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Experimental Design Methodology Applied to the Oxidation of Quinolines in Aqueous Medium by Electro-Fenton Process

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Abstract: The degradation behavior of 8-hydroxyquinoleine sulfate (8-HQS), a model molecule of quinolines, was studied in an aqueous medium by electro-Fenton process using a carbon felt cathode and a platinum anode. The great oxidation ability of this process is due to a large production of hydroxyl radical ($\cdot\text{OH}$) by electrochemically induced Fenton's reagent (H_2O_2 , Fe^{2+}). Hydroxyl radicals are very powerful oxidizing agents which react on organics up to complete mineralization. A factorial experimental design was used for determining the operating parameters on the degradation of 8-HQS in an aqueous medium. The results showed that the current intensity and the initial concentration of 8-HQS were the main factors that influenced the degradation rate. The decay in concentration of 8-HQS with the electrolysis time shows that the oxidation of 8-HQS follows pseudo-first order kinetics. The absolute rate constant for the oxidation of 8-HQS by $\cdot\text{OH}$ was determined by using competition kinetics method and found to be $1.62 \times 10^9 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$. The optimal experimental parameters for the mineralization of 8-HQS have also been investigated by the use of Doehlert matrix. It has been demonstrated that under the optimal conditions determined by this method, electro-Fenton process can lead to a quasi-complete mineralization (95% of TOC removal) of 8-HQS aqueous solution. The treatment of 8-HQS aqueous solutions leads to the formation of short-chain carboxylic acids as end-products before mineralization. Their evolution during electro-Fenton treatment was studied. The follow-up of the solution toxicity evolution shows the formation of intermediates more toxic than 8-HQS. However, the solution toxicity was totally removed after mineralization of these intermediates.

Key words: 8-hydroxyquinoleine sulfate; electro-Fenton process; hydroxyl radical; degradation; Doehlert matrix; mineralization; toxicity

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Quinolines are nitrogen heterocyclic compounds; they occur widely in coal tar, oil shale, and petroleum, and serve as raw materials and solvents in the manufacture of dyes, paints, fungicides, and wood treatment products. Quinolines and some of their derivatives were reported to be toxic, carcinogenic and mutagenic^[1-3]. Due to their good solubility and low biodegradation ability, quinolines and their derivatives have become one of the common contam-

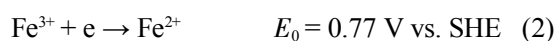
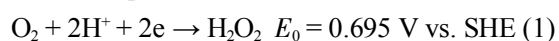
inants in ground water and soil^[4]. Therefore, it is environmentally important to find out how to remove them from water economically and effectively.

The conventional processes for the degradation of quinolines are the biological processes (activated sludge, trickling filters) which can destroy a large fraction of biodegradable organic compounds found in wastewater^[5-6]. However, many hazardous compounds are poorly removed with biological processes

due to their toxicity for microorganisms, or recalcitrance to biodegradation. Some works have reported the enhanced degradation of quinolines through utilization of screened highly effective microorganisms^[7-8]. However, these biological methods are usually time-consuming.

As an alternative, a large variety of advanced oxidation processes (AOPs) have been recently developed to remove persistent organic pollutants from waters. AOPs are environmentally friendly methods based on the in situ chemical, photochemical, photocatalytic or electrochemical productions of hydroxyl radicals ($\bullet\text{OH}$)^[9-12]. They are applied when conventional oxidation techniques become insufficient by kinetic reasons, or contaminants are refractory to chemical oxidation in an aqueous medium, or they are partially oxidized yielding stable by-products showing greater toxicity than the starting pollutants. In contrast, $\bullet\text{OH}$ radicals generated in AOPs are able to non-selectively destroy most of organic and organometallic pollutants until total mineralization. These radicals react rapidly with organics mainly either by hydrogen atom abstraction (dehydrogenation) or by addition to a non-saturated bond (hydroxylation)^[13]. Some researchers studied the degradation characteristics of quinolines using wet oxidation^[14], supercritical water^[15] and photocatalytic oxidation^[16-17].

Recently, in the framework of various methods developed for destruction of persistent organic pollutants in water, we have proposed an electrochemically induced advanced oxidation process, namely, the electro-fenton process, as an effective alternative process for wastewater treatment^[9, 13, 19]. It is based on the action of very reactive hydroxyl radicals, produced through the electrochemically in situ generated Fenton's reagent. In this process, molecular oxygen and ferric ions(Fe^{3+}) are simultaneously reduced at the cathode to generate hydrogen peroxide (Eq. 1) and ferrous ions (Eq. 2):



Then, the classical Fenton's reaction takes place in solution and generates strong oxidant $\bullet\text{OH}$:



The $\bullet\text{OH}$ generated through the process reacts then with organic pollutants in order to remove them from water. In this study, we report the degradation/mineralization of 8-hydroxyquinoline sulfate (8-HQS), as a model molecule of quinolines, in synthetic aqueous solutions by electro-Fenton process. The experimental design methodology^[20] was used to investigate the influences of the principal operating parameters (applied current intensity, concentrations of 8-HQS and catalyst, electrolysis time) on the efficiency of the electro-Fenton in degradation of 8-HQS, as well as to determine optimal mineralization conditions of 8-HQS aqueous solutions. This methodology is based on multivariable methods where the level of the independent variables is simultaneously modified from one experiment to another. It provides the means of building a statistically significant model of a phenomenon by performing a minimum set of experiments adequately distributed in the experimental matrix. It was noted that this methodology is then more effective and leads to a considerable reduction of number of experiments and a fast interpretation in results^[21-22]. Hence, it was used for planning the experimentation and analyzing the experimental results in the present study.

