

## Photocatalytic EDTA degradation on suspended and immobilized TiO<sub>2</sub>

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### Abstract

The photocatalytic degradation of EDTA solutions (5 mM) has been studied under different conditions in the presence of TiO<sub>2</sub> in suspension or immobilized on glass rings and in the absence and presence of Fe(III). Using the response surface methodology, the initial pH, amount of photocatalyst, and the Fe/EDTA molar ratio were optimized in order to obtain better degradation. Under optimized conditions, 90% EDTA degradation (at a 0.28 Fe/EDTA molar ratio) was reached after 60 min illumination at pH 3.0 and using 0.73 g L<sup>-1</sup> TiO<sub>2</sub>. Increase of the acute toxicity (Microtox) was observed in the course of the reaction, and degradation intermediates were identified by GC/MS analysis.

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### 1. Introduction

Ethylenediaminetetraacetic acid (EDTA) is widely used in industrial, pharmaceutical and agricultural applications among others. In the total chlorine free (TCF) bleaching sequence of cellulose, a large amount of EDTA is required to reduce the concentration of iron, which avoids cellulose fiber destruction caused by the Fenton reaction. EDTA is also extensively used in nuclear reactor component decontamination and cleaning.

EDTA's low biodegradability is responsible for the presence of several complexes in sewage effluents, freshwater and ground-water [1]. In natural waters, EDTA exists mainly in the form of Ca-EDTA, Zn-EDTA and Ni-EDTA.

Several attempts have been made to develop techniques for EDTA removal from waters, principally using advanced oxidation processes. Some of the explored methods have been H<sub>2</sub>O<sub>2</sub>/UV [2], radiolysis [3], photocatalysis [4,5], Fenton and photo-Fenton [6] and solar-assisted oxidation [7].

During the photocatalytic process, simultaneous reduction and oxidation reactions take place on a semiconductor particle. Titanium dioxide (TiO<sub>2</sub>) has been the most used catalyst, but other semiconductors, such as ZnO, SnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub> or CdS, have been tested for the photocatalytic process with variable results [8,9]. The band gap of anatase is 3.2 eV; therefore, UV irradiation with wavelengths below 390 nm produces electron-hole pairs (e<sup>-</sup>-h<sup>+</sup>). The TiO<sub>2</sub> valence band holes, which have an oxidation potential of 2.6 V versus normal hydrogen electrode (NHE) at pH 7, migrate to the catalyst surface where they can: (a) oxidize adsorbed species by direct hole attack, (b) oxidize water or hydroxide anions to produce hydroxyl radicals, which then proceed to oxidize other species, or (c) oxidize other species in solution.

In parallel, conduction band electrons migrate to the surface to take part in reduction reactions. They have a reduction potential of -0.4 V versus NHE at pH 7, and then they can reduce a number of oxidants, including oxygen, which can form superoxide and hydroperoxyl radicals or certain metal ions that can be reduced to their metallic form onto the catalyst [10].

This paper describes the optimization of the suspended TiO<sub>2</sub>-assisted photodegradation of EDTA in solution with the help of

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experimental factorial design. The variables studied were the pH and the amount of catalyst for different Fe/EDTA ratios. The goal of this work was to fit the set of variables in order to increase of the oxidation efficiency of the photocatalytic system. The reactions were followed by UV–vis spectrophotometry, TOC and acute toxicity, comparing the suspended and immobilized TiO<sub>2</sub> systems.

## 2. Experimental

### 2.1. Materials

Titanium dioxide Degussa P25 with surface area 50 m<sup>2</sup> g<sup>-1</sup> (BET) and 80% anatase was used as provided. Na<sub>2</sub>EDTA (Merck) was used without further purification. Iron chloride (FeCl<sub>3</sub>, Merck) was used to complex EDTA in different molar ratios. All solutions were prepared using distilled water. The initial pH was adjusted with nitric acid or sodium hydroxide. All other reagents were of the highest purity and used without further treatment.

