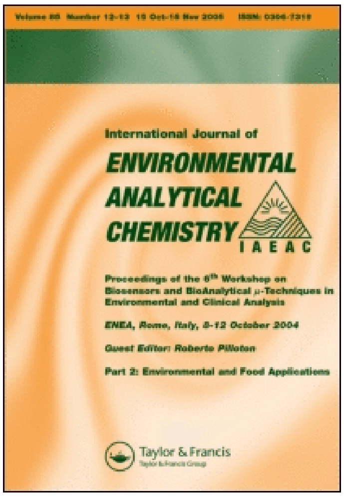

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Application of GC-MS and GC-AED to the evaluation of by-products formed by solar photo-fenton degradation of Methyl *tert*-butyl ether in water

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APPLICATION OF GC-MS AND GC-AED TO THE EVALUATION OF BY-PRODUCTS FORMED BY SOLAR PHOTO-FENTON DEGRADATION OF METHYL *TERT*-BUTYL ETHER IN WATER

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This study describes the application of solar photocatalysis by photo-Fenton reaction to the degradation of methyl *tert*-butyl ether (MTBE) in aqueous solutions at a pilot scale in a compound parabolic collector (CPC) reactor. The results show a rapid and complete oxidation of MTBE after only 35 min of treatment. However, 54% remains to be mineralized after that time, almost complete mineralization (97%) being reached only after 155 min of treatment. This indicated the formation of a large quantity of transformation products (TPs) more resistant to degradation than the parent compound. Identification and quantification of six TPs (*tert*-butyl formate, *tert*-butyl alcohol, acetone, methyl acetate, isobutene and formaldehyde) were possible with the combined use of two complementary techniques: GC-MS and GC-AED, both coupled to a purge-and-trap system. Ionic chromatography (IC) was used for the identification of organic ions usually present in the last stages of the mineralization process. Only formate ions were detected and these may be considered as the last step in the oxidation process previous to total mineralization. A degradation pathway, fixing the most critical compounds in terms of kinetic degradation, was proposed.

Keywords: Methyl *tert*-butyl ether; Photo-Fenton; By-products; Gas chromatography-Mass spectrometry; Atomic emission detector; Photodegradation

INTRODUCTION

Methyl *tert*-butyl ether (MTBE) has been used as a gasoline additive since the 1970s as an octane enhancer, producing cleaner-burning gasoline [1, 2]. Although its use has been promoted because of its low cost, simple production and characteristics that favour blending with conventional gasoline, its stability, high water solubility and volatility as well as its scarcely studied potential effect on human health and aquatic

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organisms [3, 4] make it likely to become an important environmental contaminant. Already, the presence of MTBE has been reported in the aquatic [5–9] and atmospheric [10,11] environments of regions in the US and Europe, at concentrations that range from environmental background levels in the low microgram per litre range, to high microgram per litre levels at sites affected by occasional sources. The main sources of MTBE contamination of ground and surface water are leaking storage tanks, both under and above ground, spills from gasoline-powered recreational watercraft and atmospheric deposition through precipitation of industrial or vehicular emissions. Consequently, MTBE is today one of the most frequently detected volatile organic compounds (VOCs), especially in groundwater, and techniques are needed to remove it from contaminated water.

Traditional treatments, such as air stripping, granular activated carbon (GAC) adsorption or biological filtration, have been demonstrated to be relatively ineffective at removing low concentrations of MTBE [12]. Several studies involving the degradation of MTBE in aqueous solution using advanced oxidation processes (AOPs), including ozone and ozone/hydrogen peroxide treatment [13–17], photocatalytic degradation in TiO_2 slurries [18], ultraviolet (UV)/hydrogen peroxide treatment [19–22] and hydrogen peroxide in the presence of Fe(II), otherwise known as Fenton's Reagent [23], have been conducted. Despite the efficiency of these treatments in the degradation of MTBE and other organic compounds, some aspects, such as their higher cost and, especially, formation of by-products during oxidation, require further research.