1 Experimental

1.1 Chemicals

Reagent of 8-HQS was obtained from Aldrich (purity 98%), while $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ (purity 97%) and Na_2SO_4 (purity 99%) from Acros. Carboxylic acids and other chemicals of analytical grade, used for chromatographic analysis, were purchased from Acros, Sigma, and Fluka. Analytical organic solvents were used for HPLC analysis. All solutions were prepared in tap water.

1.2 Electrochemical Apparatus and Procedures

A stabilized power supply was used for running electrolyses. Electrolyses were carried out at room temperature in a non-divided cylindrical cell of 250 mL equipped with two electrodes: a 3D carbon-felt (from Carbone Loraine, France) cathode of 70 cm²

area (14 cm length \times 5 cm height \times 0.3 cm width) and a cylindrical platinum grid of 4.5 cm height and 3 cm of internal diameter as an anode. Prior to the electrolysis, compressed air was bubbled, for 10 min, through the solution through a frit at $1 \text{ L} \cdot \text{min}^{-1}$ to reach a steady O_2 concentration. Electrolyses were carried out under current controlled conditions. A catalytic quantity of ferric iron was added to the solutions before starting the electrolysis. The current remained constant during electrolysis and samples were withdrawn at regular electrolysis times. The initial pH of the solutions was adjusted to 3 with sulfuric acid ($1 \text{ mol} \cdot \text{L}^{-1}$). The pH values were measured with a pH glass electrode calibrated with standard buffers at pH values of 4, 7 and 9. The ionic strength was maintained constant by addition of $50 \text{ mmol} \cdot \text{L}^{-1} \text{ Na}_2\text{SO}_4$.

1.3 Analysis Procedure

The evolution of 8-HQS concentration during electrolysis was monitored by high performance liquid chromatography (HPLC) using a Merck Lachrom system equipped with L-7455 diode array detector and fitted with a reverse phase Purospher RP-18 column $5 \mu\text{m}$, $4.6 \text{ mm} \times 250 \text{ mm}$. Detection of 8-HQS was carried out at 240 nm. The mobile phase was a mixture of methanol/water/acetic acid (10/89/1, $V/V/V$). It was eluted with a rate of $0.6 \text{ mL} \cdot \text{min}^{-1}$. The mineralization efficiency of treated solutions was monitored by the abatement of the total organic carbon (TOC) using a Shimadzu VCSH TOC analyzer. Calibrations were performed by using the initial 8-HQS solutions.

1.4 Toxicity Assessment

The potential toxicity of 8-HQS and its oxidation intermediates was determined using the bioluminescence test Microtox[®] according to the international standard process (OIN 11348-3). This method uses bioluminescent marine bacteria *Vibrio fischeri* (LUMISTox LCK 487) as the bioassay organism purchased from Hach Lange France. Two values of the inhibition of the luminescence (%) were calculated after 5 min and 15 min exposure to samples at $15 \text{ }^\circ\text{C}$ with a BERTHOLD AutoLumat Plus LB 953.

2 Results and Discussion

2.1 Effect of Catalyst Concentration on Degradation Kinetics

The concentration of catalyst (Fe^{3+}) is an important parameter for the electro-Fenton process. To determine the effect of the catalyst concentration on the degradation of 8-HQS, several electrolyses were carried out in acidic solutions of pH 3 at the concentration of 8-HQS being $0.2 \text{ mmol} \cdot \text{L}^{-1}$ at 100 mA and room temperature, varying Fe^{3+} concentrations in the range of $0.1 \sim 1.0 \text{ mmol} \cdot \text{L}^{-1}$ (Fig. 1). As can be seen in this figure the removal rate of 8-HQS decreases with the increase of Fe^{3+} concentration. Similar observations were reported by some publications^[23-25].