### 2.2. General procedure

The experimental set-up used in the photocatalytic experiments is shown in Fig. 1. The annular photoreactor (A) consist of a glass cylinder (75 cm length, 6 cm internal diameter, 1.4 L internal volume) equipped with a germicidal lamp (Silvania high-pressure 30 W-UV) with a maximal light intensity at 254 nm. The photon flow per unit of volume of the incident light inside the reactor (2.5 μEinstein s<sup>-1</sup> L<sup>-1</sup>) was actinometrically determined using potassium ferrioxalate. The circulation of the EDTA solution or suspension (2 L) was performed by means of a peristaltic pump (B) at a flow rate of 0.17 L min<sup>-1</sup>. Oxygen was externally bubbled into the solution (1 L min<sup>-1</sup>) 30 min prior to the beginning of the experiment by means of fritted glass located at the bottom of the vessel (C). Samples were taken in the same vessel.

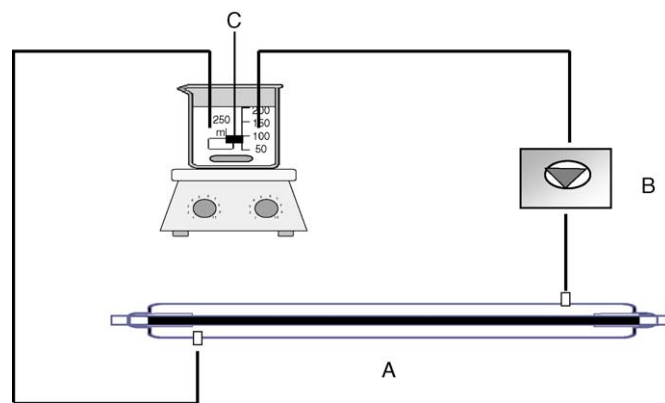


Fig. 1. General diagram of the annular photoreactor used in the photocatalytic experiments: (A) annular reactor with UV lamp; (B) peristaltic pump; (C) oxygen inlet.

In the experiments with TiO<sub>2</sub>-coated glass rings, the internal volume of the reactor was entirely filled with Raschig rings (around 2000 rings). Catalyst immobilization was carried out on glass rings (Raschig rings, 5 mm length, 5 mm internal diameter) as previously reported [11].

### 2.3. Experimental design

In the experiments with suspended catalyst, the amount of Titania, the initial pH of the EDTA solution, and the EDTA/Fe molar ratio were simultaneously varied in a 2<sup>3</sup> full-factorial central design. To fit the regression model, the MODDE 7.0 software was used. EDTA removal after 80 min of irradiation was chosen as the response factor. The titania concentration ranged between 0.5 and 1.5 g L<sup>-1</sup>, the initial pH between 3 and 5 and the Fe/EDTA molar ratio between 0.25 and 1.0. The variables were coded and 17 experiments were performed to obtain a polynomial model of the reaction. The polynomial comes from the general expression, shown below, which is applied over the

Table 1  
Experimental results from factorial design of EDTA degradation

Experiment	pH	TiO <sub>2</sub> (g L <sup>-1</sup> )	Fe/EDTA (×100)	Y <sub>exp</sub> (%)	Y <sub>calc</sub> (%)
1	3(-1)	0.5(-1)	25(-1)	91	92
2	5(+1)	0.5(-1)	25(-1)	88	94
3	3(-1)	1.5(+1)	25(-1)	91	96
4	5(+1)	1.5(+1)	25(-1)	72	59
5	3(-1)	0.5(-1)	100(+1)	28	30
6	5(+1)	0.5(-1)	100(+1)	26	31
7	3(-1)	1.5(+1)	100(+1)	80	63
8	5(+1)	1.5(+1)	100(+1)	16	25
9	2.59(-1.414)	1(0)	62(0)	85	87
10	5.41(+1.414)	1(0)	62(0)	72	62
11	4(0)	0.29(-1.414)	62(0)	85	76
12	4(0)	1.71(+1.414)	62(0)	61	74
13	4(0)	1(0)	9.5(-1.414)	56	82
14	4(0)	1(0)	115(+1.414)	57	14
15	4(0)	1(0)	62(0)	76	75
16	4(0)	1(0)	62(0)	75	75
17	4(0)	1(0)	62(0)	70	75

The response factor shown by Y, represents the degradation percentage after 80 min of irradiation on the reactor operated with TiO<sub>2</sub> in suspension.

response matrix shown in Table 1.

