

Investigation of reaction mechanisms by electrospray ionization mass spectrometry: characterization of intermediates in the degradation of phenol by a novel iron/magnetite/hydrogen peroxide heterogeneous oxidation system

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Electrospray ionization (ESI) mass spectrometry (MS) and tandem mass spectrometry (MS/MS) were used to monitor the oxidation of phenol by a novel heterogeneous Fenton system based on a Fe⁰/Fe₃O₄ composite and H₂O₂. On-line ESI-MS(/MS) shows that this heterogeneous system promotes prompt oxidation of phenol to hydroquinone, which is subsequently oxidized to quinone, other cyclic poly-hydroxylated intermediates and an acyclic carboxylic acid. A peroxide-type intermediate, probably formed via an electrophilic attack of HOO· on the phenol ring, was also intercepted and characterized. ESI-MS(/MS) monitoring of the oxidation of two other model aromatic compounds, benzene and chlorobenzene, indicates the participation of analogous intermediates. These results suggest that oxidation by the heterogeneous system is promoted by highly reactive HO· and HOO· radicals generated from H₂O₂ on the surface of the Fe⁰/Fe₃O₄ composite via a classical Fenton-like mechanism. Copyright © 2006 John Wiley & Sons, Ltd.

The Fenton reaction¹ is one of the most efficient advanced oxidation process² for the destruction of organic contaminants in wastewaters. The classical Fenton system³ uses a mixture of H₂O₂ and a soluble Fe(II) salt to generate *in situ* free hydroxyl radicals (HO·) according to the Haber-Weiss mechanism (Eqn. (1)).⁴ The reaction of the strong oxidizing HO· mineralizes the organic compounds, thus yielding CO₂ and H₂O as the final harmless products.



Recent efforts^{5–9} have been made to replace the soluble Fe(II) salt by solid iron compounds in heterogeneous Fenton-like systems. Heterogeneous processes are attractive since they can operate in a fixed-bed reactor, in a near neutral pH, with no sludge and the iron promoter can be recycled. However, most of the iron promoters so far investigated, such as goethite, hematite and ferrihydrite,^{5–9} displayed insufficient activity.

We recently showed that magnetite-based systems, i.e. Fe_{3–x}M_xO₄ (M = Mn or Co)^{10,11} and Fe⁰/Fe₃O₄,^{12,13} are

highly active in promoting Fenton chemistry. Although many heterogeneous Fenton systems have been investigated,^{14–16} information is scarce on the operating mechanisms, particularly on whether free radicals are indeed the key oxidative species and how many organic intermediates are involved.

We have used a variety of mass spectrometric techniques to reveal the mechanistic details of major water remediation processes.^{17–23} Electrospray ionization mass spectrometry (ESI-MS) has become the central technique as it often allows real-time detection and ESI-tandem mass spectrometric (MS/MS) characterization of reactants, intermediates and final products.²⁴ Major water-treatment processes have been investigated via ESI-MS techniques and even transient reaction intermediates and catalyst complexes have been intercepted and characterized.^{25–32}

This work aims to apply direct-infusion ESI-MS(/MS) to monitor the oxidation of phenol, a model aromatic compound (as well as benzene and chlorobenzene), in aqueous solution promoted by a novel heterogeneous Fenton system based on a Fe⁰/Fe₃O₄ composite and H₂O₂.

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EXPERIMENTAL

Magnetite was prepared by co-precipitation of its precursor ferric hydroxyacetate from an aqueous solution of FeCl_3 (1.65 mol L^{-1} , 85 mL), NH_4OH (28%, 100 mL) and $\text{CH}_3\text{COONH}_4$ (20%, 500 mL), followed by a thermal treatment at 430°C in N_2 for 2 h. After preparation, the magnetite was kept under an atmosphere of N_2 to avoid long-term oxidation by air.³³ Mechanically alloyed mixtures were prepared from $\alpha\text{-Fe}$ and Fe_3O_4 that were manually ground for 1 min. A detailed characterization of the mechanically alloyed mixtures by Mössbauer spectroscopy, powder X-ray diffraction, magnetization measurements, SEM (scanning electron microscopy) and TEM (transmission electron microscopy) has been presented elsewhere.^{12,13}

The chemicals were obtained from Sigma-Aldrich (Milwaukee, WI, USA) or Merck (Whitehouse Station, NJ, USA) and used without further purification. In a typical run, 0.1 mL of 30% H_2O_2 and 30 mg of the $\text{Fe}^0/\text{Fe}_3\text{O}_4$ composite were added to the aqueous solutions (prepared with Millipore MilliQ water) of the organic compounds (3.5 mL at 0.05 g L^{-1}) under stirring and at a temperature of $25 \pm 1^\circ\text{C}$. All reactions were carried out in the pH range of 5.8–6.0.