Based on previous considerations, the aim of this study was to evaluate the efficiency of the AOP known as photo-Fenton reagent, a combination of the dark $Fe(II)/H_2O_2$ reaction with UV radiation, which has scarcely been applied to MTBE degradation [24]. To obtain a more realistic evaluation of the process, a large pilot plant using sunlight as the radiation source was used. As commented above, the main disadvantage of AOPs is their high cost. The application of solar technologies to these processes could help to diminish that problem by reducing the amount of electricity required to generate UV radiation [25].

Determination of the transformation products (TPs) generated during the treatment was performed by coupling purge-and-trap gas chromatography (P&T-GC) to two powerful detection systems: mass spectrometry (MS) and atomic emission detection (AED). While GC-MS has been extensively used to determine MTBE by-products [18, 19, 26, 27], the use of GC-AED for this has not been reported. As the use of P&T-GC-AED has been successfully evaluated for determination of other volatile organic compounds [28], it may represent a good alternative in this kind of analysis [29].

EXPERIMENTAL

Standards and Reagents

Methyl *tert*-butyl ether (MTBE) (purity >99.8%) and methyl acetate (MA) (purity > 99%) were obtained from Riedel-de Haën (Seelze, Germany). *tert*-Butyl alcohol (TBA) (purity >99%), *tert*-butyl formate (TBF) (purity > 99%) and formaldehyde (FA) (37% solution) were supplied by Aldrich and Sigma (Sigma-Aldrich Chemie, Steinheim, Germany). Acetone (purity > 99.8%) was from Panreac (Barcelona, Spain). Stock and working solutions were prepared in ultrapure water (obtained by a Milli-Q water purification system, Millipore, Bedford, MA). Special care was taken to avoid volatilization during preparation. The aqueous solutions were prepared daily and discarded after analysis.

The following chemicals were used for the photo-Fenton experiments: 0.05 mM iron (II) [iron sulphate ($FeSO_4 \cdot 7H_2O$)], hydrogen peroxide reagent grade (30%) and sulfuric acid for pH adjustment (around 2.7–2.8). Catalase from Fluka Chemie AG (Buchs, Switzerland) from bovine liver (2500 U/mg) was used for eliminating the remaining H_2O_2 and quenching the reaction after sampling in photo-Fenton experiments. The water used in the experiments was obtained from the PSA Desalination Plant (conductivity $< 10\,\mu S\,cm^{-1}$).

Analytical Determinations

Purge-and-trap (P&T)

The extraction and enrichment of MTBE and its transformation products from water samples was carried out by using a Tekmar 3100 purge-and-trap (P&T) concentrator (Cincinnati, Ohio, USA). The system was equipped with a 5-mL sample container and a 30-cm × 0.312-cm i.d. absorbent trap packed with Tenax/Silica Gel. The P&T was interfaced with two different gas chromatographic systems (GC-MS and GC-AED) by means of a transfer line heated to avoid analyte condensation during the analyses. P&T operating conditions, previously optimized for maximum sensitivity [8], may be summarized as follows: sample volume, 4 mL; purge gas, He at room temperature; adsorption temperature, 30°C for 11 min; desorption temperature, 220°C for 4 min; bake conditions, 225°C for 10 min. Other temperatures: MCS, 300°C; line, 150°C; valve, 150°C.

