

Optimization of Disperse Blue 3 mineralization by UV-LED/FeTiO₃ activated persulfate using response surface methodology

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ABSTRACT

Response surface methodology based on Box-Behnken design (BBD) was successfully applied for the optimization of the UV-LED/FeTiO₃ activated persulfate (PS) process. Disperse Blue 3 (DB3) azo dye oxidation was carried out in a quartz jacketed stirred batch reactor using 405 nm UV at 10 W/m² as radiation source. The effects of temperature, catalyst concentration and persulfate dose upon the total organic carbon (TOC) removal were investigated. Optimum operating conditions were found to be: ilmenite: 320 mg/L⁻¹, PS: 1.56 g/L⁻¹ and 67 °C. Under these conditions, 96% mineralization was achieved. Ecotoxicity of the final effluent was evaluated using *Aliivibrio fischeri* bacteria, finding a negligible toxicity.

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1. Introduction

The continuous demographic growth, the steep expansion of the industrial sector and the discharge of effluents in water bodies contribute to an increasing pressure over hydrological resources, causing an irreversible reduction in fresh water availability [1]. The synthetic dyes industries are considered a representative example of water polluting industry, in which raw effluents contain recalcitrant and potentially carcinogenic compounds [2].

Nowadays, over 100,000 different dye structures have been synthesized and more than 0.7 million tons/year of dyes are produced, with applications in textile, paper, leather, cosmetics, food and pharmaceutical industries [3,4]. Worldwide, 280,000 tons of textile dyes are discharged in industrial effluents annually [5]. Among these compounds, azo dyes represent the largest group used in textile dyeing and printing industries and they account for around 70% of the world dye production. These are aromatic and heterocyclic compounds containing an azo group (–N=N–) as chromophore, linked to other groups such as –OH and –NO₂ [6,7].

Traditional treatment methods are not effective in the removal of azo dyes due to their complex structure, which confers them high stability and chromaticity. Thus, more effective water treatment technologies are required [8]. Advanced oxidation processes

(AOPs), which rely primarily on the generation of the free radicals to degrade organic compounds, have shown a great potential. These techniques consist of the activation of oxidants to provide a clean way of generating highly oxidizing radical species [9].

Recently, sodium persulfate (PS) anion has emerged as a promising oxidant, and has been effectively used for azo dye treatment [10]. PS presents high solubility, high stability and wide operative pH range in aqueous solution. However, reactions of PS with organic substances in water are generally slow at ambient temperature, therefore it is necessary to activate PS generating a stronger sulfate radical (SO₄^{•-}, $E_0 = 2.5\text{--}3.1\text{ V}$), to accelerate the degradation rate [8,11]. Generally, PS activation can be accomplished by a transition metal ion which acts as a catalyst. Because Fe is a relatively nontoxic and inexpensive specie among the transition metal catalysts, it has been widely studied for this purpose [12]. Several types of Fe-based catalysts in different AOPs have been used for the chemical activation of persulfate, including the polycrystalline FeTiO₃ (natural ilmenite) [13]. Ilmenite is an antiferromagnetic semiconductor, with a band gap between 2.3 and 2.9 eV with potential applications in chemical catalytic reactions [14].

One of the main drawbacks of this mineral is the high induction period and lower activity in comparison to other materials [14]. This problem can be solved by using UV radiation to improve the efficiency via photoreduction of Fe(III) to Fe(II) in the ilmenite surface (Eq. 1), decreasing the induction period. So far, this strategy (FeTiO₃/UV) has been tested for advanced oxidation processes us-