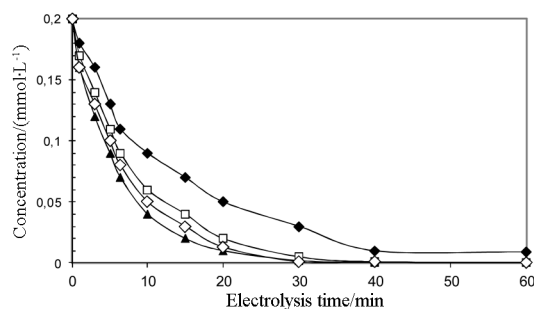
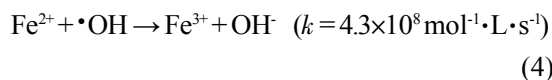


Fig. 1 Effect of catalyst (Fe^{3+}) concentration on 8-HQS decay as a function of electrolysis time during electro-Fenton treatment at 100 mA and pH 3.0 [Fe^{3+}]/(mmol·L⁻¹): 0.1 (◇-); 0.2 (-▲-); 0.5 (-□-) and 1.0 (-◆-). [8-HQS]₀ = $0.2 \text{ mmol} \cdot \text{L}^{-1}$, [Na_2SO_4] = $50 \text{ mmol} \cdot \text{L}^{-1}$, $V = 230 \text{ mL}$

The inhibition in oxidation rate of 8-HQS in the presence of higher Fe^{3+} concentrations can be explained by the enhancement of the waste reaction (4) which competes for $\cdot\text{OH}$ and reaction (5) which inhibits Fenton's reaction consuming one of its reagents, the H_2O_2 ^[26]:



2.2 Effect of Experimental Parameters on Kinetic Degradation by Means of the Experimental Design Methodology

In order to evaluate the effects of other operating parameters on the degradation rate of 8-HQS, three

main factors were chosen: electrolysis time (U_1), current intensity (U_2) and 8-HQS concentration (U_3). A two-level full factorial design $2^{k[23, 27]}$ was carried out to determine these three selected factors and their interactions on the pseudo-first order rate constant (k_{app}). In these types of designs, variables (k) are set at two levels (minimum) and (maximum) normalized as (-1) and (+1). With these designs, it was possible to calculate the average and the principle effects of each factors and their interactions 2 to 2, 3 to 3, until k factors. The experimental response (Y) associated to a 2^k factorial design (for three variables) is represented by a linear polynomial model with interaction.

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3 \quad (6)$$

Where: Y , experimental response; X_i : coded variable (-1 or +1); b_i : estimation of the principal effect of the factor i for the response Y ; b_{ij} : estimation of interaction effect between factors i and j for the response Y .

The response investigated is the apparent rate constant, k_{app} , of the reaction between 8-HQS and $\cdot\text{OH}$ during electro-Fenton processing. The coefficients of the equation model were calculated in the experimental field listed in Tab. 1. The choice of the

limits of the investigated region is referred to a previous work^[27].

The experimental design and results are presented in Tab. 2. According to the results obtained, the coefficients of the polynomial model were calculated using the new efficient methodology for research using optimal design (NEMROD) Software:

$$Y = 0.165 + 0.004X_1 + 0.043X_2 - 0.048X_3 - 0.0003X_1X_2 + 0.0003X_1X_3 + 0.006X_2X_3 - 0.0005X_1X_2X_3 \quad (7)$$

The effects and interactions of the various investigated factors are represented in Fig. 2. This figure

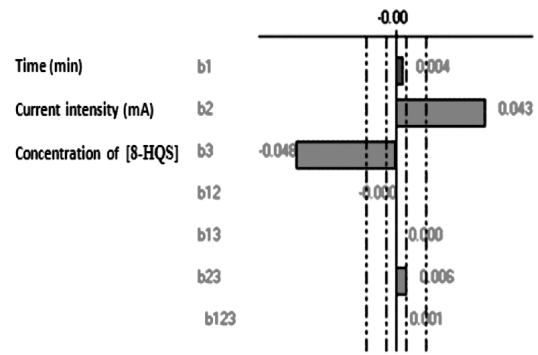


Fig. 2 Graphical analysis of the effects of electrolysis time, current intensity, and 8-HQS concentration on the degradation of 8-HQS

Tab. 1 Experimental region investigated for the 8-HQS degradation by electro-Fenton process

Coded variables (X_i)	Factors (U_i)	Unit	Unit experimental field	
			Minimum value	Maximum value
X_1	U_1 : Electrolysis time	min	20	60
X_2	U_2 : Current intensity	mA	50	100
X_3	U_3 : [8-HQS]	mmol·L ⁻¹	0.2	0.5

Tab. 2 Factorial experimental design, experimental plan, and results

Experiment N°	Experimental design			Experimental plan			Response Y k_{app}/min^{-1}
	X_1	X_2	X_3	U_1	U_2	U_3	
1	-1	-1	-1	20	50	0.2	0.172
2	1	-1	-1	60	50	0.2	0.180
3	-1	1	-1	20	100	0.2	0.248
4	1	1	-1	60	100	0.2	0.253
5	-1	-1	1	20	50	0.5	0.066
6	1	-1	1	60	50	0.5	0.073
7	-1	1	1	20	100	0.5	0.162
8	1	1	1	60	100	0.5	0.170

shows that: The degradation kinetics is greatly influenced by the initial concentration of 8-HQS which has a negative effect on the studied response. Therefore, the electrolysis duration for a complete degradation increases with increasing substrate concentration. The effect of the electrolysis time is negligible. The current intensity is the second most significant factor on the degradation kinetics of 8-HQS. Its effect is positive. The increase of current intensity leads to increase the degradation rate of the 8-HQS. There is a little interaction between term (X_2X_3), therefore, the effect of variable X_2 (current intensity) depends on the level of variable X_3 (8-HQS concentration), and vice versa, in the experimental region investigated. This interaction has a negative effect on the studied response (k_{app}).

