Solar Photoelectro-Fenton Degradation of Acid Orange 7 Azo Dye in a Solar Flow Plant: Optimization by Response Surface Methodology

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Abstract The experimental variables to optimize the solar photoelectro-Fenton (SPEF) degradation of 10 L of Acid Orange 7 (AO7) azo dye in 0.05 M Na₂SO₄ of pH 3.0 have been determined from a central composite rotatable design and response surface methodology. Trials were performed with a solar flow plant with a Pt/air-diffusion reactor generating H₂O₂ and a solar compound parabolic collector photoreactor under an UV irradiation intensity of about 31 W m⁻². Optimum variables of 4.0 A, 0.75 mM Fe²⁺, and 150 mg L⁻¹ total organic carbon (TOC) of the azo dye were found for 90 % color and 70 % TOC removals. Under optimized conditions, total decolorization was achieved in 300 min, but AO7 decay obeyed a pseudo-first-order kinetics to disappear in 80 min, pointing to the generation of recalcitrant colored aromatic products. After 360 min of electrolysis, TOC was reduced by 96 %, with 64 % mineralization current efficiency and 133 kWh kg⁻¹ TOC energy consumption. The final solution contained carboxylic acids like tartronic, oxalic, oxamic, and in larger proportion, formic. An almost total mineralization was achieved by SPEF due to the persistence of Fe(III)-formate complexes to be photolyzed by sunlight. The initial N of the azo dye was mainly released as NH₄⁺.

Keywords Acid Orange 7 · Central composite rotatable design · Response surface methodology · Solar photoelectro-Fenton · Oxidation products

Introduction

A large variety of azo dyes, which represent nearly 70 % of the world's dye production, are widely used as coloring materials in textile and food industries [1–5]. These compounds contain a chromophore group composed of one or more azo (-N=N-) groups, usually conjugated with benzene and/or naphthalene systems. As a result of the dyeing process, the textile industries release large volumes of wastewaters with high contents of dyestuffs (usually 100–250 mg L⁻¹) that are discharged into natural waters. The entrance of these pollutants into water bodies causes serious environmental risks [6], not only by the visible coloration of waters producing esthetic problems and hindering light penetration but also by health hazards on living beings due to their toxicity, mutagenicity, and carcinogenicity [5, 7, 8]. Azo dyes are very persistent upon natural oxidation and reduction conditions, light exposure, and biodegradation and are hardly removed by physicochemical and biological methods used in sewage treatment plants [9, 10]. Powerful oxidation methods are necessary to be applied to the remediation of waters contaminated with azo dyes to impede their dangerous impact in the aquatic environment.

Many authors have reported the effective treatment of aqueous solutions of azo dyes by advanced oxidation processes (AOPs) [1, 5, 10–13]. The common feature of AOPs is the in situ generation of reactive oxygen species (ROS), preeminently the hydroxyl radical ([•]OH) with so high standard reduction potential ($E^{\circ} = 2.8$ V/SHE) that can oxidize most biorefractory organics up to their mineralization to CO₂, inorganic ions, and water. An electrochemical AOP (EAOP) based on Fenton's reaction chemistry like electro-Fenton (EF) has recently received great attention for treating waters contaminated with azo dyes [3, 5, 12–16]. EF consists in the continuous cathodic generation of H₂O₂ via O₂ reduction (1) upon injection of this pure gas or air into the treated solution or

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directly at a carbonaceous cathode. Small amounts of Fe^{2+} are added to the medium to react with H_2O_2 generating Fe^{3+} and $\cdot\text{OH}$ in the bulk from Fenton's reaction (2), with optimum pH about 3. This reaction is catalytic since it can be propagated from Fe^{2+} regeneration by cathodic Fe^{3+} reduction [5, 15]. A main drawback of EF is the production of final carboxylic acids that are hardly oxidized by $\cdot\text{OH}$. This can be overcome by the photoelectro-Fenton (PEF) process, in which the solution is illuminated with UVA light ($\lambda_{\text{max}} = 360 \text{ nm}$) upgrading the degradation of organics by (i) a greater Fe^{2+} regeneration with $\cdot\text{OH}$ production from photolytic reaction (3) of photoactive hydroxy-Fe(III) complexes at pH 3 and (ii) the photolysis of Fe(III) complexes with intermediates like Fe(III)-carboxylate species from reaction (4) [3, 5, 17–21].

The oxidation ability of EF and PEF can be improved using an undivided cell with a high O_2 -overpotential anode like boron-doped diamond (BDD). This electrode possesses much greater oxidation power than common Pt and PbO_2 anodes [22–25] since it produces higher quantities of physisorbed hydroxyl radicals $\text{M}(\cdot\text{OH})$ from water discharge at the anode M by reaction (5) [22], with ability to slowly oxidize the final Fe(III)-carboxylate complexes.