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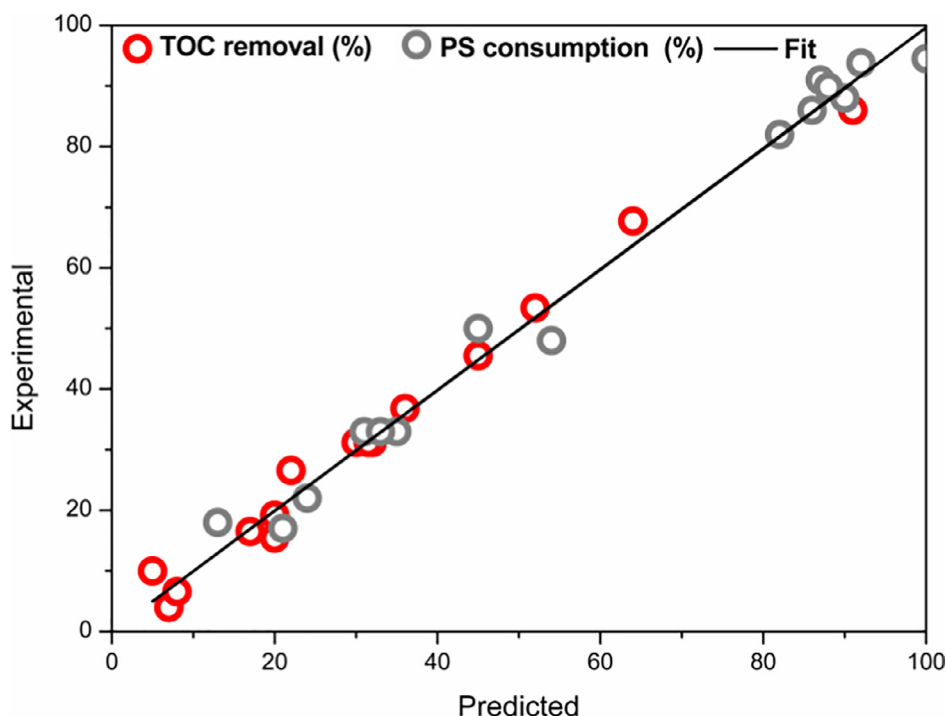


Fig. 1. Predicted versus actual plot for TOC removal and PS consumption on DB3 mineralization.

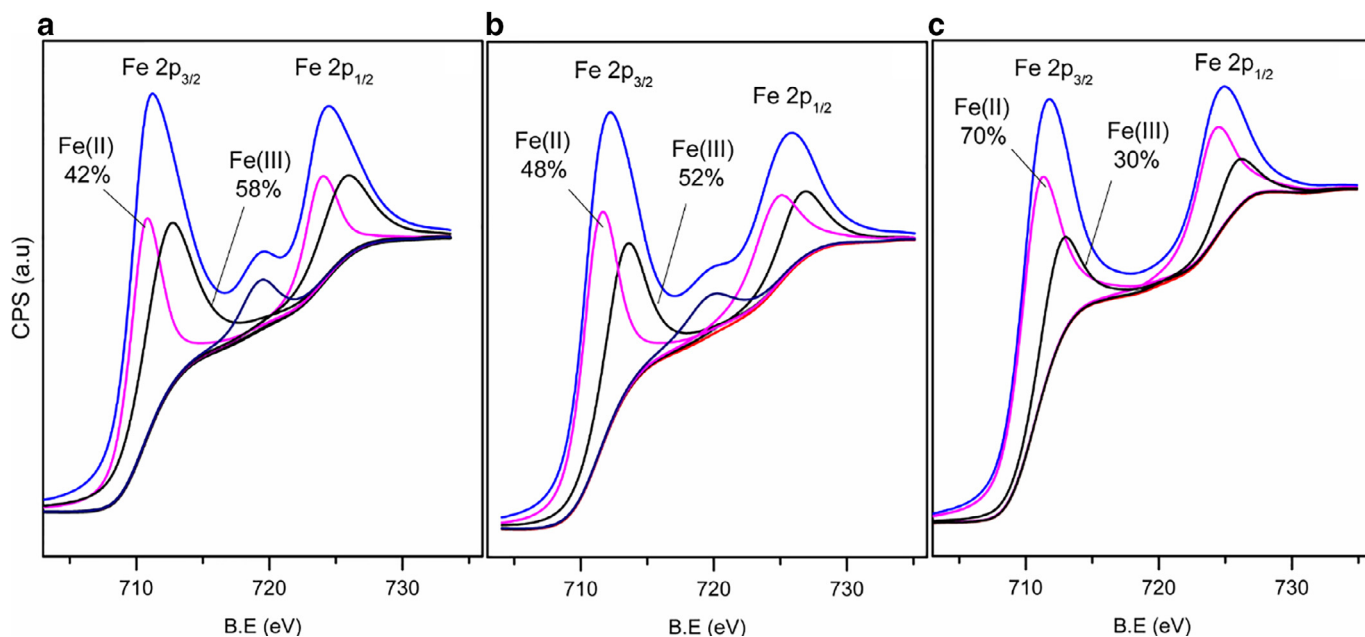


Fig. 2. XPS spectra of Fe 2p for raw ilmenite, photo-reduced and photo-reduced in dye presence. Experimental conditions: $[DB3]_0 = 80 \text{ mg/L}$, $[PS]_0 = 92\%$, ilmenite = 320 mg/L , $pH_0 = 3$, $t = 180 \text{ min}$.

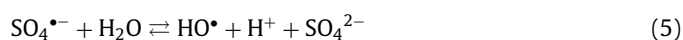
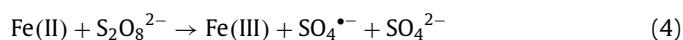
ing H_2O_2 as oxidant for the degradation of phenol [14,15].