GC-AED Analyses

GC-AED analyses were performed on an Agilent Technologies 6890 series gas chromatograph (Palo Alto, CA, USA) equipped with an Agilent Technologies G2350 AED. HP ChemStation software (B.02.05 version) was used to control the instrument and data acquisition and treatment. Two kinds of columns, of two different polarities, were used to obtain a complete separation and identification of each compound: (a) CP-Select 624 CB (6% cyanopropyl-phenyl, 94% dimethylsiloxane) capillary column (Chrompack Int.) 30 m × 0.32 mm, 1.80-μm film thickness and (b) Omegawax 250 (polyethylene glycol) capillary column (Supelco) 30 m × 0.25 mm, 0.25-μm film thickness. Helium was used as the carrier gas in the constant flow mode ($1.0\,mL\,min^{-1}$). The oven temperature program was: 40°C (8 min) to 120°C (2 min) at $18°C\,min^{-1}$ and then to 180°C (5 min) at $20°C\,min^{-1}$. Injection (2 μL) was in split mode (split ratio 20 : 1). One run with two selected wavelengths, hydrogen at 486 nm and carbon at 496 nm, and another run for oxygen determination at 171 nm, were used for each analysis. The make-up and reagent gases were oxygen at 36.0 psi and hydrogen at 11.2 psi. Make-up gas flow was set at $35\,mL\,min^{-1}$. Transfer line and cavity temperatures were both 250°C.

GC-MS Analyses

GC-MS analyses were run on an HP 6890 series gas chromatograph (Agilent Technologies) interfaced with an HP 5973 mass-selective detector. Data acquisition and processing, and instrument control, were performed by HP MSD ChemStation software. The analytical column was a CP-Select 624 CB (6% cyanopropyl-phenyl, 94% dimethylsiloxane) capillary column (Chrompack Int.) 30 m × 0.32 mm, 1.80-µm film thickness. The oven temperature program was the same as described for the GC-AED analyses. Helium was used as the carrier gas at 1.3 mL min^{-1} in the constant flow mode. A split/splitless injector, maintained at 250°C, was used in split mode (split ratio 20 : 1). The autotuning software optimized typical MS operating conditions. Electron impact (EI) mass spectra were obtained at 70 eV electron energy. The ion-source and quadrupole analyser temperatures were set at 230 and 106°C, respectively.

LC-IC

Formation of organic ions was followed by LC-IC (Dionex-120, anion column IonPAc As14, 250 mm long). The eluent was $Na_2B_4O_7$ (1 mM).

TOC

Total Organic Carbon (TOC) was analysed by direct injection of the filtered samples into a Shimadzu-5050A TOC analyser, calibrated with standard solutions of hydrogen potassium phthalate.

Photo-Fenton Degradation Assays

Photoreactor

All the experiments were carried out under sunlight at the Plataforma Solar de Almería (PSA, latitude 37°N, longitude 2.4°W) using compound parabolic collectors (CPC). The pilot plant [30] is made up of twin systems, each having three collectors, one tank and one pump. Each collector (1.03 m^2 each) consists of eight Pyrex tubes connected in series and mounted on a fixed platform tilted 37° (local latitude). The water flows at 20 L/min^{-1} directly from one module to another and finally into a tank. The total volume (V_T) of the reactor (40 L) is separated into two parts: 22 L (Pyrex tubes) total irradiated volume (V_i) and the dead reactor volume (tank + HDPE tubes). Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, model CUV3), mounted on a platform tilted 37° (the same angle as the CPCs), which provides data in terms of incident $W_{UV}\,\text{m}^{-2}$. This gives an idea of the energy reaching any surface in the same position with regard to the sun. With Eq. (1), combination of the data from several days' experiments and their comparison with other photocatalytic experiments is possible:

$$t_{30\,\text{W},n} = t_{30\,\text{W},n-1} + \Delta t_n \frac{\text{UV}}{30} \frac{V_i}{V_T}; \quad t_n = t_n - t_{n-1} \tag{1}$$

where t_n is the experiment time for each sample, UV is the average solar ultraviolet radiation measured during Δt_n, and $t_{30\,\text{W}}$ is a "normalized illumination time". In this case, time refers to a constant solar UV power of 30 W m^{-2} (typical solar UV power on a perfectly sunny day around noon).