Pareto analysis^[28] gives more significant information to interpret these results. In fact, this analysis allows calculating the percentage effect of each factor on the response, according to the relation (8):

$$P_i = \frac{b_i^2}{\sum b_i^2} \times 100 \quad (i \neq 0) \quad (8)$$

Fig. 3 presents the Pareto graphic analysis. It shows that the 8-HQS concentration and the current intensity are the most determining factors on the degradation kinetics of 8-HQS, their effect is about 99% on the investigated response. Thus, to increase the degradation efficiency, it is worth working with a low concentration ($0.2 \text{ mmol} \cdot \text{L}^{-1}$) and at a high current intensity (100 mA). These results were also reported by different authors^[25, 29-30].

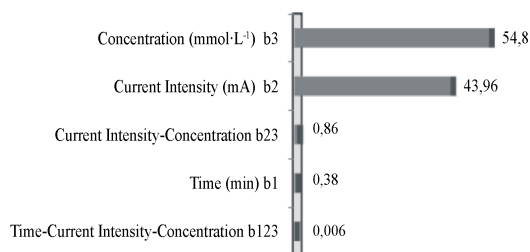


Fig. 3 Graphical Pareto analysis

2.3 Kinetics of 8-HQS Degradation by Hydroxyl Radicals

The oxidative degradation of 8-HQS with $\cdot\text{OH}$

generated by electro-Fenton process was studied under optimal conditions determined above, i.e., Fe^{3+} concentration of $0.2 \text{ mmol} \cdot \text{L}^{-1}$, current intensity of 100 mA and 8-HQS concentration of $0.2 \text{ mmol} \cdot \text{L}^{-1}$. Under these operating conditions, the complete disappearance of $0.2 \text{ mmol} \cdot \text{L}^{-1}$ 8-HQS was achieved at 15 min. Fig. 4 shows also that the decay in concentration of 8-HQS as a function of electrolysis time is exponential, indicating that the oxidation reaction obeys pseudo-first order kinetics. In fact, the reaction of 8-HQS with $\cdot\text{OH}$ can be described by pseudo-first order kinetics, assuming a quasi-stationary state for $\cdot\text{OH}$ concentration:



$$v = - \frac{d[8\text{-HQS}]}{dt} = k_{\text{abs}(8\text{-HQS})}[\cdot\text{OH}][8\text{-HQS}] \quad (10)$$

with k_{abs} and k_{app} being absolute and apparent rate constants, respectively, and $k_{\text{app}} = k_{\text{abs}}[\cdot\text{OH}]$.

The value of k_{app} was calculated to be 0.28 min^{-1} from linear regression of the pseudo-first order kinetic model (Fig. 4) with related coefficients higher than 0.99.

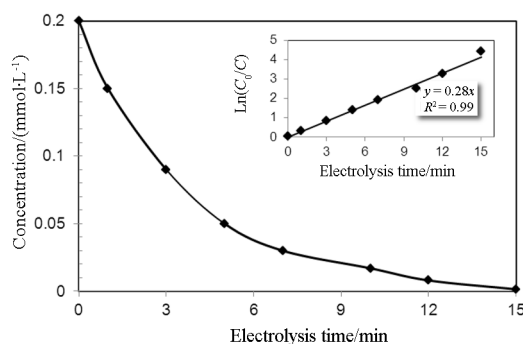


Fig. 4 Degradation kinetics for 230 mL of $0.2 \text{ mmol} \cdot \text{L}^{-1}$ 8-HQS aqueous solution at 100 mA and pH 3.0 [Fe^{3+}] = $0.2 \text{ mmol} \cdot \text{L}^{-1}$, [Na_2SO_4] = $50 \text{ mmol} \cdot \text{L}^{-1}$

The k_{abs} value of the oxidation of 8-HQS (Eq. 9) was then determined by the competition kinetics method^[25, 31-33] using a standard competition substrate (4-hydroxybenzoic acid, 4-HBA) for which k_{abs} is well known ($k_{\text{HBA}} = 1.63 \times 10^9 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$)^[34]. The competition kinetics experience was carried out under conditions given in Fig. 4. The k_{abs} value of $1.62 \times 10^9 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$ was found at 20 °C for the reaction be-

tween 8-HQS and $\cdot\text{OH}$, which is unavailable from literatures for comparison. However, this value is in agreement with k_{abs} values reported for hydroxylation reactions of aromatic compounds with $\cdot\text{OH}$ ^[34].