In addition, Cheng et al. [16] and Bokare and Choi [17] suggest that, in presence of colored substances like organic dyes, visible light irradiation can also reduce Fe(III) to Fe(II) via intermolecular electron transfer from an excited dye state, Eqs. (2,3).



The increase in source of Fe(II) promotes the activation of PS to produce $SO_4^{\bullet-}$ and $HO^{\bullet}$ (Eqs. 4,5) [18–20].



Ultraviolet light emitting diodes (UV-LEDs) are a promising source of UV radiation and become an alternative to photocatalytic reactions. They present potential advantages over conventional UV lamps such as instant on/off ability, tunable radiation to control

Table 1
Physico-chemical properties of ilmenite.

FeTiO ₃ /Rutile phases (%)	S_{BET} (m ² /g ⁻¹)	Fe(III)/Fe(II) _{surface}			Fe/Ti (%)	Band-gap (eV)
		Natural FeTiO ₃	Photo reduced	Photo/ Dye reduced		
85/15	6	58/42	52/48	30/70	36/37	2.4

the peak wavelength, compactness, long life and minimal disposal problems increases the flexibility of photoreactor designs [21–24].

In this sense, this work addresses Disperse Blue 3 degradation with UV/ FeTiO₃/PS. The process was optimized using the Box-Behnken experimental design (BBD) combined with response surface methodology (RSM) studying operating variables such as persulfate dose, ilmenite load and temperature reaction under UV-LED. Mineralization degree and PS consumption were analyzed throughout the reaction. Furthermore, the acute toxicity of the solutions was evaluated before and after treatment using *Aliivibrio fischeri*.

2. Material and methods

2.1. Materials

Azo dye DB3 was supplied from Sigma-Aldrich. Its characteristics are presented in Table S1.

All chemicals used in the experiments were analytical reagent grade. Potassium iodide (KI–99.0%), sodium carbonate (Na₂CO₃–99.0%), sodium bicarbonate (NaHCO₃–99.7%), sodium sulfate (Na₂SO₄–99.0%) and dichloromethane (CH₂Cl₂–99.8%) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Sodium persulfate (Na₂S₂O₈–98.0%) was obtained from PanReac AppliChem (Barcelona, Spain). Natural ilmenite (Ref. 50110700) was provided by Marphil S.L. (Spain). Table 1 summarizes the main physico-chemical properties of ilmenite. For the sake of comparison, this table also includes the Fe(III)/Fe(II) ratio of ilmenite after photo-reduction with and without DB3.

2.2. Catalytic oxidation procedure

A stirred tank quartz jacketed batch reactor (V:250 mL) equipped with a magnetic stirrer (Fig. S1) was employed to evaluate the catalytic activity. A commercial LED strip (SMD 5050), $\lambda = 405$ nm, with 10 W/m⁻² radiation and a power of 19 W, was placed around the external wall of the reactor. Aqueous DB3 (80 mg/L⁻¹) at pH₀ 3, adjusted with H₂SO₄, was employed as starting solution. Temperature was controlled between 30 °C and 70 °C with a thermal batch recirculation system (Julabo 13). Experiments were carried out after adding a known amount of PS between 1.7 g/L⁻¹ and 0.34 g/L⁻¹ (corresponding to 100–20% of the stoichiometric PS amount needed for complete DB3 mineralization). Ilmenite load ranged between 150 and 450 mg/L⁻¹, to match chosen experimental range and levels of independent variables (Table 2). Reaction was carried out for 180 min. Samples were taken after reaction and instantly placed in an ice bath to quench the reaction. After centrifugation (Digicen 21) at 5.294 x g for 10 min they were analyzed. All experiments were performed in triplicate.

2.3. Analysis procedure and toxicity testing method

Decolorization extents were measured by absorbance in visible spectra at the characteristic maximum wavelength ($\lambda_{\text{max}} = 640$ nm) using a UV-vis spectrophotometer (Agilent Cary 60). The mineralization of DB3 solution was analyzed using a TOC analyzer (TOC-V CSH, Shimadzu, Japan). The concentration of PS was monitored spectrophotometrically ($\lambda_{\text{max}} = 352$ nm) by a modified iodometric titration method [25]. The total iron content released from

the ilmenite was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an ICP-MS Elan 6000 PerkinElmer Sciex instrument. Ilmenite was characterized by X-ray photoelectron spectroscopy (XPS) with a K α Thermo Scientific apparatus with an Al K α ($h\nu = 1486.68$ eV) X-ray source using a voltage of 12 kV under vacuum condition (2×10^{-7} mbar). For the peak analysis, a Shirley type background was used. Peaks were fitted with Gaussian and Lorentzian functions using the XPS Peak 4.1 software [26].