In our laboratory, we are developing the solar PEF (SPEF) process that utilizes the free and renewable sunlight as energy source, becoming much more inexpensive than PEF with artificial UVA lamps [3, 26–33] and being more useful for possible application to the industrial level. The best performance of SPEF is feasible because it provides photons in the UV range of 300–400 nm and in the visible ranges of 400–650 and 400–450 nm, which can also be absorbed for reactions (3) and (4), respectively [34]. Moreover, the action of sunlight in SPEF is so potent that aromatics degradation is quite similar using a Pt or a BDD anode, with the former one being preferable by its lower price and smaller potential difference achieved by the cell yielding less energy consumption [29].

Although several azo dyes have been treated by SPEF [3, 28, 31–33], no studies about the optimization of the experimental variables applied to this process have been previously reported. To explore this possibility, we have studied the SPEF degradation of a monoazo dye such as Acid Orange 7 (AO7), also called Orange II (see its chemical structure and characteristics in Table 1), by checking its optimization from a central composite rotatable design (CCRD) coupled to

response surface methodology (RSM) [27, 30, 35, 36]. AO7 is widely used for dyeing natural fibers like cotton, silk and wool, silk and cotton, and synthetic fibers like acrylics and polyesters. It has been typically employed as model pollutant to investigate the decolorization and mineralization of azo dyes by different chemical, photochemical, and photocatalytic AOPs [37–41] and EAOPs like EF and PEF [16, 33, 42–48].

This paper presents the results obtained for the optimization of the SPEF degradation of aqueous solutions of AO7 at pH 3.0 by CCRD and RSM. Experiments were carried out with a 10-L solar flow plant containing an electrochemical cell with a Pt anode and a carbon-polytetrafluoroethylene (PTFE) air-diffusion cathode (Pt/air-diffusion cell) coupled to a photoreactor with solar compound parabolic collectors (CPCs). The decolorization, the kinetic decay and the mineralization of the azo dye, and the evolution of generated short-linear carboxylic acids and released inorganic ions for the optimized EAOP were determined to clarify the degradation process.

Experimental

Chemicals

Commercial pure Acid Orange 7 was supplied by Acros Organics and utilized without further purification. Reagent grade short-linear aliphatic carboxylic acids were purchased from Panreac and Avocado. Solutions were prepared with deionized water by adding Na_2SO_4 as supporting electrolyte and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as catalyst, both supplied by Fluka. The solution pH was adjusted to 3.0 with analytical grade H_2SO_4 from Merck. Other chemicals were of either high-performance liquid chromatography (HPLC) or analytical grade from Avocado, Fluka, Merck, and Sigma-Aldrich.

Instruments and Analytical Procedures

The solution pH was measured on a Crison GLP 22 pH-meter. At regular times, samples of 5 mL were withdrawn from the treated solutions, neutralized to pH 7–8 for quenching degradation, and filtered with Whatman 0.45 μm PTFE filters to be analyzed.

The decolorization of AO7 solutions was monitored from their absorbance (A) decay at the maximum wavelength of 484 nm in the visible region (see Table 1), determined on a Shimadzu 1800 UV–vis spectrophotometer thermostated at 35 °C. The decolorization efficiency or percentage of color removal for each sample was calculated from Eq. (6) [5]:

$$\% \text{ Color removal} = \frac{A_0 - A_t}{A_0} \times 100 \quad (6)$$

Table 1 Chemical structure and characteristics of the azo dye tested

Chemical structure	Color index name	Chemical name	Color index number	$\lambda_{\max}$ (nm)	M (g mol ⁻¹)
Acid Orange 7 (AO7)	Sodium 4-[(2E)-2-(2-oxonaphthalen-1-ylidene)hydrazinyl]benzenesulfonate	15,510	484	350.32

where A_0 and A_t are the absorbance at initial time and time t , respectively, at $\lambda_{\max} = 484$ nm.

The mineralization of the same solutions was followed from their total organic carbon (TOC) removal, measured on a Shimadzu TOC-VCSN analyzer. Aliquots of 50 μL were injected into this system and reproducible TOC values with ± 1 % accuracy were obtained. The energy consumption per unit TOC mass (EC) was obtained from Eq. (7) [27–29]:

$$\text{EC} \left(\text{kWh kg}^{-1} \right) = \frac{1000 E_{\text{cell}} I t}{V \Delta(\text{TOC})_{\text{exp}}} \quad (7)$$

where 1000 is a conversion factor (mg g^{-1}), E_{cell} is the average potential difference of the cell (in V), I is the applied current (A), t is the electrolysis time (h), V is the solution volume (L), and $\Delta(\text{TOC})_{\text{exp}}$ is the experimental TOC decay (mg L^{-1}).