Experiment Design and Sampling

Photo-Fenton experiments were carried out in the following way. At the beginning of the experiments, with collectors covered, the MTBE was added to the tank and mixed until constant concentration was achieved throughout the system (around 100 mg/L). At this moment, a first sample was taken to establish the initial concentration (C_0). After that, sulfuric acid was used to adjust pH to around 2.7–2.8. Then, the Fenton reagent (an aqueous solution of hydrogen peroxide and ferrous ions) was added, beginning the Fenton reaction in the dark [see Eq. (2)]. Once this reaction was complete, a new sample was taken for: (i) evaluation of the dark reaction and (ii) determination of the initial concentration before exposure to sunlight. Finally the collector cover was removed and the photo-Fenton reaction [see Eq. (3)] started ($t = 0$). Samples (250 mL) were then taken at regular intervals at the solar collector outlet to estimate the MTBE degradation rate and evolution over time of metabolites formed. TOC was measured and GC-MS analyses were carried out on all samples

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \tag{2}$$

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + H^+ + {}^{\bullet}OH \tag{3}$$

$${}^{\bullet}OH + MTBE \rightarrow \text{By-products} \tag{4}$$

RESULTS AND DISCUSSION

Kinetics and Mineralization of MTBE

Blank Experiments

MTBE is highly volatile (33 kPa at 298 K), so because of the special characteristics of the pilot-scale photoreactor used (outdoors, not airtight, not thermostated), loss of MTBE from volatilization may be expected. To quantify those possible losses, simultaneous blank experiments were performed along with the assays of photocatalysis in a second identical photoreactor. Water containing only MTBE at a concentration of 100 mg/L was pumped through the second reactor at the same time as the photocatalytic experiment was carried out in the first photoreactor. At the end of the photocatalytic treatment (around 155-min t_{30W}), a total of 35% of the initial MTBE and TOC in the simultaneous blank test had been lost. As disappearance of TOC and MTBE measured in this blank test was exactly the same and no TPs were detected in the water, it is logical to suppose that MTBE had been volatilized. Considering that during the photocatalysis experiments, a 35-min t_{30W} was enough to degrade MTBE almost completely, the possible volatilization in these experiments might be considered irrelevant ($<10\%$). However, this effect has to be taken into account if the rate constants of the treatment used for MTBE mineralization are low because the time of exposure of MTBE at the open air is higher so increasing volatilization losses. For example, photocatalytic treatment tests performed with TiO_2 in the same pilot plant, in which total degradation of MTBE took more than 200 min, revealed that MTBE volatilization losses were as important as photocatalytic degradation, making its application unfeasible under these experimental conditions.

As widely referenced [18,19], MTBE and solar-UV spectra do not overlap at all and so no direct photolysis of MTBE can take place. To evaluate possible hydrolysis, a 100-mg/L MTBE solution at $pH = 3$ (photo-Fenton is carried out at a pH of around 3) was kept in the dark for three days. After this time, TBA and isobutene were detected showing slight hydrolysis (less than 10%) of MTBE. From the results of these experiments, it may be concluded that photocatalytic degradation is the main cause of disappearance of MTBE during the photo-Fenton treatment in the pilot plant used.

Kinetics and Mineralization

The photocatalytic disappearance of MTBE (100 mg/L) in water during treatment with photo-Fenton followed apparent zero-order kinetics until 90% of degradation was attained, as shown in Fig. 1.