Degradation byproducts were detected by mass spectra and their fragmentation pattern. For that purpose, a gas chromatography coupled with a mass spectrometry (GC-MS) was used (CP-3800/Saturn 2200, Varian). Sample preparation includes a liquid-liquid extraction using 5 mL of the initial or mineralized DB3 and 15 mL of dichloromethane and preconcentration evaporating at 40 °C. The by-product 1-amino-4-(methyldamino) anthracene-9,10-dione with m/z 252 was identified using the National Institute of Standards and Technology (NIST) database. A more detailed analytical methodology is described elsewhere [27]. Toxic effect of DB3 after the treatment was evaluated using a commercially available bio-test (MicroTox®) based on reduction of bio-luminescence of aquatic bacteria *A. fischeri*. Changes in bacteria concentration is sensed by means of natural bio-luminescence that is measured using a photometer [28]. The response established for the toxicity test with *A. fischeri* was the mean lethal concentration (EC₅₀) meaning the sample initial concentration which reduced 50% of the total biological effect (light emission). Once the results are inversely proportional the EC₅₀ data was transformed to Toxic Units (TU) and was used to evaluate the toxicity of collected samples [29].

2.4. Response surface methodology experimental design

The model performance is expressed using a second-order polynomial equation (Eq. 6).

$$R = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^k \sum_{j=1+1}^k \beta_{ij} x_i x_j + \varepsilon \quad (6)$$

where R is the predicted response for TOC removal, β_0 is the intercept parameter, β_i , β_{ii} and β_{ij} are parameters for linear, quadratic and interaction factor effects, x_i and x_j are independent variables and ε is the error. The number of experiments (N) required for the development of this design is defined as $N = 2k(k+1) + C_0$, where k is the factor number and C_0 is the replicate number of the central point [30].

Ilmenite concentration (A), persulfate dose (B) and reaction temperature (C) were analyzed as independent variables at three levels, coded as -1 , 0 , and 1 (low, center and high) would be 27 (3^3), which has been reduced to 15 experiments using BBD experimental design, summarized in Table 2, to get the DB3 mineralization.

Three-dimensional response surface plots were used to gain insight about the effect of each variable and interactive effect. The fit between the model and the experimental data was evaluated by ANOVA (analysis of variance). The F-test was applied to verify whether the model could predict a significant variation in the experimental data. The Probability p value was used to estimate whether F is large enough to indicate statistical significance

Table 2

The BBD design matrix and experimental results.

Run	Actual conditions			Coded factors			TOC removal (%)		PS consumption (%)	
	Ilmenite (mg/L ⁻¹)	Persulfate (%)	Temperature (°C)	A	B	C	Exp	Pred	Exp	Pred
1	450	20	50	+1	-1	0	20	15.4	92	93.8
2	150	100	50	-1	+1	0	22	26.6	24	22
3	150	60	30	-1	0	-1	7	4.0	21	17
4	300	60	50	0	0	0	30	31.2	35	33
5	150	20	50	-1	-1	0	8	6.6	45	50
6	450	60	30	+1	0	-1	17	16.5	82	82
7	450	100	50	+1	+1	0	52	53.4	54	48
8	450	60	70	+1	0	+1	64	67.75	87	91
9	300	20	70	0	-1	+1	36	36.8	100	94.5
10	300	20	30	0	-1	-1	5	10	90	88
11	300	100	70	0	+1	+1	91	86	88	89.8
12	150	60	70	-1	0	+1	45	45.5	86	86
13	300	100	30	0	+1	-1	20	19.2	13	18
14	300	60	50	0	0	0	32	31.2	31	33
15	300	60	50	0	0	0	31.5	31.2	33	33

Table 3

ANOVA test for TOC removal efficiency TOC and PS consumption.

SOURCE	Sum of squares		Df	Mean square		F-value		p ^a -value Prob > F	
	TOC	PS		TOC	PS	TOC	PS	TOC	PS
Model	7505.82	13,478.18	9	833.98	1497.58	31.73	42.36	.0007	.0003
A	1682.00	2738.00	1	1682.00	2738.00	63.99	77.45	.0005	.0003
B	630.13	2415.12	1	630.13	2415.12	23.97	68.32	.0045	.0004
C	4371.13	3003.13	1	4371.13	3003.13	166.31	84.95	<.0001	.0003
AB	81.00	72.25	1	81.00	72.25	3.08	2.04	.1395	.2122
AC	400	1056.25	1	400	1056.25	15.22	29.88	.0114	.0028
BC	20.25	900.00	1	20.25	900.00	0.77	25.46	.4202	.0039
A ²	0.78	554.08	1	0.78	554.08	0.030	15.67	.8703	.0108
B ²	100.16	266.77	1	100.16	266.77	3.81	7.55	0.1084	.0404
C ²	196.31	2792.31	1	196.31	2792.31	7.47	78.99	.0411	.0003
Residual	131.42	176.75	5	26.28	35.35				
Lack of fit	129.25	168.75	3	43.08	56.25	39.77	14.06	.0246	.0671
Pure error	2.17	8.00	2	1.08	4.00				
Cor total	7637.23	13,654.93	14						