2.4 Mineralization of 8-HQS

The mineralization of 8-HQS aqueous solutions can be monitored by measuring the TOC removal during treatment by electro-Fenton process. In order to find optimal conditions for the mineralization of 8-HQS, three influent factors including current intensity (U_1), catalyst concentration (U_2) and electrolysis time (U_3) have been studied. We have chosen, at first, the approach of Doehlert^[21, 35-36]. Indeed, Doehlert matrix has some interesting qualities; it presents a uniform distribution of the experimental points within the space of the coded variables. Uniform networks are especially useful if one seeks to cover an experimental field with a set of uniformly distributed points, and if one seeks to explore the whole field

(limits and the interior) without proposing any prior model.

The experimental response associated to Doehlert matrix for 3 variables (Tab. 3) is represented by a quadratic polynomial model:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_{12} + b_{22}X_{22} + b_{33}X_{32} + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad (11)$$

where b_i is the estimation of the main effects of the factor i ; b_{ii} is the estimation of the second order effects, and b_{ij} is the estimation of the interactions between factor i and factor j .

The experimental response studied was the TOC removal ratio (Y) which is calculated according to the following equation:

$$Y(\%) = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_t} \times 100$$

The total experimental domain is explored through a minimum number of experiments which depends on the number of factors studied. Indeed, k

Tab. 3 Experimental region investigated for the 8-HQS mineralization.

Coded variables (X_i)	Factors (U_i)	Unit	Experimental region	
			Minimum value	Maximum value
X_1	U_1 : Current intensity	mA	100	500
X_2	U_2 : $[\text{Fe}^{3+}]$	mmol·L ⁻¹	0.05	0.5
X_3	U_3 : Electrolysis time	h	2	8

Tab. 4 Doehlert matrix experiments and experimental results

Experiment N°	Experimental region			Experimental plan			Result Y(%)
	X_1	X_2	X_3	U_1	U_2	U_3	
1	1.000	0.000	0.000	500	0.275	5	41.6
2	-1.000	0.000	0.000	100	0.275	5	36.5
3	0.500	0.866	0.000	400	0.470	5	47.4
4	-0.500	-0.866	0.000	200	0.080	5	60.5
5	0.500	-0.866	0.000	400	0.080	5	28.4
6	-0.500	0.866	0.000	200	0.470	5	65.2
7	0.500	0.287	0.816	400	0.340	8	74.4
8	-0.500	-0.287	-0.816	200	0.210	2	18.8
9	0.500	-0.287	-0.816	400	0.210	2	15.7
10	0.000	0.577	-0.816	300	0.405	2	54.6
11	0.500	0.287	0.816	200	0.340	8	87.0
12	0.000	-0.577	0.816	300	0.145	8	63.7
13	0.000	0.000	0.000	300	0.275	5	48.4

factors will require a minimum of $(k^2 + k + 1)$ experiments. For three variables, a set of 13 experiments is required (Tab. 4). This method allows an optimal organization of experiences and, consequently, a reduction of time and cost.

The experimental values of U_i are calculated from the coded variables X_i using Eq. (13):
where:

$$X_i = \frac{U_i - U_{i,0}}{\Delta U_i} \times \alpha \quad (13)$$

$U_{i,0} = \frac{U_{i,max} + U_{i,min}}{2}$ is the value of U_i at the centre of the experimental region;

$\Delta U_{i,0} = \frac{U_{i,max} - U_{i,min}}{2}$ is the step with $U_{i,max}$ and $U_{i,min}$, maximum and minimum values of the effective variable U_i , respectively. α is the maximum coded value of X_i with $X_1 = 1$; $X_2 = 0.866$; $X_3 = 0.816$.

The experimental design and results are represented in Tab. 4. Replicates at the central level

of the variables are performed in order to validate the model by means of an estimate experimental variance. The experiment at the center (experiment N° 13) was carried out three times in order to obtain an estimation of the experimental error (Tab. 5).

According to these results, the coefficients of the polynomial model were calculated using the NEM ROD Software^[37]:

$$Y = 49.2 - 0.39X_1 + 10.6X_2 + 29.8X_3 - 10.15X_1^2 - 4.72X_2^2 + 5.97X_3^2 - 2.71X_1X_2 + 9.41X_1X_3 - 30.11X_2X_3 \quad (14)$$

The predicted contour plots (curves of constant responses) and the three-dimensional representation of the same plots are given in Figs. 5, 6 and 7.