ESI-MS(/MS) experiments in the positive ion mode were performed using a 2000 QTrap MDS mass spectrometer from Applied Biosystems (Foster City, CA, USA). The major conditions were as follows: scan range, m/z 50–500; heater temperature, 375°C ; flow of the nitrogen carrier gas, 70 L min^{-1} ; sheath gas (60 L min^{-1}) and curtain gas (30 L min^{-1}); nebulizer potential, 3000 V; declustering potential, 30 V; and entrance potential, 9 V. The reaction samples were analyzed by direct infusion of aliquots into the ESI source via a syringe pump at a flow rate of $5 \mu\text{L min}^{-1}$.

ESI-MS(/MS) experiments in the negative ion mode were performed using a commercial LCQ Advantage ion trap mass spectrometer (ThermoElectron, San Jose, CA, USA). The spectra were obtained as an average of 50 scans, each requiring 0.2 s. Typical ESI conditions were as follows: heated capillary temperature, 150°C ; sheath gas (N_2) flow rate, 20 units (ca. 0.50 L min^{-1}); spray voltage, 4.5 kV; capillary voltage, 25 V; tube lens off-set voltage, 25 V. For ESI-MS(/MS), the precursor ion of interest was first isolated by applying an appropriate waveform across the end cap electrodes of the ion trap to resonantly eject all trapped ions except those ions of the m/z ratio of interest. The isolated ions were then subjected to a supplementary ac signal to resonantly excite them and so cause collision-induced dissociation (CID). The collision energy was set to a value at which product ions were produced in measurable abundance. The isolation width used for ESI-MS(/MS) was 2 Th.

RESULTS AND DISCUSSION

Figure 1 displays representative ESI(–)-MS spectra acquired for the $\text{Fe}^0/\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ oxidation of phenol (1). At the beginning (zero reaction time, Fig. 1(a)), phenol is detected solely as $[1 - \text{H}]^-$ of m/z 93. After longer reaction times [20 min (Fig. 1(b)) and 80 min (Fig. 1(c))], however, other anions are clearly detected and assigned as $[2 - \text{H}]^-$ of m/z