^avalues of "Prob > F" less than .05 indicate model terms are significant.

[31]. The model was developed using the software Design Expert v.8.0.7.1.

3. Results and discussion

3.1. Box-Behnken analysis: model evaluation

The experimental matrix (Table 2) was conducted to establish a model to obtain the highest degree of DB3 mineralization. The accuracy of model fitting in the form of ANOVA (F-test and *p*) are displayed in Table 3. The ANOVA results confirm the significance of the model in each case along with its individual factor at the level of Prob > F less than .05.

The model F-values of 31.73 and 42.36 pointed out that it was significant at *p* < .0007 and .0003 for TOC removal and PS consumption, respectively. Also, A, B, C, AC, BC, A², C² are significant model terms in TOC removal and A, B, C, AC, BC, A², B² and C² are significant terms in PS consumption. The adequate precision is a measure of the range in predicted response relative to its associated error, being desirable a signal-to-noise ratio greater than 4.0 [32].

The ratio found values 19.74 and 15.88 are adequate signals for the validity model. Furthermore, the determination coefficient (*R*² = 0.982 and 0.987 for mineralization and oxidant decay, respectively) indicates that 1.8% and 1.3% variability cannot be satisfactorily explained by the empirical model in the range of operating parameters. A large value of *R*² does not imply that the regression model is a good one. However, *R*²_{adj} is preferred to determine the

fit of a regression model, as it does not always increase when variables are added. A good agreement has been obtained between the predicted TOC removal and PS consumption and the experimental value with *R*²_{adj} of 0.952 and 0.964 respectively. The model fitted was expressed by comparing the experimental TOC removal and PS consumption and the predicted values, parity plots were used to estimate the accuracy of the regression model are collected in Fig. 1, which indicated that the proposed model had adequate approximation to the actual value [33].

3.2. Preliminary tests

Preliminary tests were performed to assess the contribution of adsorption, photolysis and photocatalytic activity (due to the electron/hole pair caused by irradiating the ilmenite as seen in Eq. (7)) in absence of PS. The results showed a negligible contribution to the reaction, yielding TOC reduction lower than 3% after 180 min reaction time. Garcia-Munoz et al. [15] suggested that the high Fe/Ti molar ratio produces an elevated electron/hole pair recombination, thus reducing the photocatalytic activity.



Besides, the temperature hardly activated PS (Eq. 8) in the range 30–50 °C, achieving less than 10% mineralization. Nonetheless, this value increased up to 39% at 70 °C. Under these latter conditions, in presence of ilmenite, the mineralization increased up to 55%, corroborating the synergistic effect of combining an iron source

