

## APPLIED CHEMISTRY

# Photocatalytic Degradation of Phenol and Trichloroethylene: On-Line and Real-Time Monitoring via Membrane Introduction Mass Spectrometry

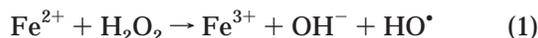
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Membrane introduction mass spectrometry (MIMS) has been applied to monitor and compare in real time the extent by which three photocatalytic remediation processes—Fenton's reagent/UV, ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV, and TiO<sub>2</sub>/UV—destroy two common water pollutants—phenol and trichloroethylene (TCE). Continuous MIMS and selected ion monitoring (MIMS–SIM) of both phenol and TCE degradation and CO<sub>2</sub> production show first-order kinetics for the three processes. Phenol half-life times indicate that Fenton's reagent/UV and ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV destroys phenol 10 times faster than TiO<sub>2</sub>/UV, that is, Fenton's reagent/UV ≈ ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV ≫ TiO<sub>2</sub>/UV. For TCE, half-life times for the three remediation processes are ordered as follows: ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV ≫ Fenton's reagent/UV > TiO<sub>2</sub>/UV. For phenol, the extent of mineralization measured via total organic carbon analysis was lower than the extent of degradation measured by MIMS–SIM; hence, for the three processes, the intermediate products of phenol photocatalytic degradation are slowly destroyed. For Fenton's reagent/UV and ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV, GC/MS analysis detected pyrocatechol as the main intermediate of phenol degradation and *p*-benzoquinone for TiO<sub>2</sub>/UV.

## Introduction

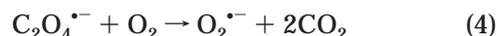
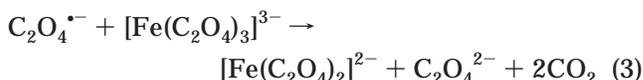
Increased industrial activity has created an undesirable byproduct—chemical pollution. Hence, to efficiently destroy the increasing number and amounts of chemical pollutants in air, water, and soil, many remediation processes have been developed. Photocatalytic processes<sup>1–16</sup> are among the most powerful able to mineralize a large variety of pollutants, including recalcitrant chemicals. The TiO<sub>2</sub>/UV photocatalytic process, for instance, mineralizes efficiently many common organic contaminants such as phenols, organochlorides, alcohols, surfactants, and dyes.<sup>1–5</sup> The long known Fenton's reagent,<sup>6</sup> owing to its broad oxidizing power, is also used extensively.<sup>7–10</sup> In the Fe(II)/H<sub>2</sub>O<sub>2</sub> acidic media, oxidation occurs via hydroxyl radicals (eq 1). When combined



with UV–vis irradiation, the degradation efficiency of the photo-Fenton's reagent is considerably enhanced<sup>10–13</sup> as the result of continuous photoreduction of Fe(III) to Fe(II).

A novel photocatalytic remediation process using an organic complex of Fe(III)—the ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV process—has been recently developed.<sup>14,15</sup> Complexes of Fe(III) show normally high absorption bands in the UV–vis region, and potassium ferrioxalate, i.e., K<sub>3</sub>[Fe-

(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>], has been used extensively as a chemical actinometer for light-intensity measurement.<sup>16</sup> In the ferrioxalate process, Fe(III) is reduced to Fe(II) by the reaction sequence summarized in eqs 2–4; Fe(II) as [Fe-