Considering the following theoretical mineralization reaction of AO7 anion to CO_2 , SO_4^{2-} , and NH_4^+ as pre-eminent ion:

the mineralization current efficiency (MCE) for each trial was estimated from Eq. (9) [28]:

$$\text{MCE}(\%) = \frac{n F V \Delta(\text{TOC})_{\text{exp}}}{4.32 \times 10^7 m I t} \times 100 \quad (9)$$

where n is the number of electrons involved during AO7 mineralization (68 according to reaction (8)), F is the Faraday constant ($96,487 \text{ C mol}^{-1}$), 4.32×10^7 is a factor for units homogenization ($3600 \text{ s h}^{-1} \times 12,000 \text{ mg mol}^{-1}$), and m is the number of carbon atoms of AO7 (16 atoms).

For the optimized SPEF run, the AO7 concentration decay was followed by reversed-phase HPLC with a Waters 600 LC fitted with a Spherisorb ODS2 5 μm , 150 mm $\times$ 4.6 mm, column at 35 $^\circ\text{C}$ and coupled with a Waters 996 photodiode array detector set at $\lambda = 310$ nm. Aliquots of 20 μL were injected into the LC and a 30:70 (v/v) acetonitrile/water (2.4 mM *n*-butylamine) mixture was eluted at 0.6 mL min⁻¹ as mobile phase. The chromatograms displayed a peak for AO7 anion with a retention time (t_r) of 7.6 min. The generated short-linear carboxylic acids were determined by ion-exclusion HPLC with the same LC fitted with a Bio-Rad Aminex HPX 87H, 300 mm $\times$ 7.8 mm, column at 35 $^\circ\text{C}$, and the detector was selected at $\lambda = 210$ nm. Aliquots of 20 μL were injected into the LC and 4 mM H_2SO_4 at 0.6 mL min⁻¹ was used as mobile phase. The chromatograms exhibited peaks related to oxalic ($t_r = 7.0$ min), tartronic ($t_r = 7.9$ min), maleic ($t_r = 8.2$ min), tartaric ($t_r = 8.5$ min), pyruvic ($t_r = 9.2$ min), oxamic ($t_r = 9.4$ min), formic ($t_r = 13.4$ min), and fumaric ($t_r = 14.7$ min). Released NH_4^+ , NO_3^- , and SO_4^{2-} ions were quantified by ion

chromatography following the method reported elsewhere [31].

Solar Flow Plant

The solar flow plant constructed by us for the treatment of 10 L of AO7 solutions in batch mode has been described before [28]. The solution introduced in the reservoir was recirculated through the system by a peristaltic pump. It passed through a flow meter and two heat exchangers to maintain a liquid flow rate of 200 L h⁻¹ and 35 °C, respectively. Further, the effluent circulated through the electrochemical cell and, finally, through the solar CPC photoreactor before coming back to the reservoir. The electrochemical cell was a filter-press reactor equipped with a 100-cm² Pt sheet (99.99 % purity) and a 100-cm² carbon-PTFE air-diffusion electrode for H₂O₂ electrogeneration from reaction (1), separated 1.2 cm by a PVC liquid compartment with a central window of 9.5 cm × 9.5 cm (90.3 cm²). The cathode was fed with compressed air at 4.5 L min⁻¹ regulated with a back-pressure gauge. The constant current to the cell was provided by a Grelco GDL3020 power supply, which directly displayed the potential difference between electrodes. The solar CPC photoreactor had an irradiated volume of 1.57 L, with a concentration factor of 1 and 0.4 m² area. It was mounted in an aluminum frame on a platform tilted 41° (local latitude) to better collect direct sun rays. Solar assays were made in sunny and clear days of summer 2015, and the UV irradiation intensity from 300 to 400 nm provided by sunlight was measured on a Kipp & Zonen CUV 5 radiometer. Before performing the assays, the air-diffusion cathode was activated by polarizing 10 L of 0.05 M Na₂SO₄ at pH 3.0 and 5 A for 240 min.

