4.5	140.45	96.9	96.3
16	0	0	0	3 000	4.5	90	76.5	52.3
17	0	0	0	3 000	4.5	90	74.9	55.7
18	0	0	0	3 000	4.5	90	74.4	60.8
19	0	0	0	3 000	4.5	90	69	82.4
20	0	0	0	3 000	4.5	90	78.3	86.1
21	+1.41	0	0	3840,9	4.5	90	51.1	34.4
22	-1.41	0	0	2 159	4.5	90	71.5	66.4
23	0	+1.41	0	3 000	7	90	92.1	92

24	0	-1.41	0	3 000	1.98	90	51.3	41.1

Table 4. Comparison between theoretical and experimental results during the oxidation of EG by ECO process under optimal conditions (I= 5.3 A, t=110 min, [EG] = 2 500 mg/L, [Na_2SO_4] = 7g/L).

Solution	**Factors**				**Theoretical Results**		**Experimental Results**	
	U1 (mg/L)	**U2 (A)**	**U3 (min)**	**U4**	**COD removal (%)**	**TOC removal (%)**	**COD removal (%)**	**TOC removal (%)**
	2500	**5.3**	**110**	**Na_2SO4**	**87.5**	**89**	**91 ± 2.2**	**80 ± 4**

Table 5. Identification and quantification of EG by-products produced during ECO treatment of EG under optimal conditions (I= 5.3 A, t=110 min, [EG] = 2 500 mg/L, [Na_2SO_4] = 7g/L).

Treatment time (min)	**Oxalic acid (mg/ L)**	**Formic acid (mg/ L)**
0	< 10	< 10
10	< 10	< 10
20	11	86
30	20	131
40	26	157
60	38	189
90	46	171
110	40	119