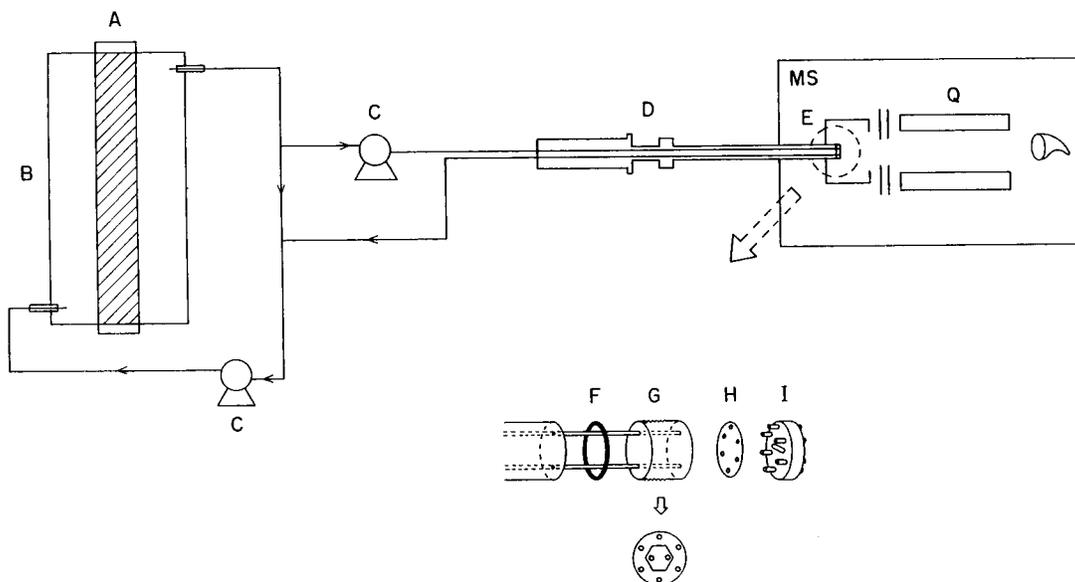
(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> generates OH<sup>•</sup> on reaction with H<sub>2</sub>O<sub>2</sub> (eq 1).

To evaluate and compare the many remediation processes for chemical pollutants, efficient analytical techniques are needed. Ideally, these techniques should be fast and of high sensitivity, thus allowing on-line and real-time monitoring. Membrane introduction mass spectrometry (MIMS) has emerged as a simple, fast, and very sensitive method for the real-time, on-line monitoring of volatile and semivolatile organic compounds (VOCs) in water and wet soil.<sup>17–19</sup> MIMS, which is currently under extensive evaluation, has been shown to be very promising for monitoring many industrial and environmental processes.<sup>20–25</sup> In MIMS, enrichment of aqueous VOC samples occurs owing to preferential migration of VOCs through a semipermeable membrane—usually of silicone polymer—that also acts as the interface between the aqueous solution and the high vacuum of the mass spectrometer. Relatively nonpolar and low molecular weight compounds permeate efficiently the hydrophobic membrane; hence, they are detected by

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**Figure 1.** Photoreactor/MIMS system composed of (A) UV lamp, (B) photoreactor, (C) peristaltic pumps, (D) MIMS probe, (E) ion source, (F) O-ring, (G) source front block, (H) silicone membrane, and (I) membrane holder.

MIMS without extraction or preconcentration steps at very low detection limits—low ppb and ppt. Also with MIMS, real-time and simultaneous multicomponent analysis of VOCs is performed.

In this work, MIMS is used to compare the extent by which three photocatalytic processes—TiO<sub>2</sub>/UV, Fenton's reagent/UV, and ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV—destroy two common water pollutants—phenol and trichloroethylene (TCE). With MIMS, the destruction of the organic compound and the production of the final mineralization product—CO<sub>2</sub>—have been monitored on-line and in real time.

## Materials and Methods

**Materials.** Potassium ferrioxalate was obtained by reacting 6 mL of potassium oxalate solution (1.5 mol L<sup>-1</sup>) with 2 mL of Fe(NO<sub>3</sub>)<sub>2</sub> solution (1.5 mol L<sup>-1</sup>) under vigorous stirring. After recrystallizing the crude potassium ferrioxalate several times in water, a 0.25 mol L<sup>-1</sup> aqueous stock solution was prepared and used in the ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV experiments. Titanium dioxide powder was obtained from Degussa (P-25) with a particle diameter of 30 nm, a crystal structure of primarily anatase, and a surface area of 50 ± 15 m<sup>2</sup> g<sup>-1</sup>. The TiO<sub>2</sub> catalyst was used in the immobilized form, that is, supported on the inner surface of a glass cylinder.<sup>26</sup> Hydrogen peroxide, 30% (Riedel de Haen, p.a.), was used as received. A 1 g L<sup>-1</sup> stock solution of Fe(II) in 0.2 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> was used for the Fenton's reagent/UV process. Deionized water solutions of phenol (2.0 mmol L<sup>-1</sup>) and TCE (0.4 mmol L<sup>-1</sup>) were used in the photodegradation experiments.