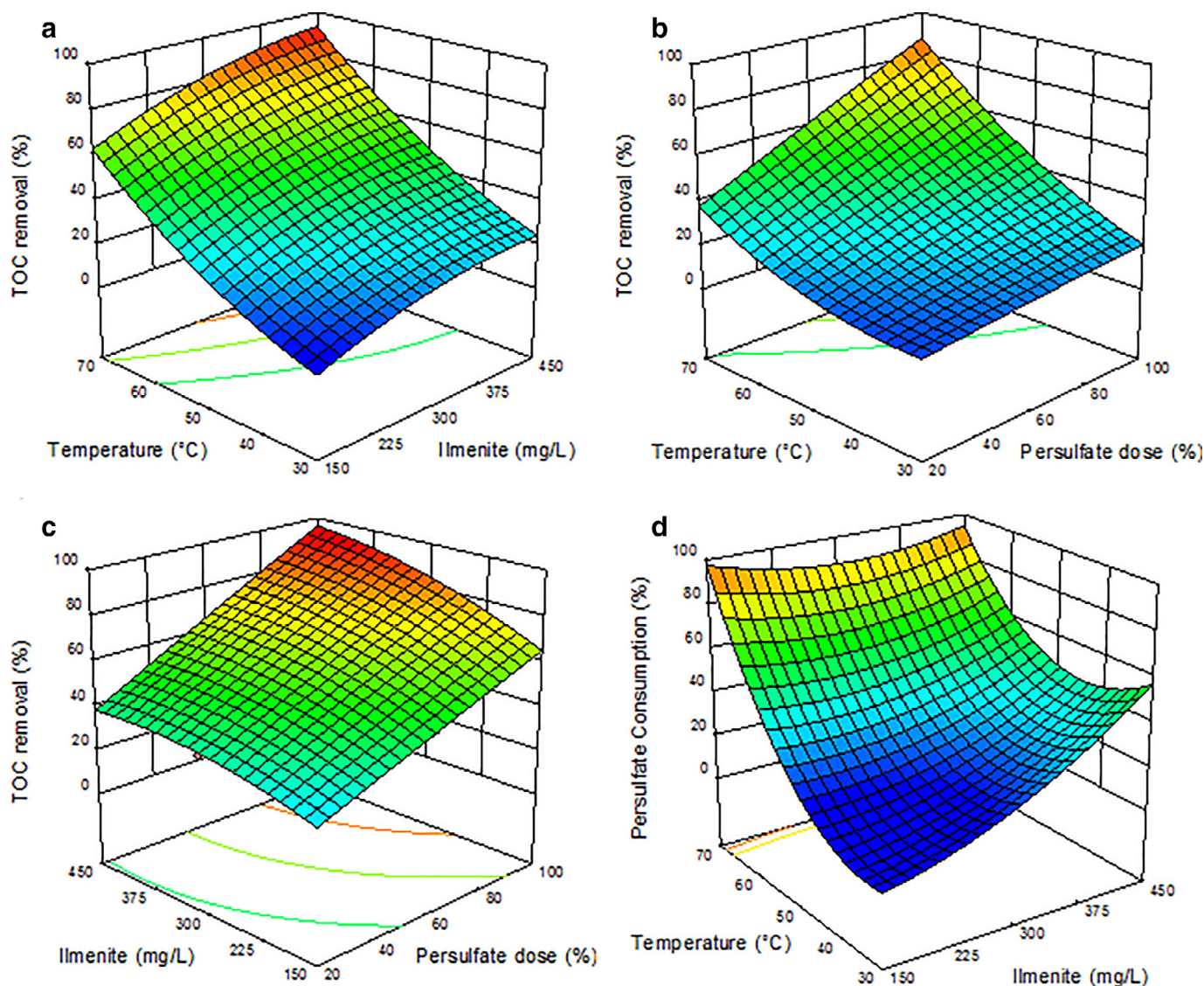


Fig. 3. Response surface plot showing interaction of ilmenite concentration and temperature (a), persulfate dose and temperature (b), persulfate dose and ilmenite concentration (c) on TOC removal and ilmenite concentration and temperature on PS consumption (d).

and temperature (Table S2).



The system based on persulfate with multiple activators (heat/ilmenite/UV-LED) improves the overall mineralization degree. UV-LED plays an important role in the ilmenite surface, due the photoreduction of Fe(III) to Fe(II). The Fe(II)/Fe (III) ratio was 0.72 in the natural ilmenite and was increased from 0.92 to 2.33 respectively after radiation alone and radiation in presence of dye (Fig. 2).

3.3. Optimization design

The performance of the process was optimized considering the operating costs ascribed to persulfate consumption and reaction temperature. In this sense, Fig. 3 shows 3D response surface, depicting the relation between UV-LED radiation and PS dose, ilmenite concentration and reaction temperature on TOC removal and PS consumption. The non-linear contour of all response surfaces suggested the interactions between each of the independent variables [34]. We used the second-order polynomial equation

(based on the RSM model, Eq. (6)) to optimize the process. The final predicted model can be described by the Eqs. (9,10) in terms of coded values.

$$\begin{aligned} \text{TOC removal (\%)} = & +31.17 + 14.50A + 8.88B + 23.38C \\ & + 4.50AB + 10.00AC + 2.25BC \\ & - 0.46A^2 - 5.21B^2 + 7.29C^2 \end{aligned} \quad (9)$$

$$\begin{aligned} \text{PS consumption (\%)} = & +33 - 18.50A + 17.38B + 19.38C \\ & - 4.25AB + 16.25AC - 15.00BC + 12.25A^2 \\ & - 8.50B^2 + 27.50C^2 \end{aligned} \quad (10)$$

A 30% increase in the mineralization degree was achieved when the concentration of ilmenite increased from 150 to 450 mg/L (Fig. 3a) and approx. 50% when the PS varied between 20% and 100% of the theoretical stoichiometric dose at 70 °C (Fig. 3b). With respect to the ilmenite and PS concentration (Fig. 3c), the photoreduction of Fe(III) to Fe(II) in the reaction with high PS dose increases the $\text{SO}_4^{\bullet-}$ generation [35,36].