Experimental Design and Response Surface Methodology

The optimum conditions for the decolorization and mineralization of AO7 solutions by SPEF was ascertained by CCRD and RSM. The time required for 90 % color removal (*t*_{90 %CR}) was taken as a response because it determines the effluent decolorization before release. Besides, the time needed for 70 % TOC removal (*t*_{70 %TOC}) and the EC for 70 % TOC removal (EC_{70 %TOC}) were taken as responses because it has been corroborated that after attaining 70 % of TOC removal, the aromatic by-products are completely removed, remaining only highly biodegradable short-linear aliphatic carboxylic and dicarboxylic acids. A current from 3.0 to 8.4 A, Fe²⁺ content from 0.08 to 1.92 mg L⁻¹, and dye concentration from 75 to 209 mg L⁻¹ TOC were selected as independent variables, with five coded levels as *x*_{*i*} = -1.68, -1, 0, 1, and 1.68, as shown in Table 2. The CCRD consisted of eight factorial points, six axial points, and three central points, in a total of 17 runs [49]. The relation between each response and the

independent variables was given by the following second-order model [49, 50]:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^k \sum_{i \neq j=1}^k \beta_{ij} x_i x_j + \varepsilon \quad (10)$$

where *Y* is the response; β_0 is a constant coefficient; β_i , β_{ii} , and β_{ij} are the coefficients for the linear, quadratic, and interaction effects, respectively; *x_i* and *x_j* are the coded levels for the independent variables; *k* is the number of independent variables; and ε is the random error.

The three replicates in the central point (runs 15 to 17 in Table 2) allowed estimating the pure error. The response surfaces [35, 36, 49] were generated by a StatSoft Statistica v6 program. The resulting polynomial models were statistically validated by analysis of variance (ANOVA), with their statistical significances checked from *F* test and their fit quality from *R*² coefficients.

Results and Discussion

SPEF Degradation of AO7 Solutions

Blank experiments made with 10 L of AO7 solutions under recirculation in the solar flow plant, but without current pass, did not evidence any color and TOC removals, indicating that the azo dye is not directly photolyzed by sunlight.

When SPEF was applied, the strong orange color of starting solutions lost intensity turning into a dark brown color that slowly became clearer up to colorless solutions. This suggests the gradual production of colored conjugated products slowly destroyed mainly by •OH formed in the bulk from Fenton's reaction (2) and in a smaller extent by Pt(•OH) produced from reaction (5) [5, 12, 13]. Since the solution pH dropped during electrolysis due to the production of acidic products like carboxylic acids, it was continuously regulated at pH 3.0 by adding small volumes of 0.5 M NaOH. The mineralization rate of AO7 solutions was much slower than its decolorization by the generation of more recalcitrant products, difficultly removed by hydroxyl radicals and sunlight. From this behavior, times related to 90 % color and 70 % TOC removals were taken to optimize the independent variables in CCRD for the decolorization and mineralization processes, respectively. The EC for 70 % TOC removal was also chosen to minimize the energy consumption of SPEF. The observed responses for all coded levels checked are collected in Table 2. This table also shows that all runs always received a quite analogous average UV irradiation intensity between 30.2 and 32.4 W m⁻².

Table 2 Coded levels and real values for the CCRD and RSM analysis of the SPEF treatment of AO7 solutions in 0.05 M Na₂SO₄ at pH 3.0 and 35 °C using a 10-L solar flow plant

Run	Coded levels			Real values			Observed responses			
	x_1	x_2	x_3	X_1^a	X_2^b	X_3^c	$t_{90} \%CR$ (min)	$t_{70} \%TOC$ (min)	EC ₇₀ %TOC (kWh kg ⁻¹ TOC)	UV ^d (W m ⁻²)
1	-1	-1	-1	3.0	0.45	75	68.9	195	122.2	30.2
2	1	-1	-1	7.0	0.45	75	43.2	90	167.5	32.4
3	-1	1	-1	3.0	1.55	75	89.0	188	91.6	30.4
4	1	1	-1	7.0	1.55	75	71.5	103	201.2	31.2
5	-1	-1	1	3.0	0.45	150	159.5	310	75.7	32.1
6	1	-1	1	7.0	0.45	150	64.7	153	130.8	31.3
7	-1	1	1	3.0	1.55	150	216.5	450	109.4	30.2
8	1	1	1	7.0	1.55	150	140.9	282	221.0	31.1
9	-1.68	0	0	1.6	1.00	125	136.3	314	34.2	30.4
10	1.68	0	0	8.4	1.00	125	52.2	107	113.4	30.7
11	0	-1.68	0	5.0	0.08	125	138.0	228	155.0	31.8
12	0	1.68	0	5.0	1.92	125	168.7	309	224.2	32.5
13	0	0	-1.68	5.0	1.00	41	52.2	67	153.5	30.5
14	0	0	1.68	5.0	1.00	209	153.3	339	157.8	31.4
15	0	0	0	5.0	1.00	125	108.14	177	134.2	30.6
16	0	0	0	5.0	1.00	125	115.7	183	141.4	32.2
17	0	0	0	5.0	1.00	125	113.0	182	139.0	30.7

^a Current (A)^b Fe²⁺ concentration (mM)^c Initial dye concentration (mg L⁻¹ TOC)^d Average UV irradiation intensity supplied by sunlight during the SPEF trial