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1^2 + \dots$$

In this methodology the variable values are codified and put in the matrix  $X$  and the experimental response factor for each run are placed in the matrix  $y$ . By using matrix algebra it is possible to obtain the matrix  $b$ , which represents the values of the polynomial expression that fits the model [12].

$$b = (X^tX)^{-1}X^ty$$

#### 2.4. Analytical methods

EDTA degradation was monitored by HPLC analysis using the procedure reported by Nowack et al. [13]. Before the chromatographic analysis, 100  $\mu\text{L}$  of the EDTA solution was diluted with 4.7 mL of distilled water and 2 mL of 5 mM ferric chloride. The solution was injected in a Rheodyne injector model 7125 equipped with a Knauer 64 pump and a LiChrosphere 100 RP18 (125 mm  $\times$  5  $\mu\text{m}$ ) column. Methanol/formate buffer 0.02 M, pH 3.3 (90:10 v/v) was used as eluent. The EDTA-iron complex was detected using UV-vis detector at 258 nm. The retention time for the EDTA complex under such conditions was  $3.3 \pm 0.2$  min.

Total organic carbon was determined in a Shimadzu 5000 TOC analyzer. Acute toxicity was measured by exposing the solutions during 15 min to *Vibrio fischeri* in a MICROTOX instrument model 500. The results are expressed as toxicity units (TU) defined as 100/EC<sub>50</sub>. For the analysis of the oxidation products, the photocatalyzed sample was derivatized with diazomethane. The methyl ester derivatives were extracted twice with dichloromethane and injected in a HP-5890 Series gas chromatograph equipped with a HP 5972 Mass Selective Detector.

### 3. Results and discussion

#### 3.1. Preliminary results

EDTA degradation was studied at an initial concentration of 5 mM, a very high value when compared to values typically found in natural waters. However, similar values can be found in nuclear reactor effluents when EDTA is extensively used to avoid metal presence in process waters [14,15].

Preliminary experiments were carried out to evaluate the effect of iron and TiO<sub>2</sub> on the degradation kinetics of 5 mM EDTA solutions. Initial conditions were pH 3 and 1 g L<sup>-1</sup> TiO<sub>2</sub>. Fig. 2 shows that 60% of the EDTA was degraded by direct photolysis after long irradiation periods (>180 min). Under photocatalytic conditions (1 g L<sup>-1</sup> TiO<sub>2</sub>), around 80% degradation was obtained after 130 min irradiation. Finally, in the presence of Fe(III) and TiO<sub>2</sub>, the same result (80% degradation) was reached after 90 min irradiation. These results indicate that titania catalyzes the photolytic degradation of EDTA, and it is favored when EDTA is complexed with iron. Similar results have been observed by the presence of other metals [16–18]. EDTA forms very stable metallic complexes, especially at pHs in the range

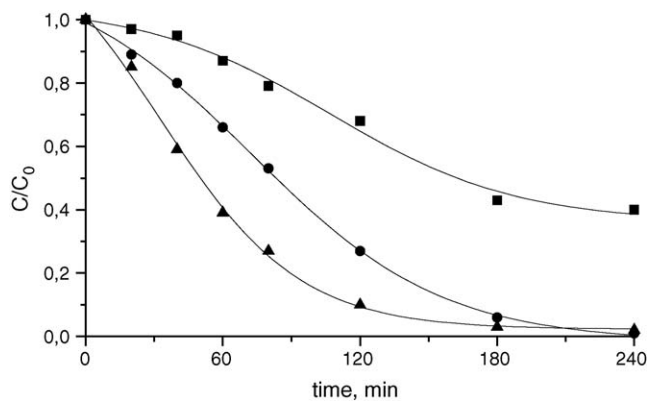
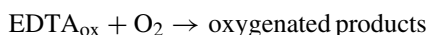
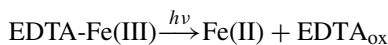


Fig. 2. EDTA degradation (5 mM, initial pH 3 and O<sub>2</sub> saturated): (■) UV photolysis; (●) [TiO<sub>2</sub>] = 1 g/L; (▲) [Fe<sup>3+</sup>] = 5 mM; [TiO<sub>2</sub>] = 1 g/L.

4–5 [19]. When iron-EDTA complexes are irradiated, a charge transfer reaction can occur from EDTA to iron, forming Fe(II) and EDTA radicals, which in turn can be oxidized by oxygen in a chain reaction:



In parallel, an increase of the solution pH was observed during the course of EDTA degradation under different conditions, indicating the formation of basic compounds, probably amines. This effect has been also reported by Furlong et al. [20].