However, the excess of catalyst concentration, for ilmenite loads above 320 mg/L, increases the turbidity of the DB3 solution, reduc-

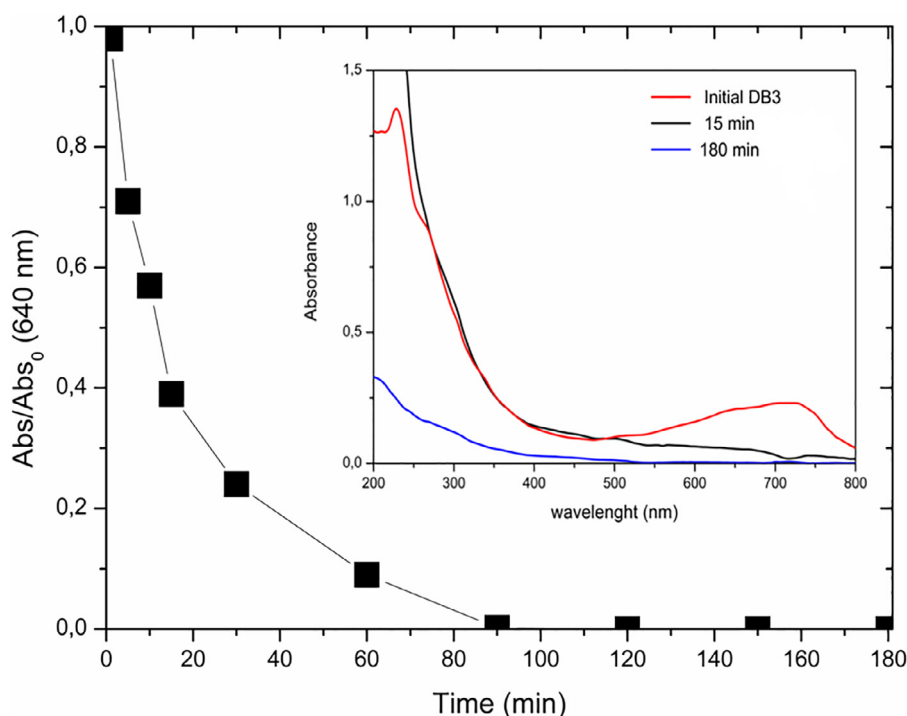


Fig. 4. UV-vis absorption spectra of DB3 before and after degradation treatment. Inset change in the spectra of DB3 between 200 and 800 nm.

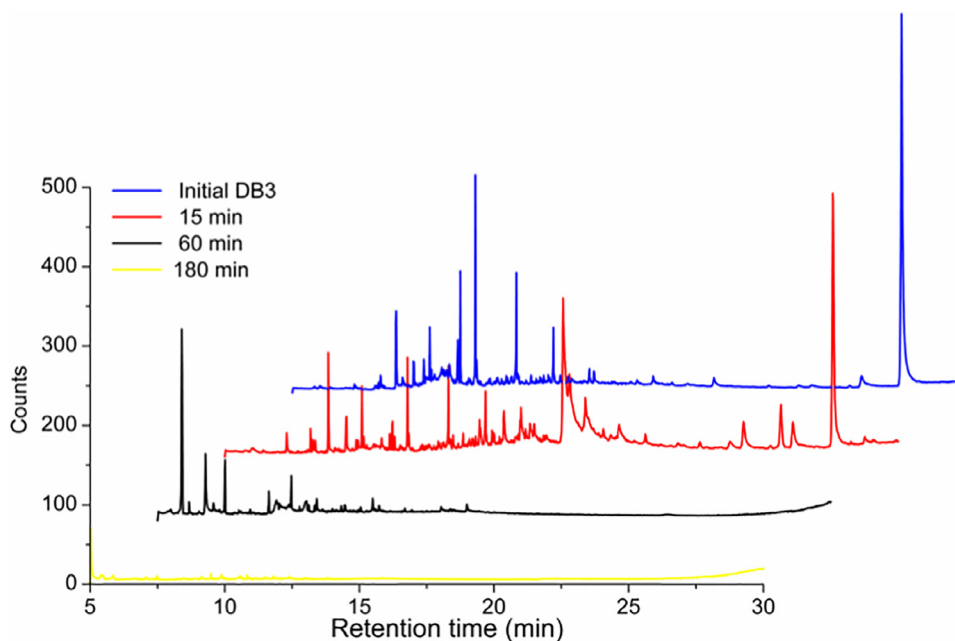


Fig. 5. GC-MS analysis of DB3 before and after experiment.

ing the light penetration of light through the dye solution. Hence, the source of Fe(II) decreases as photoreduction is hindered [37]. During the mineralization of DB3, persulfate consumption gradually increased with the temperature and ilmenite concentration (Fig. 3d). The amplitude of PS consumption varied from 20 to 90% after 180 min.