Effect of Independent Experimental Variables on the SPEF Process

Analysis of the observed responses given in Table 1 using Eq. (10) led to the following second-order models with 95 % confidence level:

$$t_{90} \%CR = 112.9 - 25.99x_1 + 17.06x_2 + 35.08x_3 - 8.64x_1^2 + 12.23x_2^2 - 5.64x_3^2 - 3.42x_1x_2 - 15.9x_1x_3 + 10.62x_2x_3 \quad (11)$$

$$t_{70} \%TOC = 181.2 - 63.2x_1 + 30.1x_2 + 78.8x_3 + 8.6x_1^2 + 29.1x_2^2 + 5.9x_3^2 + 1.1x_1x_2 - 16.8x_1x_3 + 32.9x_2x_3 \quad (12)$$

$$EC_{70} \%TOC = 138.2 + 33.3x_1 + 17.8x_2 - 2.8x_3 - 22.7x_1^2 + 18.2x_2^2 + 6.2x_3^2 + 15.1x_1x_2 + 1.5x_1x_3 + 15.1x_2x_3 \quad (13)$$

where x_1 , x_2 , and x_3 are the current, Fe^{2+} concentration, and azo dye concentration, respectively. Note that Eqs. (11)–(13) only include the most significant terms obtained from ANOVA. Figure 1 shows the response surfaces generated from the above equations.

The great negative contribution of x_1 in Eqs. (11) and (12) indicates shorter times for 90 % decolorization and 70 % mineralization when current increased, as shown in Fig. 1a, b, d, e. The negative coefficient of x_1^2 in Eq. (11) also favored the color removal as current grew. Nevertheless, the positive coefficient for the same parameter in Eq. (12) yielded the opposite trend, although its low value compared with that of x_1 slightly decelerated the drop of $t_{70\% \text{TOC}}$ at high current (Fig. 1d, e). This

suggests the production of more quantities of oxidizing hydroxyl radicals with increasing current by acceleration of electrode reactions (5) and (1), originating more $\text{Pt}(\text{OH})$ and H_2O_2 , respectively, which enhances the generation of $\cdot\text{OH}$ from Fenton's reaction (2) [5, 28, 31]. The faster oxidation of products leads to higher amounts of photoactive products that are more quickly destroyed upon solar irradiation, thus upgrading mineralization and diminishing $t_{70\% \text{TOC}}$ [31]. However, the growth in current caused a variable influence on $\text{EC}_{70\% \text{TOC}}$ by the high positive contribution of x_1 and the relatively smaller negative coefficient of x_1^2 in Eq. (13), predominating at low and high current, respectively. Figure 1g, h evidences the compensation of both contributions at about 6–7 A giving a

Fig. 1 CCRD response surfaces after the SPEF degradation of 10 L of Acid Orange 7 (AO7) solutions in 0.05 M Na_2SO_4 at pH 3.0 and 35 °C using a solar flow plant at a liquid flow rate of 200 L h^{-1} . **a–c** Time required for 90 % color removal, **d–f** time needed for 70 % total

organic carbon (TOC) removal, and **g–i** energy consumption per unit TOC mass (EC) for 70 % TOC removal as a function of applied current and dye and Fe^{2+} concentrations as independent variables

maximum $EC_{70} \%TOC$ value. At higher current, the decay of this response can be related to a much more efficient TOC removal by the quicker photolysis of higher amounts of products formed upon the potent action of sunlight.

Equations (11)–(13) also point to a notable effect of Fe^{2+} concentration over all responses, owing to the positive contributions of x_2 and x_2^2 . The response surfaces (Fig. 1a, c, d, f, g, i) reflect the existence of minimum values of $t_{90} \%CR$, $t_{70} \%TOC$, and $EC_{70} \%TOC$ at about 0.75 mM Fe^{2+} . This behavior can be related to the competence of Fenton's reaction (2) to produce $\cdot OH$ in the bulk with the consumption of this radical by Fe^{2+} through reaction (14) [28]:

The lower responses when the Fe^{2+} content grew from 0.08 to 0.75 mM can be associated with the gradual acceleration of Fenton's reaction (2) by the presence of more Fe^{2+} in the effluent. The greater generation of $\cdot OH$ enhanced the decolorization and mineralization of AO7, diminishing the energy consumption as well. In contrast, the excess of added Fe^{2+} from 0.75 to 1.92 mM caused a rapid and progressive acceleration of reaction (14), dropping the quantity of $\cdot OH$ able to oxidize organics and, consequently, prolonging $t_{90} \%CR$ and $t_{70} \%TOC$ and upgrading $EC_{70} \%TOC$.