#### 3.2. Factorial design

To obtain a more efficient EDTA degradation over TiO<sub>2</sub>, optimization experiments were carried out. The response surface methodology was chosen as the mathematical tool to optimize the EDTA degradation, where pH, quantity of TiO<sub>2</sub>, and the Fe(III)/EDTA molar ratio were the parameters to be optimized. In preliminary experiments, it was observed that the presence of iron increased the EDTA degradation rate (Fig. 2). A 2<sup>3</sup> model was proposed considering the three variables and two levels: high and low (+ and -). The pH ranged between 3 and 5, TiO<sub>2</sub> concentration between 0.5 and 1.5 g L<sup>-1</sup> and Fe/EDTA molar ratio between 0.25 and 1. Table 1 shows the real and coded values of the variables simultaneously changed in the 17 experiments performed, arranged in a spherical mathematical model. The first eight experiments represent the vertices of a cube, the next six experiments are located in the centered faces of the cube, and the last three assays represent the central point of the cube that gives the statistical validity of the model. The independent variable or response factor ( $Y$ ) was chosen as the percent of EDTA degradation after 80 min of irradiation.

With the use of the software MODDE 7.0, the data shown in Table 1 was adjusted to a polynomial equation. The calculated polynomial (Eq. (1)) gives the weight of the variables under study ( $x_1$ ,  $x_2$ ,  $x_3$  or pH, TiO<sub>2</sub>, Fe/EDTA molar ratio):

$$Y = 74.9(\pm 4.3) - 8.9x_1(\pm 3.3) - 24.0x_3(\pm 4.0) - 13.4x_3^2(\pm 5.9) - 9.8x_1x_2(\pm 4.0) + 7.3x_2x_3(\pm 4.0) \quad (1)$$

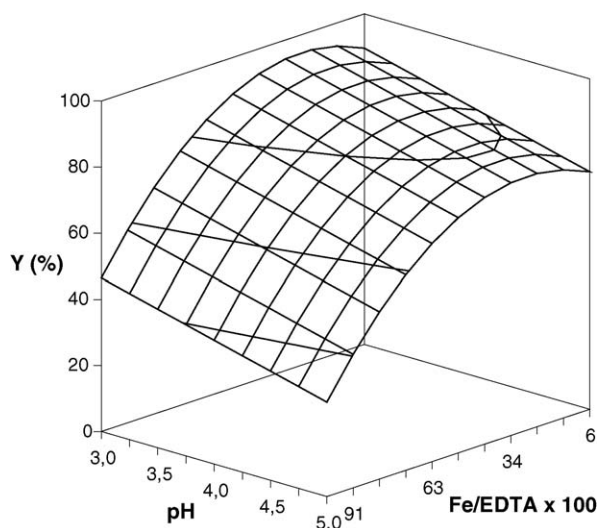


Fig. 3. Response surface showing the EDTA degradation percentage (5 mM) after 80 min light irradiation as a function of pH and % of EDTA chelation.

Taking in consideration only the first order effect, it is evident that the highest EDTA removal can be obtained when a low amount of iron in the complex ( $x_3$ ) and a low pH ( $x_1$ ) are fitted. The  $\text{TiO}_2$  concentration is not a significant variable for EDTA removal, showing only crossed effects with  $x_1$  and  $x_3$ . A significant quadratic effect is presented by the Fe/EDTA ratio meaning that an optimal region can be obtained for this parameter ( $x_3$ ). From the polynomial, it can also be concluded that an antagonistic effect is observed between the combinations of the variables pH- $\text{TiO}_2$  ( $x_1x_2$ ). A low synergistic effect is observed between the last two variables ( $x_2x_3$ ). In summary, the most noticeable effect on the EDTA degradation is related with the Fe/EDTA molar ratio.

The EDTA degradation after 80 min of irradiation was calculated from the polynomial equation (Table 1, last column), and compared with the experimental data to verify the validity of the mathematical model. From the figures shown in the table, the model's statistical consistence is evident. A lack of fit is observed only at extreme values of  $x_3$  (experiments 13 and 14). These experiments were not considered in the determination of the polynomial. Under those conditions, the calculated variance was 87.7% for a confidence level of 95%, indicating that the polynomial calculated with the performed experiments agreed with the experimental data.