We can note from these figures that the maximum TOC removal ratio is obtained with an electrolysis time located in the maximum of the experimental region and a catalyst concentration between 0.20 to 0.35 mmol·L⁻¹. In addition, the TOC removal ratio is improved for current intensities

Tab. 5 Estimation of experimental error

Experimental N°	Current intensity/mA	[Fe ³⁺]/(mmol·L ⁻¹)	Electrolysis time/h	Y/%
14	300	0.275	5	48.4
13	300	0.275	5	50.0
15	300	0.275	5	49.2

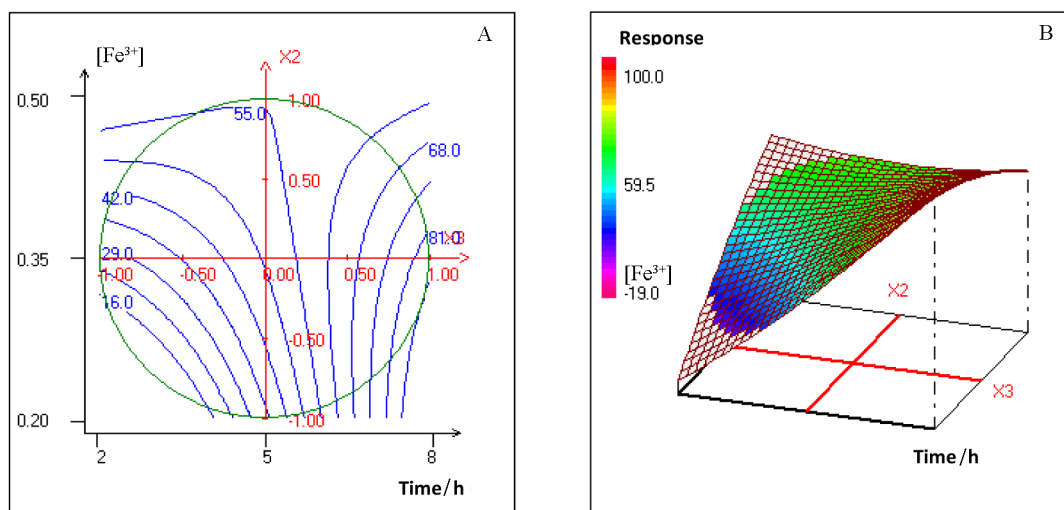


Fig. 5 Contour plots of TOC removal versus the catalyst concentration (mmol·L⁻¹) and electrolysis time (h) (A); Corresponding three-dimensional plot, results obtained from Doehlert matrix (Tab. 3) (B) [8-HQS]₀ = 0.2 mmol·L⁻¹, pH 3.0

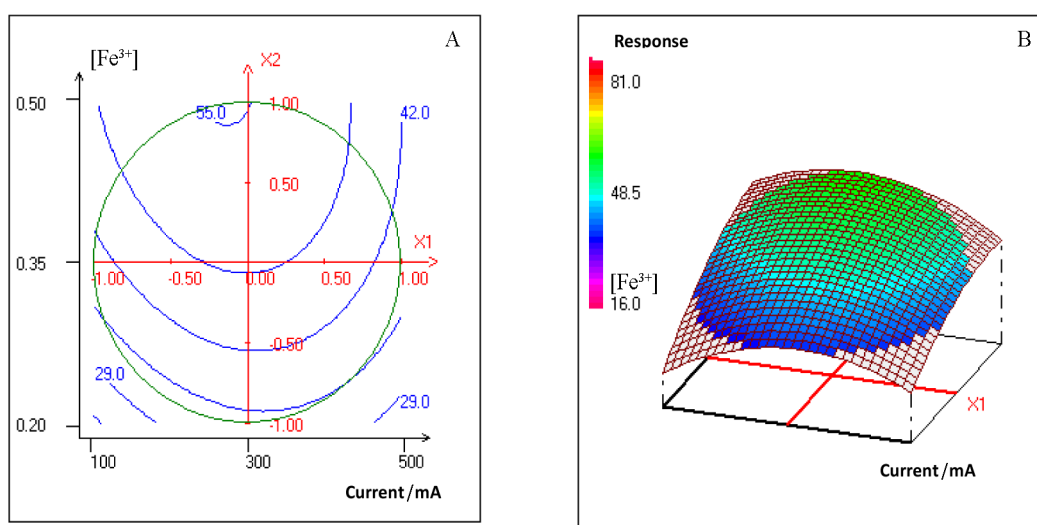


Fig. 6 Contour plots of TOC removal versus the catalyst concentration($\text{mmol} \cdot \text{L}^{-1}$) and current intensity(mA) (A); Corresponding three-dimensional plot, results obtained from Doehlert matrix (Tab. 3) (B) $[\text{8-HQS}]_0 = 0.2 \text{ mmol} \cdot \text{L}^{-1}$, pH 3.0