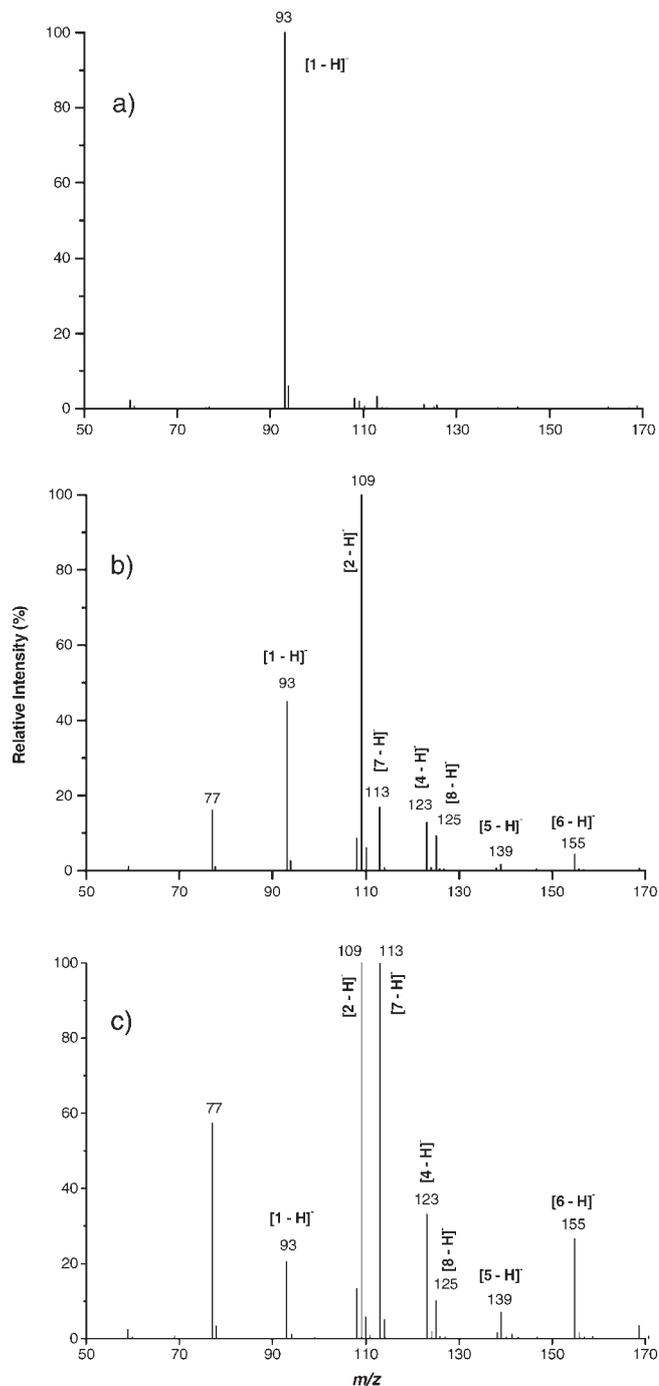
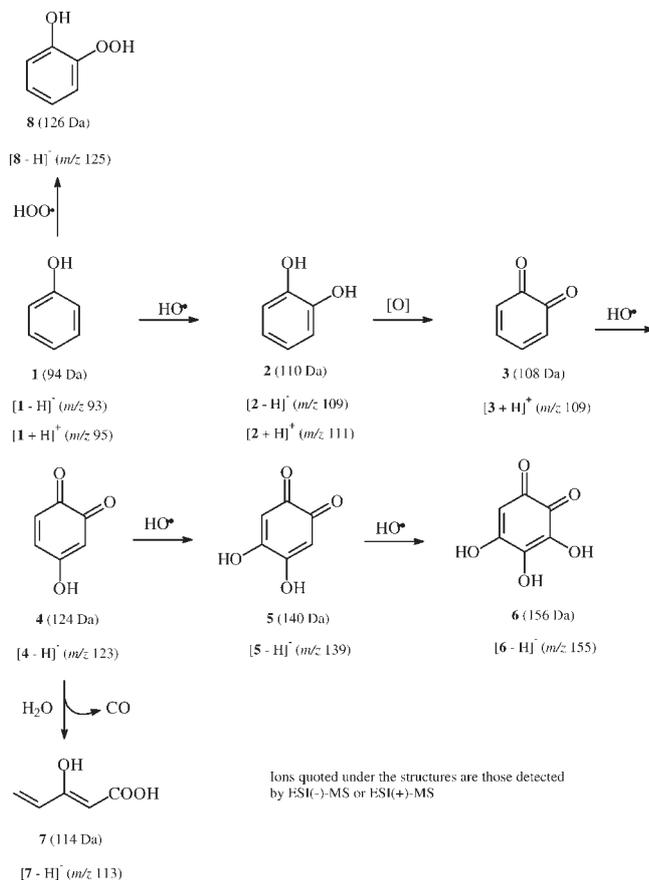


Figure 1. ESI(–)-MS monitoring of the oxidation of phenol in water by the $\text{Fe}^0/\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ heterogeneous system at different reaction times: (a) 0 min; (b) 20 min; and (c) 80 min.

109, $[4 - \text{H}]^-$ of m/z 123, $[5 - \text{H}]^-$ of m/z 139, $[6 - \text{H}]^-$ of m/z 155, $[7 - \text{H}]^-$ of m/z 113, and $[8 - \text{H}]^-$ of m/z 125.

Based on the ESI-MS data, we propose a reaction sequence for the oxidation of phenol by the $\text{Fe}^0/\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ system (Scheme 1). First, an initial hydroxyl radical attack, probably at the activated positions (*ortho* and *para*) of the phenol ring, yields the hydroquinone 2. Subsequent oxidation of 2 generates the quinone 3, which undergoes successive hydroylations to yield 4, 5, and 6. Finally, the acyclic carboxylic acid 7 is formed from the cyclic intermediate 4 via



Scheme 1.

nucleophilic attack of a water molecule on the carbonyl carbon of 4, followed by ring opening and CO release.

To test the putative structural assignments for intermediates 2–8, ESI(-)-MS/MS spectra were acquired. Figure 2 displays the ESI(-)-MS/MS spectra for [7 - H]⁻, which is shown to dissociate nearly exclusively by the loss of CO₂ (44 Da). This loss supports the structural assignment of 7 as a carboxylic acid. For the [2 - H]⁻, [4 - H]⁻, [5 - H]⁻ and [6 - H]⁻ anions, dissociation occurs mainly by the loss of CO and/or H₂O (spectra not shown). These losses are also in agreement with their postulated structures (Scheme 1)