Degradation of MTBE was especially fast during the first 30 min. About a 60% reduction in the initial MTBE concentration was reached during the "dark" Fenton reaction, before illumination, despite the small amount of Fe^{2+} used (0.05 mM). This indicates that MTBE is highly susceptible to degradation by $^{\bullet}OH$ radicals. Removal of the initial MTBE concentration was nearly complete after only 50 min of treatment (15 min in the dark and t_{30W} of 35 min). At that point, however, measured TOC values were still high (41 mg/L) indicating the presence of a considerable amount of by-products generated during the process. In fact, the slow decay of TOC during the first 30 min (15 min in the dark and 15 min under illumination) can be attributed to coincidence with the period of major formation of by-products, and mineralization is very slow. From this point up to the end of the experiment TOC abatement was more pronounced, attaining

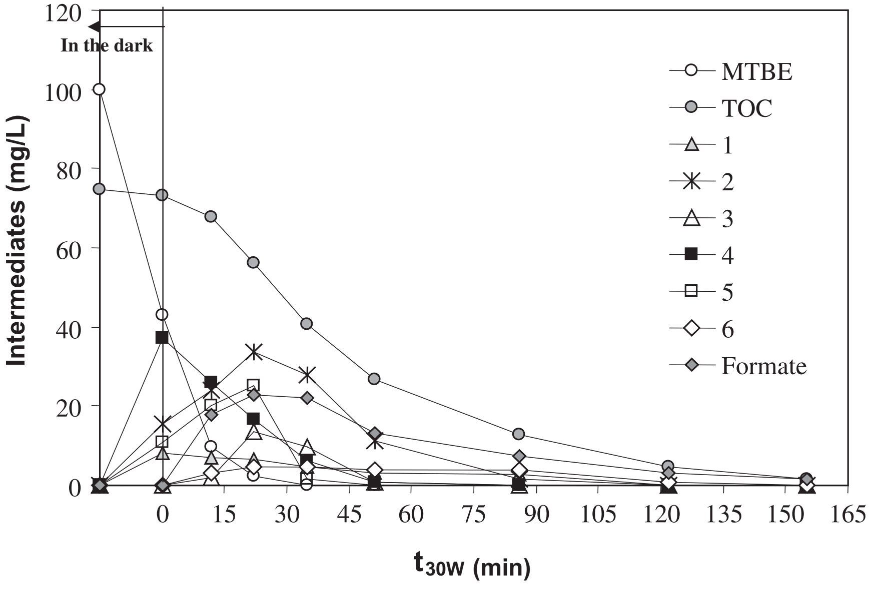

FIGURE 1 Evolution of MTBE, TOC and transformation products generated during photo-Fenton treatment of an MTBE water solution (initial concentration 100 mg/L) over time.

more than 97% of mineralization (1.6 mg/L) in approximately 155 min of treatment. The photo-Fenton rate allows photocatalytic degradation of MTBE without significant loss from volatilization under the experimental conditions and in the pilot plant used. Longer treatment times would require the design of new reactors to guarantee non-volatilization, in which case they must be airtight and/or refrigerated. Furthermore, more Fe could be added to the water to enhance the reaction rate, but with small amounts of Fe, its removal is not necessary before disposing of the water.

Identification and Quantification of TPs

For complete evaluation of the photocatalytic degradation process under pilot-scale conditions, formation of MTBE transformation products was studied using two analytical techniques, GC-MS and GC-AED, which were fine-tuned to evaluate their performance in the identification and quantification of the TPs generated. Both instruments were then connected to a P&T system with which six purgeable compounds were readily identified as primary intermediates: *tert*-butyl formate (TBF), *tert*-butyl alcohol (TBA), acetone, methyl acetate, isobutene and formaldehyde.

GC-EI-MS analysis, in *full scan* mode and under the chromatographic conditions described in the experimental section, allowed the unequivocal identification of five of the six TPs cited. Mass spectra obtained were favourably compared (match 99.9%) with a commercial database (NIST) and the retention times were further confirmed with analytical standards. Figure 2 shows the overlapping GC-MS chromatograms corresponding to the analysis of two samples taken at 1.95 and 35.5 min of treatment. The first peak in the chromatogram of Fig. 2 corresponds to CO_2 generated during the oxidation process.

Similarly, samples were also analysed by GC-AED. Previous work [29] has demonstrated the potential of this technique for the identification and quantification of unknown compounds, even when analytical standards are not available, making the MS/AED combination one of the most powerful alternatives for this kind of analysis.