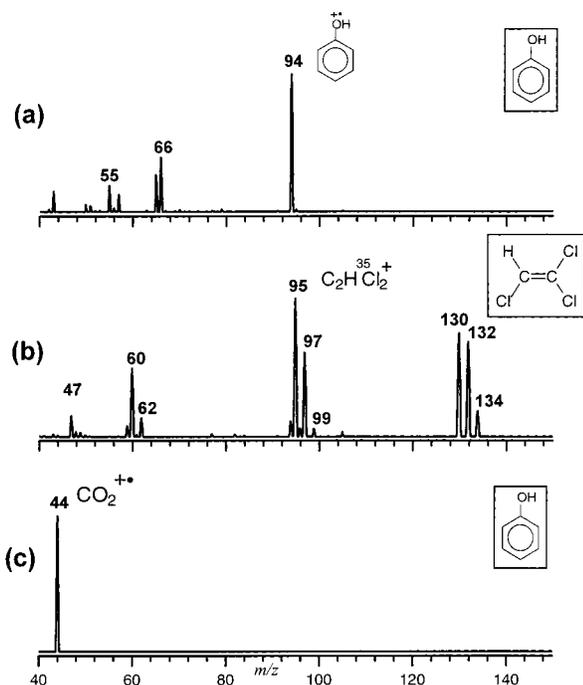
**Chemical Analysis.** Monitoring was performed using a MIMS system (Figure 1) composed mainly of a peristaltic pump (Ismatec, flow rate of 40 mL min<sup>-1</sup>) with Tygon tubes and a MIMS probe using a 0.010-in. Silastic silicone membrane (from Dow Corning Co.) directly connected to a Extrel pentaquadrupole (QqQqQ) mass spectrometer.<sup>27</sup> Aqueous solutions, sampled from the photoreactor (Figure 1), were directly pumped through the silicone MIMS probe. No extraction or preconcentration steps were required for MIMS analysis.

Both the destruction of phenol and TCE and CO<sub>2</sub> formation were monitored as a function of time via multiple selected ion monitoring (SIM) controlled by a PC-based data system.<sup>28</sup> Molecules were ionized using 70-eV electron ionization (EI).

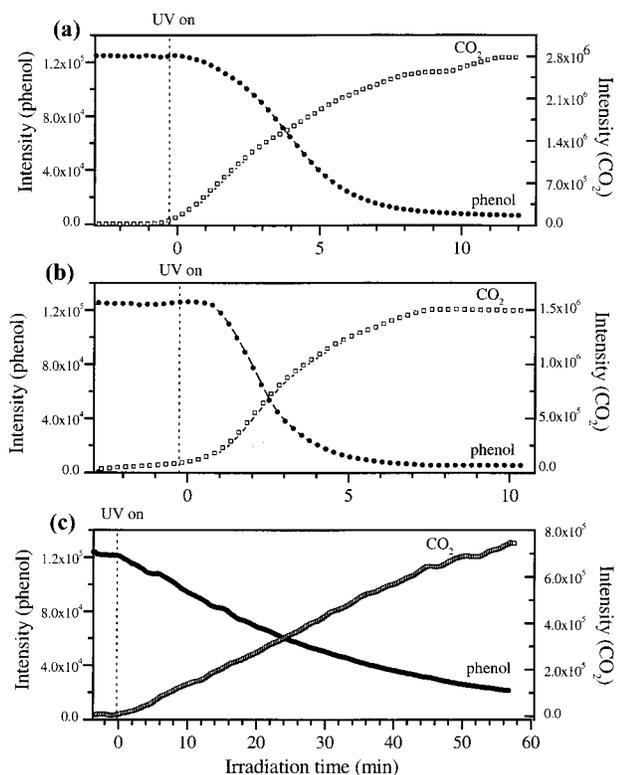
The mineralization of the compounds was also evaluated by total organic carbon (TOC) analysis performed on a total carbon analyzer (Shimadzu TOC 5000). Samples (10 mL) were taken at 5-min intervals and analyzed immediately. The intermediates in the phenol degradation were detected by gas chromatography/mass spectrometry (GC/MS) after sampling 10 mL of the photoirradiated solution and extracting the organic material with three portions of dichloromethane (3 mL). GC/MS analysis was performed on a Hewlett-Packard 5890 Series II equipment with a fused silica capillary column, Ultra-2 (HP) (25 m × 0.2 mm × 0.33 μm). The oven temperature was initially kept at 35 °C for 2 min and then heated at a rate of 20 °C/min up to 280 °C; the injector and detector were kept at 250 °C.