Considering the three studied variables and using the polynomial, it was possible to draw a 3D representation of the response surface, keeping constant the  $\text{TiO}_2$  concentration ( $1 \text{ g L}^{-1}$ ), which is the less significant variable ( $x_2$ ). Fig. 3 shows the three-dimensional relationship between the pH and Fe/EDTA ratio with respect to the response factor  $Y$ . It is clearly observed that the most significant variable for EDTA removal is the Fe/EDTA molar ratio. More than 85% of EDTA removal was observed when around 20–40% of EDTA was chelated with iron. It has been pointed out that the presence of iron could promote the photolytic degradation driven by photochemical induced charge transfer to Fe(III) initiating thus the EDTA decarboxylation [21],

which means that heterogeneous and homogeneous photochemical reactions are simultaneously occurring in the presence of iron. A possible explanation to the detrimental effect of iron excess is that it can act as electron or hole scavenger. Additionally, when all the EDTA is chelated with iron, the removal is less than 40% suggesting that the increase of Fe(III) in the complex decreases the net negative charge, depleting the interaction with the positively charged  $\text{TiO}_2$ , consequently decreasing photocatalytic activity. The response surface shows that good EDTA degradation can be achieved when the appropriate Fe/EDTA ratio is used throughout the pH range. From mathematical and graphical considerations, the conditions to obtain good EDTA degradation were 0.25–0.30 Fe/EDTA molar ratio (25–30% chelation), initial pH <3.5, and  $\text{TiO}_2$  loading around  $1 \text{ g L}^{-1}$ . For experimental purposes, the values chosen as optimum for the variables Fe/EDTA, pH and  $\text{TiO}_2$  loading were 0.28, 3.0 and 0.73, respectively. Under those conditions, degradation values over 90% can be observed after 80 min irradiation (see experiments 1 and 3).

### 3.3. Effect of the initial EDTA concentration

To determine the significance of the EDTA adsorption in the photocatalytic process, EDTA solutions at different initial concentrations were irradiated in the presence of  $\text{TiO}_2$ . It is well known that the photocatalytic degradation of many organic compounds follows the Langmuir–Hinshelwood (L–H) mechanism [22]. A linearized L–H model was used to determine the kinetic ( $k_{\text{vel}}$ ) and adsorption ( $K_{\text{ads}}$ ) constants for EDTA degradation. To determine these constants, experiments were carried out using a titania concentration of  $1 \text{ g L}^{-1}$ .

The  $k_{\text{vel}}$  and  $K_{\text{ads}}$  values, determined from plots of the initial degradation rate versus EDTA concentration in the linearized L–H model, were  $3 \times 10^{-5} \text{ mol L}^{-1} \text{ min}^{-1}$  and  $1.8 \times 10^3 \text{ L mol}^{-1}$ , respectively. These values agree well with previous results obtained for a similar system [4,23]. This fact confirms the importance of adsorption as the first step in the photocatalytic process influenced by the complex and  $\text{TiO}_2$  charges.

### 3.4. Reactions under optimized conditions

#### 3.4.1. EDTA degradation

EDTA degradation was carried out in suspension under optimized conditions, pH 3,  $\text{TiO}_2$   $0.73 \text{ g L}^{-1}$  and Fe/EDTA ratio 0.28 (Fig. 4). For comparison, the results obtained for similar photocatalyzed reactions in absence of Fe(III) are also included in the figure. The presence of Fe notably accelerates EDTA degradation, with virtually total EDTA elimination being achieved after 70 min irradiation. On the other hand, the photocatalytic reaction in suspension and in absence of Fe required 180 min to reach complete EDTA degradation. These results confirm that the formation of the complex Fe/EDTA has a positive effect in EDTA degradation when an adequate Fe/EDTA molar ratio is used. As it was pointed out in the discussion of Fig. 2, total disappearance of EDTA was reached after 240 min under non-optimized conditions, indicating that optimization is an appropriate tool to establish the best experimental conditions.