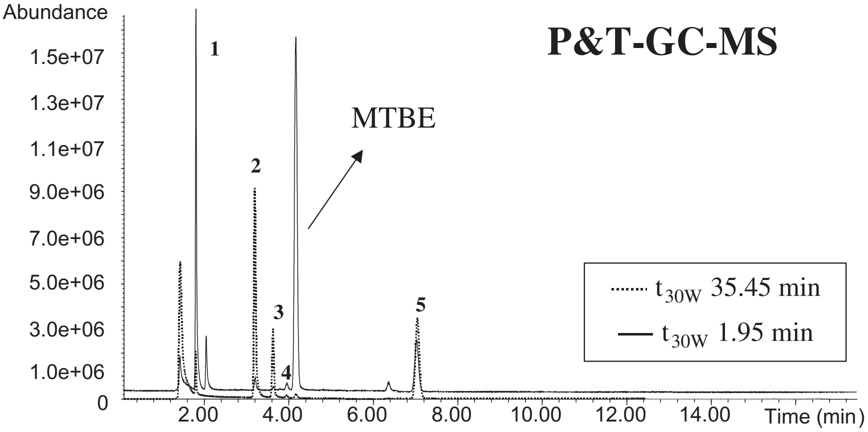

FIGURE 2 GC-MS chromatograms of two real samples taken at different illumination times during MTBE photo-Fenton treatment. Numbers correspond to the compounds shown in Fig. 4.

For element-specific detection, three wavelengths, corresponding to carbon (496 nm), hydrogen (486 nm) and oxygen (171 nm) emissions were monitored. Chromatographic conditions similar to GC-MS were used initially for compound separation. However, the analytical column had to be changed to avoid the appearance of a broad peak (from 6 to 10 min), from water vapour in the purge gas, which made the use of hydrogen and oxygen signals unfeasible. The use of a polyethylene glycol capillary column (Omegawax 250) was able to overcome this problem and, thanks to its higher polarity, allowed the detection of a new compound (Peak 6 in Fig. 3). The compound-independent element response of the atomic emission detector allowed elemental mole ratios to be measured so as to obtain the empirical formula. The compound was tentatively identified as formaldehyde and further confirmed with the injection of the analytical standard. An example of a GC-AED multi-element chromatogram showing C, H and O emission lines is given in Fig. 3 for a sample taken after 22.3 min of photocatalytic treatment.

Although the qualitative results obtained basically agree with the results of other AOP studies, differences in the concentration of each compound detected were found. Whenever the analytical standard was available (Compounds 2 to 6), quantitative determination of the by-products identified was performed by GC-MS external standard calibration, selecting one or two of the more significant fragment ions. In the case of isobutene (Compound 1), however, the analytical standard was not available. Quantification, in this case, was carried out by GC-AED, making use of one of the major advantages of this technique, the possibility of elemental calibration with surrogate standards. This feature is a result of the AED compound-independent elemental response that makes elemental responses theoretically independent of the concentration levels and the molecular structure of the compounds. The response factors for each element are constant within the linear range of the detector. Thus compound-independent calibration (CIC) using a standard mixture of two selected