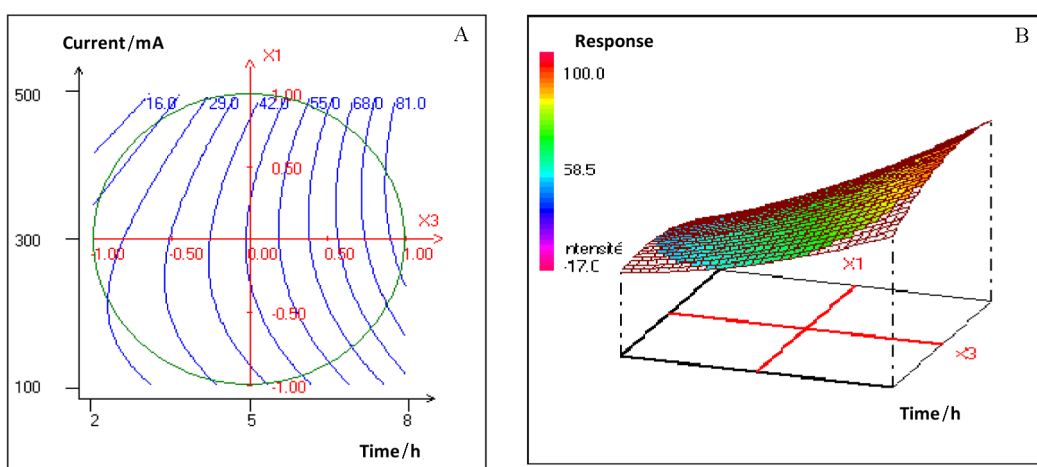


Fig. 7 Contour plots of TOC removal versus the current intensity (mA) and electrolysis time (h) (A); Corresponding three-dimensional plot, results obtained from Doehlert matrix (Tab. 3) (B) $[\text{8-HQS}]_0 = 0.2 \text{ mmol} \cdot \text{L}^{-1}$, pH 3.0

located in the center of experimental region. Consequently, to determine the optimal conditions for the 8-HQS mineralization, the experiment was done under the following conditions: $I = 300 \text{ mA}$, $t = 8 \text{ h}$, $[\text{Fe}^{3+}]_0 = 0.20 \text{ mmol} \cdot \text{L}^{-1}$. These conditions led to a maximum mineralization efficiency (95% of TOC removal).

2.5 Identification of Generated Carboxylic Acids

Generation of short chain carboxylic acids is expected from the oxidative breaking of the aryl moiety

of aromatic compounds^[33, 38-39]. The evolution of short chain carboxylic acids during the treatment of $0.20 \text{ mmol} \cdot \text{L}^{-1}$ 8-HQS aqueous solution of pH 3.0 by electro-Fenton process was followed by ion-exclusion chromatography. Oxalic, acetic, maleic and glyoxylic acids were detected under our analysis conditions. Fig. 8 shows their evolution as a function of electrolysis time during electro-Fenton process. As can be seen from Fig. 8, carboxylic acids were generated as soon as the electrolysis started. Maleic acid reached its maximum concentration at 3 h (Fig. 8A), being

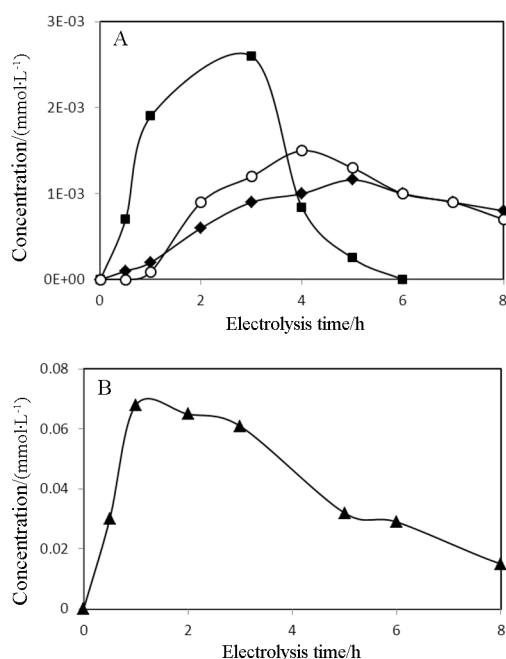


Fig. 8 Time-course of carboxylic acids produced during the mineralization of 230 mL 0.20 mmol·L⁻¹ 8-HQS aqueous solution: (a) maleic (-■-), acetic (-○-), glyoxylic (-◆-) acids, and (b) oxalic acid (-▲-). I = 300 mA, [Fe³⁺] = 0.2 mmol·L⁻¹, [Na₂SO₄] = 50 mmol·L⁻¹

subsequently quickly degraded. Glyoxylic acid started to be formed at the first minutes reaching its maximum concentration at 6 h (Fig. 8A). The disappearance of this acid led to the formation of oxalic acids (Fig. 8B). The transformation of glyoxylic acid into oxalic acid by electrochemical-advanced oxidation methods was previously reported by Boye et al.^[40] and Pimentel et al.^[33]. On the other hand, oxidation of acetic acid to oxalic acid was also reported^[41]. Oxalic acid is usually found as final by-product before complete mineralization during electrochemical AOPs^[23, 42-43] because it forms, with Fe³⁺, stable ferric-oxalate complexes which are difficult to mineralize by •OH^[23]. Because the formation by different paths and its recalcitrance due to formation of iron(III)-oxalic acid complex allows its accumulation at large extent compared to other carboxylic acids (Fig. 8 A and B).