The high positive contributions of x_3 in Eqs. (11) and (12) indicate a gradual increase of $t_{90} \%CR$ and $t_{70} \%TOC$ with increasing azo dye concentration. This can be observed in the response surfaces of Fig. 1b, c, e, f, at constant current and Fe^{2+} content, and can be related to the reaction of lower percentages of color and TOC removals with similar amounts of hydroxyl radicals. However, the low negative coefficient of x_3 and the slightly higher positive coefficient of x_3^2 gave lower $EC_{70} \%TOC$ for azo dye contents $>150 \text{ mg L}^{-1}$ TOC, as clearly shown in Fig. 1h, i. This opposite tendency to the other two increasing responses is due to the gradual destruction of more quantity of TOC. The oxidation ability of the SPEF process is then progressively upgraded because more $Pt(\cdot OH)$ and $\cdot OH$ are able to oxidize organics, feasible by the deceleration of waste reactions of both radicals. Examples are the oxidation of $Pt(\cdot OH)$ to gas O_2 from reaction (15) and the consumption of $\cdot OH$ by Fe^{2+} and generated H_2O_2 from reactions (14) and (16), respectively [5, 12, 15].

Validation of the Polynomial Models

The statistical validation of the polynomial regressions of Eqs. (11)–(13) was made by the Fisher distribution (F test) of ANOVA. The significance of the models was assessed from the

ratio of the mean squares of regressions with residuals (difference between the observed and predicted values). The adjustment of the same models was evaluated from the ratio of the mean squares of lack of fit with pure error. The F ratio determined for the models was 23.15 for $t_{90} \%CR$, 166.59 for $t_{70} \%TOC$, and 24.49 for $EC_{70} \%TOC$, higher than 3.29 theoretically established for 95 % confidence level [36], confirming the statistical significance of the obtained regressions. The F ratio obtained for the lack of fit of the models was 16.59 for $t_{90} \%CR$, 15.17 for $t_{70} \%TOC$, and 17.15 for $EC_{70} \%TOC$, values smaller than 19.30 tabulated for a 95 % confidence level [35, 36], evidencing a lack of fit of the developed regressions. Figure 2a–c depicts excellent linear straight between the predicted and observed responses of $t_{90} \%CR$, $t_{70} \%TOC$, and $EC_{70} \%TOC$, respectively, with corresponding R^2 values of 0.978, 0.995, and 0.979. These good coefficients, close to unity, also corroborate the statistical significance of Eqs. (11)–(13).

Fig. 2 Predicted values determined for **a** time required for 90 % color removal from Eq. (11), **b** time needed for 70 % TOC from Eq. (12), and **c** EC for 70 % TOC removal from Eq. (13) vs. the observed values

The residual-observed plots for these three regressions are presented in Fig. 3a–c, respectively. A random distribution of the residuals around the mean value of zero can be always observed as a result of the good agreement of the regressions without systematic errors. The statistical values determined from ANOVA and collected in Table 3 demonstrate the insignificance of the lack of fit with p values >0.05 for all the three responses. The coefficient of determination R^2 is the parameter to determine the overall efficiency of model prediction, showing high values (>0.98), and hence, ensuring good correlations between observed values and model-predicted values is ensured. For the three developed models, R^2_{adjusted} and $R^2_{\text{predicted}}$ do not differ considerably. Table 3 also shows an adequate precision (AP) >10 in all cases, evidencing the good models developed, and an excellent reproducibility assessed by low coefficient of variance (CV) values below 5 %.

Fig. 3 Residual values calculated as the difference between the observed and predicted ones for **a** time required for 90 % color removal, **b** time needed for 70 % TOC removal, and **c** EC for 70 % TOC removal as a function of the observed ones

Optimization of the SPEF Process of AO7

The optimum conditions for the SPEF treatment of AO7 solutions were determined from the RSM results considering the lower times for color and TOC removals with the smaller energy consumption, i.e., the maximum effectiveness of oxidation with hydroxyl radicals and sunlight. Acceptable responses were found for a current of 4.0 A, 0.75 mM Fe^{2+} , and azo dye content of 150 mg L⁻¹ TOC, which were selected as the best experimental conditions for the SPEF process. It should be highlighted that under these operational conditions, the models predicted values of $t_{90\% \text{CR}} = 158.9$ min, $t_{70\% \text{TOC}} = 290$ min, and $\text{EC}_{70\% \text{TOC}} = 148$ kWh kg⁻¹ TOC, which are quite similar to the experimental values of $t_{90\% \text{CR}} = 160$ min, $t_{70\% \text{TOC}} = 296$ min, and $\text{EC}_{70\% \text{TOC}} = 150$ kWh kg⁻¹ TOC, thereby demonstrating a good agreement with the RSM model defined.