**Photoreactor.** The upflow photoreactor (Figure 1) uses a glass cylinder of 3.8-cm i.d. and 42-cm height. For the TiO<sub>2</sub>/UV process, the TiO<sub>2</sub> catalyst was supported on the inner wall of the glass cylinder. Sample solutions were recirculated through the photoreactor using a peristaltic pump (Flex-Flo, model A-1845V-7N).

Photoactivation was provided by a commercially available 15-W UV-visible lamp (Sankyo Denki Japan BLB), which also serves as the inner surface of the annulus. Light intensities measured using a Cole Parmer radiometer for 254- and 365-nm wavelengths were 0 and 22.1 W m<sup>-2</sup>, respectively. For the Fenton's reagent/UV and ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV experiments, the pH of the phenol and TCE solutions was adjusted to 2.5 with sulfuric acid, and Fe(III) solution was added to a final Fe(III) concentration of 0.4 mmol L<sup>-1</sup>. After the solution was stirred for a few minutes, hydrogen peroxide was added to a final concentration of 10 mmol L<sup>-1</sup>, and the fresh solution was immediately pumped into the reactor. The TiO<sub>2</sub>/UV experiments were performed with phenol and TCE aqueous solutions with no pH adjustments.<sup>1-5</sup>



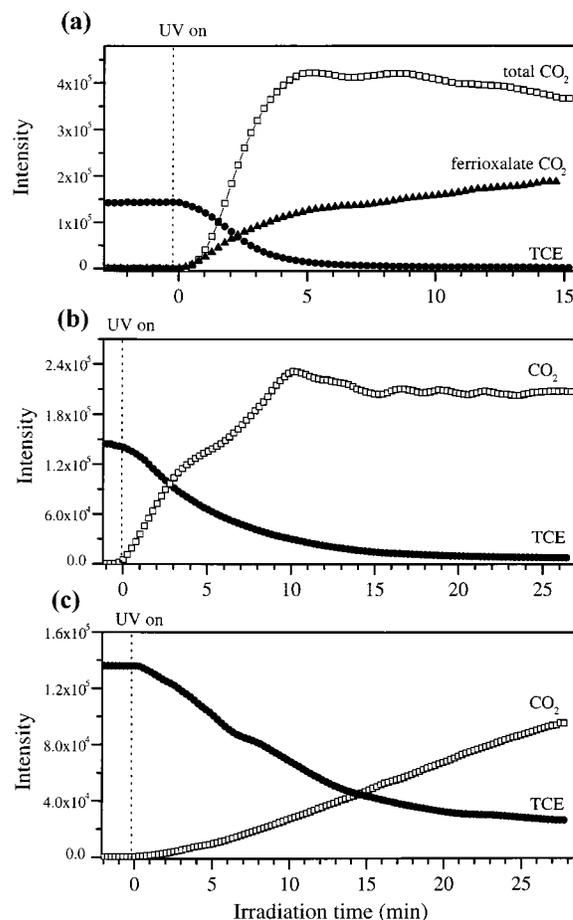
**Figure 2.** MIMS 70-eV EI spectra of phenol (a) and trichloroethylene (b) plus Fenton's reagent solutions before TiO<sub>2</sub>/UV remediation. (c) MIMS 70-eV EI spectra of phenol solution after 30 min of Fenton's reagent/UV remediation.



**Figure 3.** MIMS-SIM on-line monitoring of phenol photocatalytic degradation by (a) ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV, (b) Fenton's reagent/UV, and (c) TiO<sub>2</sub>/UV.