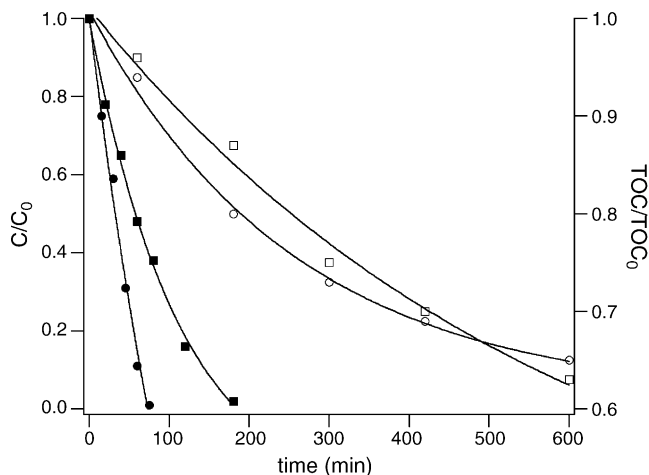


Fig. 4. TOC profiles and EDTA removal under optimal conditions found for EDTA and EDTA-Fe degradation: (□) TOC (EDTA) with TiO<sub>2</sub> in suspension; (○) TOC (EDTA-Fe) with TiO<sub>2</sub> in suspension; (■) EDTA removal with TiO<sub>2</sub> in suspension; (●) EDTA-Fe removal with TiO<sub>2</sub> in suspension.

A comparison between Fe/EDTA and EDTA degradation was also performed using immobilized TiO<sub>2</sub> on Raschig rings (Fig. 5). Under experimental conditions similar to those used for suspended catalyst, total EDTA removal was achieved after 360 min irradiation. The only difference was that the content of TiO<sub>2</sub> on the rings was 0.64 g L<sup>-1</sup> considering the total volume (2L), or 0.9 g taken into account only reactor volume (1.4 L). In the case of Fe/EDTA solution, complete EDTA abatement was reached after 120 min of irradiation. As in the case of suspended catalyst, a significant improvement in the reaction rate was observed by using iron-chelated EDTA. This reaction is even faster than the one observed for TiO<sub>2</sub> suspensions in absence of iron. The behavior of the catalytic system with immobilized catalyst still turns out to be more efficient than the system with the catalyst in suspension, considering the mass of TiO<sub>2</sub> used in the reactor. In an earlier report, Shibata et al. [24] reported that the addition of Fe(III)-EDTA to a TiO<sub>2</sub> photocatalytic system

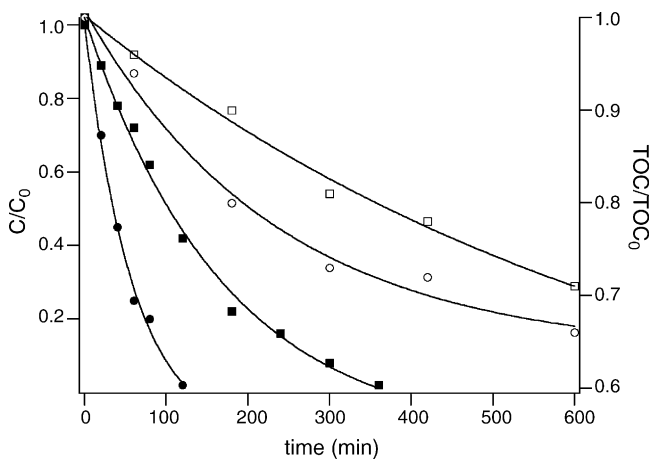


Fig. 5. TOC profiles and EDTA removal under optimal conditions found for EDTA and EDTA-Fe degradation (□) TOC (EDTA) with TiO<sub>2</sub> immobilized; (○) TOC (EDTA-Fe) with TiO<sub>2</sub> immobilized; (■) EDTA removal with TiO<sub>2</sub> immobilized; (●) EDTA-Fe removal with TiO<sub>2</sub> immobilized.

increase notably the generation of OH radicals because the complex acts as an electron acceptor, which is more efficient than oxygen.

### 3.4.2. TOC decrease

EDTA's mineralization profiles for the different systems are shown in Figs. 4 and 5. The elimination of organic matter reached approximately 40% of the initial carbon after 10 h of irradiation in all cases. This result indicates a similar efficiency regarding the mineralization for the immobilized catalyst in comparison with titania in suspension. Despite the fast EDTA elimination in the optimized system in the presence of Fe, a slow mineralization rate was detected for the four studied systems, which could be due to the nature of EDTA degradation intermediates that are very stable and smaller in size than the parent EDTA. Thus, the efficiency of all the studied systems would be similar independent of the mineralization mechanism.