Figure 4a highlights that the decolorization efficiency underwent a continuous, but slow, growth with prolonging electrolysis time, reaching total decolorization after 300 min. As stated above, Eq. (11) predicted a $t_{90\% \text{CR}} = 158.9$ min, very close to 160 min experimentally obtained, pointing to a good agreement of the regression developed by RSM. However, a very different behavior from AO7 decay was found by reversed-phase HPLC, since the azo dye disappeared in only 80 min, as shown in Fig. 4b. The much quicker AO7 removal compared to its decolorization evidences that its fast oxidation with $\text{Pt}(\text{OH})$ and mainly $\cdot\text{OH}$ yields large amounts of colored aromatic products, which absorb at the same $\lambda_{\text{max}} = 484$ nm and are much more slowly destroyed by hydroxyl radicals with insignificant participation of sunlight [28, 31]. Moreover, AO7 obeyed a pseudo-first-order kinetics reaction, as shown in the inset panel of Fig. 4b. From this analysis, an apparent rate constant of 0.043 min⁻¹ with $R^2 = 0.991$ was found. This suggests that the azo dye reacts with a low and steady concentration of hydroxyl radicals, at least in the starting of the SPEF run.

Figure 5a shows an S shape for TOC decay, with a long delay time close to 210 min where it was only reduced by 13 %. At a longer time, TOC was very rapidly removed until attaining 96 % decay at 360 min. This tendency agrees with the large decolorization suffered by the effluent with the formation of colored products that are slowly destroyed by $\text{Pt}(\text{OH})$ and $\cdot\text{OH}$ from 80 to 300 min (Fig. 4a, b). The smaller molecules originated from these colored products are much more rapidly removed under the synergistic action of such generated hydroxyl radicals and sunlight, causing a quick TOC reduction up to almost total mineralization. Note that a time of 296 min was required for 70 % TOC removal, close to 290 min obtained from Eq. (12), confirming its good fit to predict this response.

As expected from the S shape of TOC abatement, very low MCE values and very high EC values were determined up to

Table 3 Analysis of variance for each response optimized

Source	Sum of squares	DF	Mean square	F value	p	
Decolorization at t_{90} %CR						
Model	37,110.1	9	4123.3	23.2	0.0002	Significant
Residual	1246.9	7	178.1			
Lack of fit	1217.5	5	245.5	16.6	0.0578	Not significant
Pure error	29.3	2	14.7			
$R^2_{\text{adjusted}} = 0.9992$	$R^2_{\text{predicted}} = 0.967$		AP = 14.7	CV = 3.54 %		
Mineralization at t_{70} %TOC						
Model	172,355.0	9	19,151.0	166.6	<0.0001	Significant
Residual	804.7	7	114.9			
Lack of fit	784.0	5	156.8	15.2	0.0630	Not significant
Pure error	20.7	2	10.3			
$R^2_{\text{adjusted}} = 0.9998$	$R^2_{\text{predicted}} = 0.995$		AP = 10.3	CV = 2.78 %		
Energy consumption at EC ₇₀ %TOC						
Model	37,441.0	9	4160.1	24.5	0.0001	Significant
Residual	1188.8	7	169.8			
Lack of fit	1161.8	5	232.4	17.2	0.0560	Not significant
Pure error	27.1	2	13.5			
$R^2_{\text{adjusted}} = 0.9992$	$R^2_{\text{predicted}} = 0.967$		AP = 14.7	CV = 3.54 %		

210 min of SPEF. Figure 5b depicts the gradual growth in current efficiency by the acceleration of mineralization as

Fig. 4 **a** Percentage of color removal and **b** AO7 concentration decay with electrolysis time for the optimum treatment found by RSM of 10 L of a 0.781-mM (150 mg L⁻¹ TOC) AO7 solution in 0.05 M Na₂SO₄ with 0.75 mM Fe²⁺ at pH 3.0 and 35 °C by SPEF with a solar flow plant at 4.0 A and liquid flow rate of 200 L h⁻¹

the intermediates are transformed into more easily oxidizable products. The MCE value grew from 13 % at 210 min to 57 % at the end of the run, when an almost total mineralization with 96 % TOC reduction was achieved. Similarly, Fig. 5c shows the progressive drop of EC with prolonging electrolysis. Its value decayed from 580 kWh kg⁻¹ TOC at 210 min to 133 kWh kg⁻¹ TOC at 360 min. For 70 % TOC removal, 150 kWh kg⁻¹ TOC was experimentally found, similar to 148 kWh kg⁻¹ TOC expected from Eq. (13), indicating the good agreement of this equation to describe this parameter.