## Results and Discussion

**Full MIMS Analysis.** Figure 2 shows typical MIMS spectra before irradiation for the phenol (Figure 2a) and TCE (Figure 2b) plus Fenton's reagent solutions and for the phenol/Fenton's reagent solution after 30 min of UV irradiation (Figure 2c). The most abundant peak in



**Figure 4.** MIMS-SIM on-line monitoring of TCE photocatalytic degradation by (a) ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV, (b) Fenton's reagent/UV, and (c) TiO<sub>2</sub>/UV. MIMS monitoring of photocatalytic degradation processes.

Figure 2a is the phenol molecular ion ( $m/z$  94). In Figure 2b, the TCE molecular ion of  $m/z$  130 (C<sub>2</sub>H<sup>35</sup>Cl<sub>3</sub><sup>+</sup>) and its two isotopomers of  $m/z$  132 (C<sub>2</sub>H<sup>35</sup>Cl<sub>2</sub><sup>37</sup>Cl<sup>+</sup>) and 134 (C<sub>2</sub>H<sup>35</sup>Cl<sup>37</sup>Cl<sub>2</sub><sup>+</sup>) are quite abundant, but the TCE fragment ion (C<sub>2</sub>H<sup>35</sup>Cl<sub>2</sub><sup>+</sup>) of  $m/z$  95 is the base peak. After the phenol/Fenton's reagent solution was irradiated for 30 min or more, only an ion of  $m/z$  44 is observed (Figure 2c), which indicates that phenol has been totally destroyed and (at least partially) mineralized to CO<sub>2</sub>.

**On-Line Monitoring by MIMS-SIM.** MIMS and multiple selected ion monitoring (SIM) was then applied to monitor on-line and simultaneously both the destruction of the target compounds and the extent of mineralization via formation of CO<sub>2</sub>. For phenol, its molecular ion of  $m/z$  94 was selected for monitoring; for TCE, its most abundant fragment ion of  $m/z$  95; and for CO<sub>2</sub>, its molecular ion of  $m/z$  44.

Figure 3 (for phenol) and Figure 4 (for TCE) compare the degradation power of the three processes via MIMS-SIM monitoring. Phenol is nearly completely destroyed after 8 min of ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV treatment (Figure 3a) and after 6 min of Fenton's reagent/UV treatment (Figure 3b). More CO<sub>2</sub> is produced as phenol is destroyed, and the CO<sub>2</sub> production ends a few minutes after phenol has been totally removed. For TiO<sub>2</sub>/UV (Figure 3c), however, phenol is destroyed considerably more slowly: after 10 min of irradiation, for instance, phenol has been totally destroyed by ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV and Fenton's reagent/UV but only to a 32% extent by TiO<sub>2</sub>/UV.

**Table 1. Performance of Photocatalytic Degradation Processes for Phenol and TCE in Aqueous Solutions after 15 min of UV Irradiation**

process	phenol			TCE		
	$t_{1/2}$ , min	extent of		$t_{1/2}$ , min	extent of	
		degradation, <sup>a</sup> %	mineralization, <sup>b</sup> %		degradation, <sup>a</sup> %	mineralization, <sup>b</sup> %
ferrioxalate/H <sub>2</sub> O <sub>2</sub> /UV	2.0	95.6	14.0	1.4	97.7	92.0
Fenton's reagent/UV	1.2	96.5	13.0	7.3	89.8	66.0
TiO <sub>2</sub> /UV	21.5	32.2	22.0	12.5	68.8	42.0

<sup>a</sup> Extent of degradation was monitored by MIMS–SIM. <sup>b</sup> Extents of mineralization was calculated from TOC analysis.

The extent of TCE degradation for the three processes also varies considerably (Figure 4). After 7 min of irradiation, TCE is totally destroyed by ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV, but only partial TCE degradation occurs for both Fenton's reagent/UV (near 65%) and TiO<sub>2</sub>/UV (near 40%). The contrasting extents of degradation of the three photocatalytic processes are also clearly noted when measuring the half-life times ( $t_{1/2}$  in Table 1). Note also that in TCE degradation by TiO<sub>2</sub>/UV (Figure 4c), production of CO<sub>2</sub> displays a considerably longer induction period, which indicates that intermediate products are more slowly destroyed.