### 3.4.3. Toxicity evolution

The evolution of acute toxicity during 10 h irradiation under optimized conditions of the systems EDTA/TiO<sub>2</sub> and EDTA-Fe(III)/TiO<sub>2</sub> for the suspended catalyst are shown in Fig. 6. Initial EDTA solution toxicity values were very low and increased progressively, reaching a maximum value of 18 TU after 360 min of irradiation. They then diminished until complete toxicity removal after 600 min of irradiation. Similarly, initial Fe/EDTA toxicity was very low and grew rapidly to reach a maximum of 17 TU at 300 min of irradiation, but it remained constant (≈16 TU) until 600 min of irradiation. These results differ from those reported by Sillampää et al. [25], who observed a moderate initial toxicity as much for EDTA as for the complex Fe/EDTA using MICROTOX bioassay. EDTA toxicity has been broadly discussed in the literature, either as free compound or forming complexes with diverse transition metals [26–28]. The EDTA solution does not present acute toxicity at the initial work con-

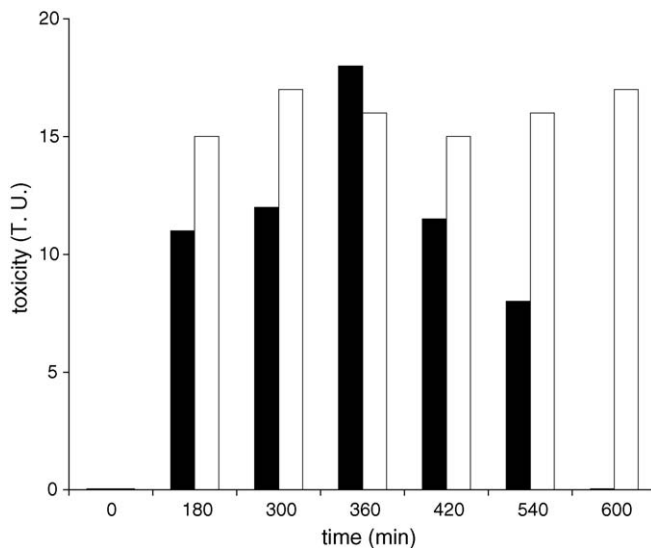


Fig. 6. Acute toxicity (MICROTOX) during the course of the photocatalytic reactions under optimal conditions for: EDTA (filled bars) and EDTA-Fe (open bars).

centration as demonstrated by their TU value (almost zero) and previous reports [28].

#### 3.4.4. Electric energy per order determinations

The figure-of-merit EE/O (electric energy per order) has been used as a comparative figure to evaluate the efficiency of photocatalytic organic compound degradation [29]. It measures the energetic cost to abate the initial concentration of a certain pollutant in one order of magnitude. These experiments were performed under the optimized conditions for Fe/EDTA, and the same pH and TiO<sub>2</sub> loading was used for the degradation in absence of Fe. The EE/O values were calculated for the photocatalytic systems with suspended and immobilized TiO<sub>2</sub> are shown in Table 2. This values show that Fe/EDTA complex degradation by TiO<sub>2</sub> suspended photocatalysis consumes 18 kWh m<sup>-3</sup>, while the immobilized system requires

Table 2

Electric energy per order values calculated for the different photocatalytic systems

System	EE/O (kWh m <sup>-3</sup> )
UV/TiO <sub>2</sub>	49
UV/TiO <sub>2</sub> immobilized	74
UV/TiO <sub>2</sub> /Fe	18
UV/TiO <sub>2</sub> immobilized/Fe	27

27 kWh m<sup>-3</sup> to achieve the same degradation. This result indicates a very good EDTA degradation efficiency for the immobilized catalyst, and is comparable to the suspended catalyst, in spite of the expected loss of efficiency for a fixed TiO<sub>2</sub> amount over inert substrates. These observations are concordant with experimental results for other systems [30], which validate the advantage of using an immobilized catalyst.