2.6 Evolution of the Toxicity of 8-HQS Aqueous Solution during Electrolysis

In order to determine the potential toxicity of

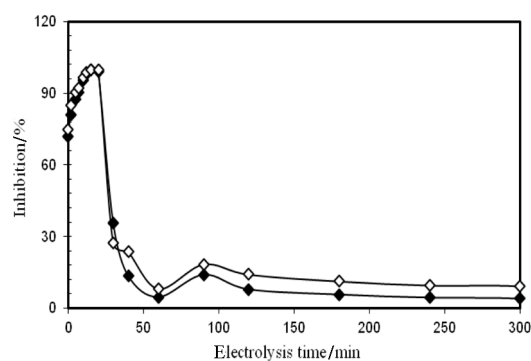


Fig. 9 Evolution of the inhibition of luminescence of bacteria *Vibrio fischeri* (Microtox[®] test) during electro-Fenton treatment of 230 mL of 0.20 mmol·L⁻¹ 8-HQS aqueous solution at 300 mA and pH 3 for the exposition times of 5 min (-◆-) and 15 min (-◇-) [Fe³⁺] = 0.2 mmol·L⁻¹, [Na₂SO₄] = 50 mmol·L⁻¹

8-HQS and its intermediates, the changes in toxicity of a 0.20 mmol·L⁻¹ 8-HQS solution during treatment by electro-Fenton method at 300 mA were followed by Microtox method. The evolution of the luminescence inhibition as a function of electrolysis time for two exposition time (5 and 15 min) is presented in Fig. 10. As shown from this figure, two curves have a similar shape. It can also be noted that the initial solution of 8-HQS has an inhibition of 40% of luminescence. The inhibition reaches 99% after 20 min treatment, indicating the formation of significantly more toxic oxidation intermediates^[14] at the beginning of the treatment and then the solution toxicity decreases with the disappearance of aromatics. At the end of the treatment, the inhibition is lower than 10%, which shows that the solution toxicity is in relation with aromatic compounds and that the mineralization leads to the detoxification of treated solution.

3 Conclusions

Experimental design methodology has been used to determine the optimal experimental conditions for degradation of 8-HQS aqueous solutions by electro-Fenton process. Factorial designs demonstrated that the current intensity and the initial concentration of 8-HQS are the most influential parameters on the electro-Fenton degradation. Degradation of 8-HQS was found to follow pseudo-first order reaction kinetics in an aqueous acid medium. The apparent rate

constant (k_{app}) for the oxidation of 8-HQS by $\bullet\text{OH}$ was determined as 0.28 min⁻¹ under the current experimental conditions. The absolute rate constant (k_{abs}) was then found to be $1.62 \times 10^9 \text{ mol}^{-1} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ at 20 °C by competition kinetic method using 4-hydroxybenzoic acid as a reference compound. Moreover, the Doehlert matrix was employed to define the optimal operating conditions for mineralization of 8-HQS aqueous solutions. It has been demonstrated that electro-Fenton process can lead to a quasi-complete mineralization of 8-HQS aqueous solution since 95% of TOC removal was reached after 8 h. These results show that electro-Fenton process is a viable environmentally friendly technology for the remediation of wastewaters containing organic pollutants.

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应用于水溶液介质中喹啉氧化的电芬顿工艺 实验设计方法

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摘要: 采用碳毡阴极和铂阳极的电芬顿工艺研究了喹啉模型分子—8-羟基喹啉硫酸盐(8-HQS)在水溶液介质中的降解行为. 由于电化学诱导芬顿药剂($\text{H}_2\text{O}_2, \text{Fe}^{2+}$)产生大量的羟基活性基($\cdot\text{OH}$), 成为与有机物发生反应直到有机物完全矿化的强有力氧化剂, 因此, 电芬顿工艺具有很强的氧化能力. 采用正交实验设计确定了水溶液介质中 8-HQS 降解的操作参数. 结果表明, 电流密度和 8-HQS 的初始浓度是影响降解速度的主要因素. 8-HQS 浓度随着电解时间而减少, 说明 8-HQS 的氧化遵循准一级反应动力学. 通过竞争动力学方法确定的由 $\cdot\text{OH}$ 引起 8-HQS 氧化的绝对反应速度常数为 $1.62 \times 10^9 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$. 通过 Doehlert 矩阵研究了 8-HQS 矿化的最佳实验参数, 由此确定最佳条件下电芬顿工艺能导致 8-HQS 在水溶液中的准完全矿化 (总有机成分去除率 95%). 对 8-HQS 水溶液的处理, 使得 8-HQS 矿化前的最终产物为短链羧酸. 同时研究了电芬顿处理中短链羧酸的演变行为. 溶液毒性演变的跟踪研究发现, 中间产物的毒性比 8-HQS 强, 但溶液的毒性在中间产物矿化后可以完全消除.

关键词: 8-羟基喹啉硫酸盐; 电芬顿工艺; 羟基活性基; 降解; Doehlert 矩阵; 矿化; 毒性