When monitoring the extent of degradation for the ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV process, it must be considered that CO<sub>2</sub> is also co-generated by photolysis of ferrioxalate (eqs 2–4). Hence, a blank experiment was performed, and the extra CO<sub>2</sub> curve (▲) in Figure 4a shows the CO<sub>2</sub> monitored in such an experiment, that is, by photolysis of ferrioxalate.

**Extent of Photodegradation.** For the three processes and for the two chemicals—phenol and TCE—log *C* vs time plots (not shown) show linear correlations, thus indicating first-order kinetics. From these plots, the half-life times of the chemical contaminants were then calculated; they are summarized in Table 1. To facilitate comparison, Table 1 also lists the degradation and mineralization extents after 15 min of irradiation. Note that the extent of degradation was calculated from MIMS–SIM data on the removal of the chemical contaminant, but the extents of mineralization were measured from total organic carbon analysis in which both target compounds and intermediate degradation products are detected.

For both ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV and Fenton's reagent/UV, phenol is destroyed to a great extent (>95%) after 15 min of irradiation, but the extent of mineralization is lower, barely reaching 15% (Table 1). TiO<sub>2</sub>/UV displays, after 15 min of irradiation, the lowest extent of degradation (32%) but the highest extent of phenol mineralization (22%). For TCE, the extent of mineralization for the three processes was much higher, particularly for ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV and Fenton's reagent/UV.

The extent of degradation, i.e., the oxidation power of Fenton's reagent/UV and ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV, in both cases results from the action of the HO• radical, which is formed by the reaction of Fe(II) with H<sub>2</sub>O<sub>2</sub>. For the ferrioxalate system, this reaction occurs after photolysis of the iron complex by photons up to 450 nm. Under the present experimental conditions, the greater extent by which ferrioxalate/H<sub>2</sub>O<sub>2</sub>/UV destroys TCE can be attributed to a more efficient use of the UV light, since ferrioxalate absorbs strongly up to 450 nm with high quantum yield.<sup>14,16</sup> Although the maximum emission of the UV lamp corresponds to the band-edge of TiO<sub>2</sub>, the TiO<sub>2</sub>/UV process was the least effective. TiO<sub>2</sub>/

**Table 2. Intermediates of Photocatalytic Degradation of Phenol Detected by GC/MS Analysis**

intermediate	$t_r$ , <sup>a</sup> min	major peak, <i>m/z</i>	rel abund, %		
			Fenton's reagent/UV	ferrioxalate/H <sub>2</sub> O <sub>2</sub> /UV	TiO <sub>2</sub> /UV
benzoquinone	5.0	108	13.0	11.7	100
pyrocatechol	7.2	110	100	100	none
hydroquinone	7.8	110	36.7	none	29.6

<sup>a</sup> Retention time in the chromatography run.

UV is a heterogeneous process, and the catalyst is used in the immobilized form; hence, mass transfer is limited, and this can reduce its degradation power.

**GC/MS Analysis.** Owing to their high polarity, intermediates that are known to be generated in the oxidation of phenol—benzoquinone, pyrocatechol, and hydroquinone<sup>28,29</sup>—could not be efficiently monitored by MIMS. These intermediates were detected, instead, by liquid–liquid extraction and GC/MS analysis, and the results are summarized in Table 2. These products result from the first oxidation step in which HO• adds to the aromatic ring, forming pyrocatechol and hydroquinone; these two compounds are then further oxidized to benzoquinones and finally mineralized to CO<sub>2</sub>.<sup>29,30</sup>

## Conclusions

On-line and real-time monitoring of photocatalytic degradation processes of volatile organic pollutants in water can be effectively performed by applying the MIMS–SIM technique. Both the extent of degradation of the organic contaminant and the extent of mineralization (via formation of CO<sub>2</sub>) can be simultaneously monitored by MIMS–SIM. Relative extents of degradation and mineralization and kinetic information such as half-life times are therefore easily obtained, thus allowing the degradation power of different remediation processes to be appropriately compared.

## Acknowledgment

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