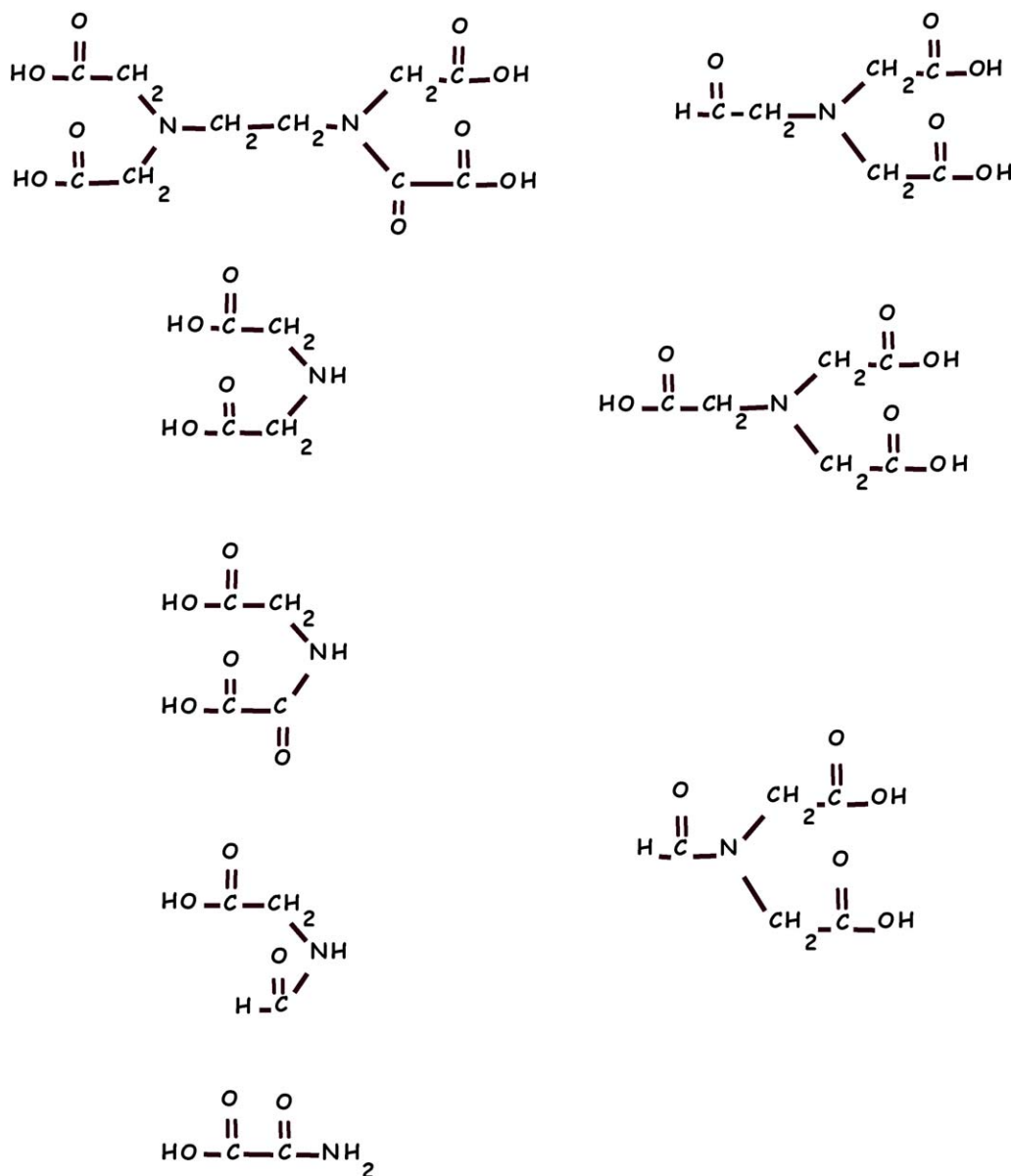


Fig. 7. Compounds identified in the photocatalytic EDTA oxidation in the presence of Fe(III).

### 3.4.5. Identification of reaction intermediates

Previous results suggest different EDTA degradation routes, generating different intermediates, which are more toxic than the original EDTA solutions [4]. For EDTA degradation in the system with Fe(III), some of the intermediates were determined by GC/MS. The identified structures are shown in Fig. 7. The low molecular weight oxidation intermediates with functional groups such as amines, aldehydes and carboxylic acids, could be the cause of the solution toxicity evolution.

## 4. Conclusions

The paper shows that the photocatalytic EDTA degradation can be improved by using optimization procedures to identify the most important variables involved in the EDTA oxidation and to fit the ideal degradation conditions in a determined medium. Experiment modeling results in a single mathematical expression, which is in good agreement with experimental results. The use of an immobilized catalyst does not significantly reduce the TiO<sub>2</sub>-photocatalytic activity, opening the possibility of scaling-up for potential applications. When EDTA is chelated with iron in an appropriate ratio, the photocatalytic oxidation presents the best results either for suspended or immobilized TiO<sub>2</sub>. A very important parameter that must be taken into account is the acute toxicity evolution during the photocatalytic process, mainly when EDTA forms iron complexes.

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