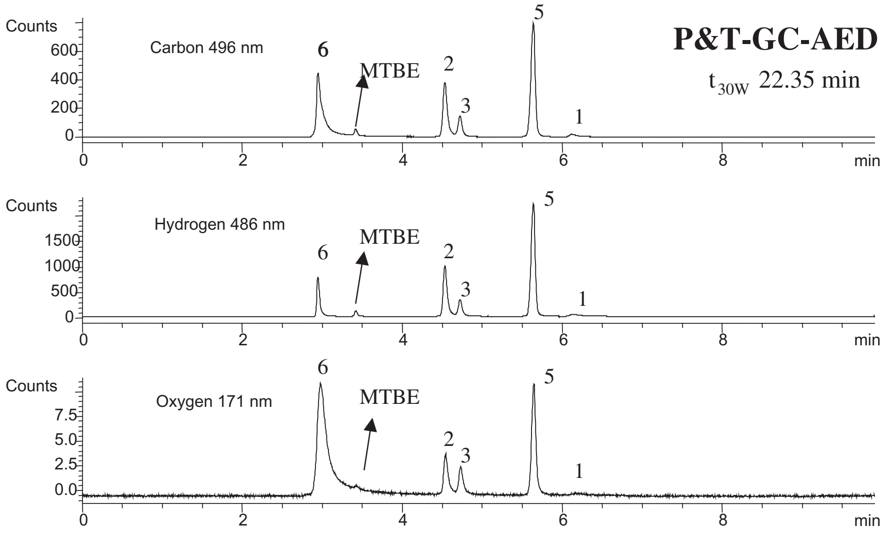

FIGURE 3 GC-AED chromatogram of a real sample after 22.35 photo-Fenton treatment. Numbers correspond to compounds shown in Fig. 4.

compounds (MTBE and TBA) at five different concentrations was used to obtain the calibration curves. The carbon-specific response of these compounds was used in the calibration plots.

The quantitative evaluation of the TPs generated during the process yielded the results shown in Fig. 1, where evolution of the intermediates over time is represented. It may be observed that TBA and acetone were the two major TPs formed by photo-Fenton reaction, differentiating it from other oxidation procedures that yield TBF as the main intermediate [14, 18, 20]. Presence of TBA is more significant in the first stage of the process, coinciding with the main formation of this compound during the "dark" Fenton reaction, before illumination. Hydroxyl radicals provided by the Fenton reactant [(Eq. (2)] and the possible contribution of hydrolysis of MTBE explains the rapid formation of this compound.

Once the photocatalytic reaction is initiated, the predominant kinetics of formation corresponds to other TPs, such as TBF and acetone. TBF formation could be a consequence of the $^{\bullet}OH$ attack on MTBE β-hydrogen. An alternative route of MTBE degradation could be the $^{\bullet}OH$ attack on the *t*-butyl group with the subsequent formation of methyl acetate, but this can be considered less kinetically favoured because of the low concentrations of methyl acetate found.

Acetone and traces of isobutene have previously been reported as intermediates of TBA photocatalysis [14,18]. Acetone is the main TP detected throughout oxidative treatment. This can be explained by its slow rate of mineralization during photo-Fenton reaction, as previously reported [31]. Therefore, acetone is the most stable intermediate under the reaction conditions, becoming a reaction bottleneck. The presence of isobutene is consistent with the mechanism reported by Barreto *et al.* [18], who explain its formation from TBA as a consequence of dehydration in strong acidic media.

Carboxylic acids and other smaller species are usual in the last stages of oxidation prior to mineralization [29]. Formation of formic acid was therefore verified by ion chromatography in the presence of the formate anion. This molecule was detected very early in the process, reaching maximal concentration values at around 22 min and coinciding with the main TP formation period. From this moment, after a period of stabilization, formate concentration then underwent slow decay, a concentration of around 1.5 ppm remaining at the end of the experiments. Acetic acid has been also described in the literature as a product of TBA oxidation by O_3 and O_3/H_2O_2 [14] but it was not detected in our assays, probably because of the design of the photoreactor, which is made up of dozens of metres of glass tubes connected in series and to a recirculation tank. Furthermore, the residence time in the illuminated zone is relatively long. So the small quantities of acetic acid produced in the illuminated zone may be converted into formic acid, which is a more $^{\bullet}OH$-resistant compound and, therefore, detectable and quantifiable in the samples. Formaldehyde was also identified as an intermediate in the degradation of acetone [31]. Overall concentrations reached during the process (around 4 ppm) remained stable during most of the experiment and it was still detectable (0.12 ppm) at the end of the experiments, contributing to the residual TOC values.