Evolution of Short-Linear Carboxylic Acids and Released Inorganic Ions

Ion-exclusion chromatograms of the above treated azo dye solution displayed peaks related to maleic, fumaric, tartaric, pyruvic, tartronic, oxamic, oxalic, and formic acids. The five former acids are originated from the breaking of the benzenic and naphthalenic rings of aromatic intermediates, further being oxidized to oxalic and formic acids [26–31]. The degradation of intermediates with a -NH₂ group can yield oxamic acid. Oxalic, formic, and oxamic acids are directly mineralized to CO₂ [5, 12]. It is expected that all acids form Fe(III)-carboxylate complexes due to the production of Fe³⁺ in a large extent from Fenton's reaction (2) under the SPEF conditions tested [3, 5, 31]. These complexes are very stable in front of the attack of hydroxyl radicals, and most of them can be photolyzed by UV light of sunlight irradiation via reaction (4).

Fig. 5 a TOC decay and changes of **b** mineralization current efficiency and **c** EC with electrolysis time for the optimized SPEF run of Fig. 4

Figure 6a illustrates a low accumulation of maleic, fumaric, and pyruvic acids during the optimized SPEF process. While Fe(III)-maleate and Fe(III)-fumarate complexes only persisted for 150 min because of their quick photo-oxidation by sunlight, Fe(III)-fumarate species were more slowly photolyzed and completely removed at the end of treatment. In contrast, Fig. 6b shows a much larger accumulation of tartaric, tartronic, oxalic, oxamic, and formic acids starting from 120 to 180 min of electrolysis, just when TOC began to be strongly reduced due to the fast mineralization of intermediates (Fig. 5a). The Fe(III) complexes of the four former acids were rapidly photodecomposed until attaining final contents <3 mg L⁻¹, but the photo-oxidation of Fe(III)-formate species was so slow that 16 mg L⁻¹ of formic acid remained in the final solution. A mass balance at the end of the optimized SPEF run points to 6 mg L⁻¹ of TOC related to all final acids, in agreement with the experimental TOC of the resulting solution (see Fig. 5a). The final effluent was then only composed of a mixture of final short-linear carboxylic acid, whose persistence, pre-eminently of formic acid, impedes its total mineralization.

It is well-known that the S atoms of azo dyes with -SO₃⁻ groups, like AO7, are released as SO₄²⁻ [3, 28, 31, 33] by

Fig. 6 Evolution of the concentration of **a** maleic (filled inverted triangle), pyruvic (filled diamond), and fumaric acids (filled triangle) and **b** tartaric (open triangle), tartronic (open square), oxamic (open inverted triangle), oxalic (filled square), and formic acids (filled circle) detected during the optimized SPEF trial of Fig. 4. **c** Time course of NH₄⁺ (filled circle) and NO₃⁻ (open circle) ions detected during the same assay

EAOPs, as stated in reaction (8). The evolution of NH₄⁺ and NO₃⁻ ions coming from the N atoms (22.1 mg L⁻¹) of the azo dye during the optimized SPEF was followed by ion chromatography. No other nitrogenated ions like NO₂⁻ were detected using this technique. Figure 6c reveals a continuous release of NH₄⁺ during the process to reach a concentration of 23.3 mg L⁻¹ (82.1 % of initial N). This evidences that NH₄⁺ is the pre-eminent ion originated during SPEF, as proposed in the theoretical mineralization reaction (9) of AO7 anion. In contrast, Fig. 6c also shows a poor production of NO₃⁻, with a maximal of 4.6 mg L⁻¹ at 210 min that is further reduced to 1.6 mg L⁻¹ (1.6 % of initial N). This surprising phenomenon has been observed for the SPEF treatment of other dyes [28, 32], being associated with the reduction of NO₃⁻ by intermediates upon activation with solar irradiation to give volatile species such as N₂ and/or N_xO_y.

Conclusions

The SPEF process of AO7 solutions in 0.05 M Na₂SO₄ of pH 3.0 can be optimized from the application of a CCRD coupled to RSM. Experiments were carried out with a 10-L solar flow plant equipped with a Pt/air-diffusion reactor and a solar CPC photoreactor operating under an average UV irradiation intensity near 31 W m⁻². The optimum variables were 4.0 A, 0.75 mM Fe²⁺, and 150 mg L⁻¹ TOC of azo dye, determined for 90 % decolorization and 70 % mineralization. Under these conditions, total decolorization was achieved in 300 min, whereas AO7 was removed in only 80 min, indicating the formation of large amounts of colored aromatic products. Moreover, TOC was reduced by 96 % in 360 min with 64 % mineralization current efficiency and 133 kWh kg⁻¹ TOC energy consumption. The polynomial models developed by RSM predicted adequately the observed experimental data. The final treated solution contained a mixture of short-linear carboxylic acids like tartaric, oxalic, oxamic, and formic acids. The large persistence of Fe(III) complexes of formic acid to be photolyzed by UV light of sunlight explains the almost total mineralization attained by SPEF. The initial N was majority released as NH₄⁺, with a very small proportion of NO₃⁻.

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