To assess the PS consumption, we have quantified the PS yield (ϵ) defined as the amount of TOC converted (mg) per unit weight of PS fed (g) [38]. The theoretical maximum value of ϵ for complete mineralization when using the stoichiometric PS would be 33.5 mg

TOC/g PS. The experimental ϵ value slightly overestimated (around 6%) the theoretical maximum ϵ value, which can be justified by the contribution of additional oxidation processes.

Optimum operating conditions were found to be: ilmenite: 320 mg/L, PS: 1.56 g/L and 67 °C. Under these conditions, experimental TOC removal was slightly overestimated in relation to the model (X_{TOCmodel} : 0.92 versus X_{TOCexp} : 0.96). The TOC removal as a function of reaction time is represented in Fig S2. Under these conditions, the leached iron (measured by ICP) was less than 1% of the total iron contained in the catalyst (approx. 0.8 mg/L⁻¹).

3.4. Dye removal evaluation

Dye removal was evaluated by the normalized absorbance decrease (at 640 nm) and the change in the spectra of DB3 (200–800 nm) as a function of treatment time is represented in Fig. 4. The peak at 640 nm is responsible for the blue color and absorbance peak at 254 nm is related to the anthraquinone structure [39]. As can be observed, the absorbance at 640 nm was easily removed after 15 min treatment (about 60%). The degradation of DB3 mainly related to the destruction of chromophore structures and the increase in the absorbance peak at 254 nm can be related to the formation of persistent aromatic by-products during the early oxidation stages.

Intermediates formed during the process were analyzed by GC–MS. Fig. 5 depicts the chromatograms of the reaction samples obtained throughout the experiments. After 15 min treatment, 1-amino-4-(methilamino) anthracene-9,10-dione with *m/z* 252 was identified, probably generated by homolytic rupture of C–N bond [40,41].

The effect of DB3 removal upon the toxicity was assessed using *Aliivibrio fischeri* (Fig. S3). The starting DB3 solution exhibits a toxicity of 22 TU. This value increased up to 28 after 15 min reaction, confirming the formation of more toxic byproducts. Thereafter, its toxicity decreased to nearly zero at 180 min as those compounds were almost completely mineralized.

3.5. Deactivated ilmenite surface

Stability of ilmenite was tested in consecutive runs under the optimum experimental conditions. Ilmenite showed a negligible activity in the third run (mineralization < 5%). Concerning the XPS of the O1s and S2p spectrum (Fig. S4) an increase in the signal intensity peaks of the deactivated catalyst was observed. Sulfur was not detectable on the fresh catalyst. Al-Shamsi and Thomson [42] detected FeSO₄ at a binding energy of 531.5 eV in O 1s (the peak between 529.8 and 532.3 eV corresponds to the surface lattice oxygen of metal oxides, the surface hydroxyl species and the adsorbed oxygen or water [43]) and 168.6 in S 2p spectra on deactivated nZVI surface exposed to persulfate. Descostes et al. [44] showed that FeSO₄ and Fe₂(SO₄)₃ were formed at 168.95 eV and 169 eV respectively. On the other hand, the deactivation could be attributed to the presence of iron sulfate generated on the ilmenite surface [45].

4. Conclusion

The irradiation with UV-LED allows overcoming the drawbacks associated with the use of natural ilmenite (FeTiO₃) in AOPs. Mineralization of DB3 azo dye by UV/FeTiO₃/PS was conducted analyzing the influence of temperature reaction, ilmenite concentration and persulfate dose. Application of Box-Behnken design combined with the RSM model equations satisfactorily described the inter-relationships between independent and dependent variables. The combined UV-LED/ FeTiO₃/heat to active PS shows synergetic effect compared to the individual processes, achieving DB3 mineralization around 96% under the optimum operating conditions (ilmenite: 320 mg/L⁻¹, PS: 1.56 g/L⁻¹ and 67 °C under UV-LED radiation) which is very close to the predicted values (92% mineralization). In addition, the mineralization of DB3 in the UV-LED/ilmenite/persulfate system is efficient in removing the toxic properties of the dye as shown by the *Aliivibrio fischeri* bacteria assay. Nevertheless, after three consecutive runs, the FeTiO₃ suffered loss of activity due the formation of an iron sulfate passivation layer on the catalyst surface.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtice.2017.12.015.

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