The pathway for oxidation of MTBE by photo-Fenton shown in Fig. 4 was proposed based on the literature and the quantitative and qualitative data obtained in the experiments.

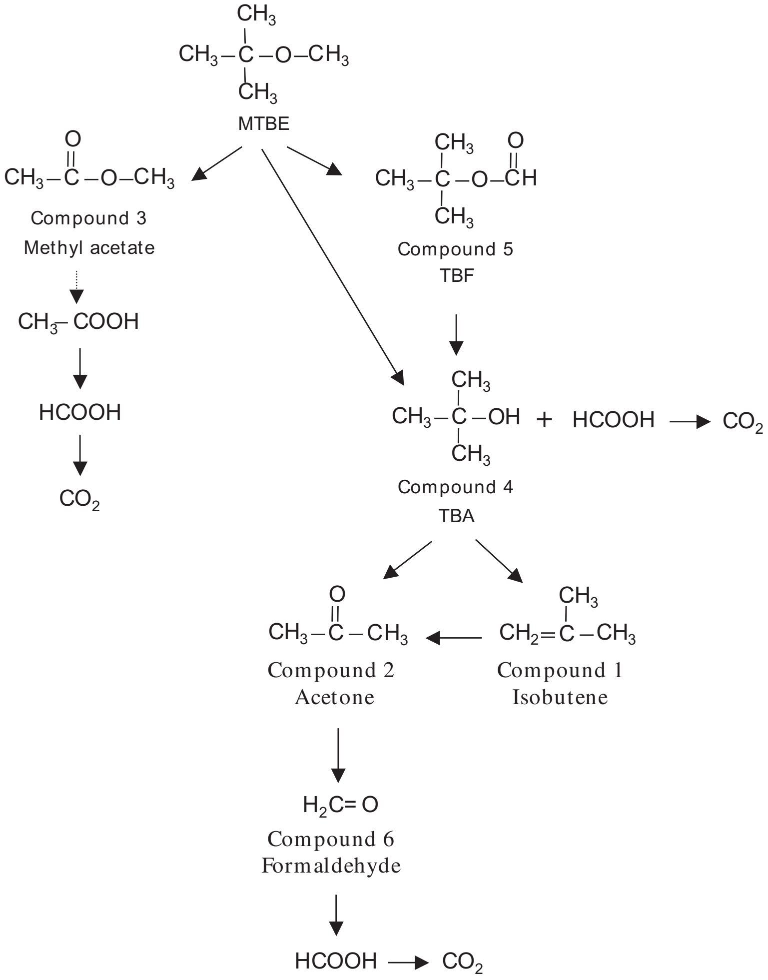

FIGURE 4 Drawing of the proposed pathway for degradation of MTBE in water during photocatalytic treatment by photo-Fenton reaction.

CONCLUSIONS

The application of solar photocatalysis by photo-Fenton to the degradation of MTBE in aqueous solutions resulted in the complete disappearance of the initial MTBE concentration (100 mg/L) after only 35 min of treatment. However, many intermediates still remained in the water at this time and almost complete mineralization was attained only after 155 min. These results demonstrate that the solar-driven photo-Fenton treatment may be considered suitable to guarantee complete detoxification of MTBE-contaminated water. A solar pilot plant operating under real conditions and using very small amounts of Fe demonstrated the feasibility of this application.

A combination of GC-MS and GC-AED analytical techniques coupled to a P&T system, represents a good option in the qualitative and quantitative evaluation of the volatile intermediates generated during the process. GC-AED analysis, after compound-independent calibration, allows the estimation of empirical formulas and the quantitative determination of compounds in absence of the analytical standard. This feasibility represents a great advantage because of the great variety of compounds, not always commercially available, generated during the degradation processes, and so GC-AED can be considered a very useful complementary technique in this kind of studies.

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