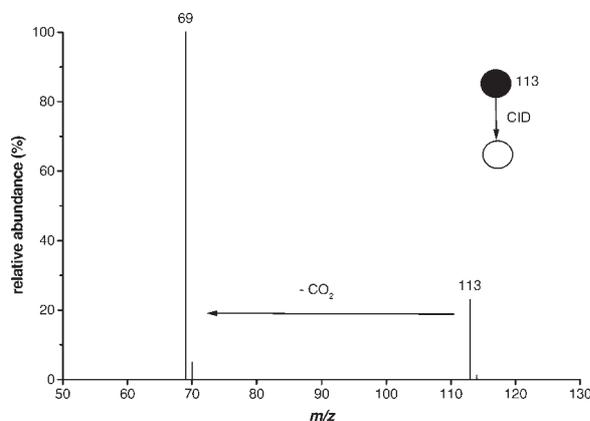


Figure 2. ESI(-)-MS/MS spectrum of the anion of *m/z* 113 attributed to [7 - H]⁻ and intercepted during the Fe⁰/Fe₃O₄/H₂O₂ oxidation of phenol in water.

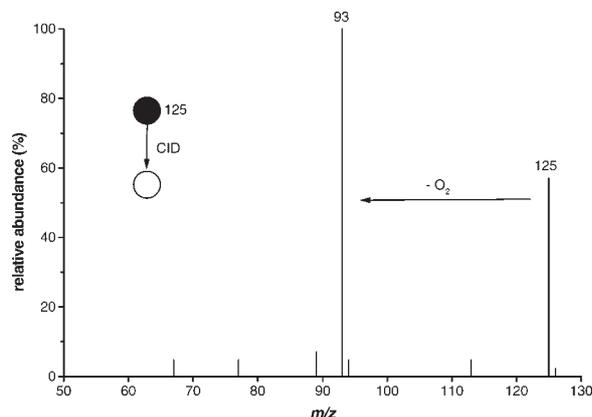


Figure 3. ESI(-)-MS/MS spectrum of the anion of *m/z* 125 attributed to [8 - H]⁻ and intercepted during the Fe⁰/Fe₃O₄/H₂O₂ oxidation of phenol in water.

Dissociation of the [8 - H]⁻ anion of *m/z* 125 is also in line with the proposed peroxide-type intermediate 8 as it occurs almost exclusively by O₂ loss to form the product ion of *m/z* 93 (Fig. 3). This intermediate could be formed via an electrophilic attack of the highly reactive HOO• on phenol, probably on the activated *ortho* and *para* ring positions (Scheme 1).

We also monitored the Fe⁰/Fe₃O₄/H₂O₂ oxidation of phenol by ESI(+)-MS. Figure 4 shows a representative ESI(+)-MS spectrum acquired after a reaction time of 5 min. Note that the same set of cations was detected by ESI(+)-MS during 60 min of reaction with only small variations in their relative abundances. Three ions are clearly detected, namely, [1 + H]⁺ of *m/z* 95, [2 + H]⁺ of *m/z* 111 and [3 + H]⁺ of *m/z* 109 (Scheme 1). Benzoquinone 3 contains carbonyl groups and no acidic hydrogens, and these characteristics are therefore in line with its detection by ESI(+)-MS of 3 as [3 + H]⁺ (protonation at the CO group), whereas ESI(-)-MS (Fig. 1) fails to detect the [3 - H]⁻ anion of *m/z* 107.

Figure 5 shows the ESI(+)-MS/MS spectra of the putative [2 + H]⁺ ion of *m/z* 111 and the [3 + H]⁺ ion of *m/z* 109. [3 + H]⁺ dissociates mainly by CO loss and [2 + H]⁺ by consecutive losses of H₂O (18 Da) and CO (28 Da). These

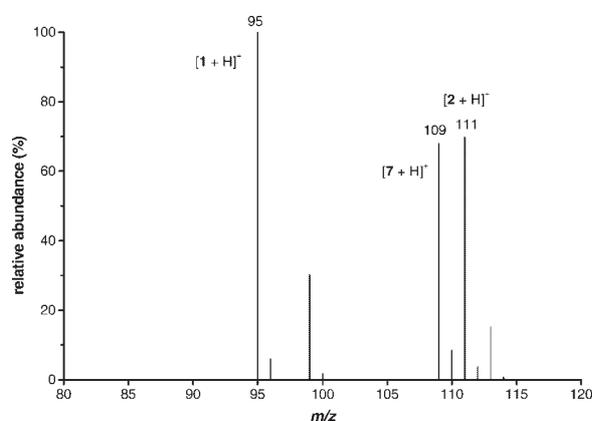


Figure 4. ESI(+)-MS monitoring of the oxidation of phenol in water by the Fe⁰/Fe₃O₄/H₂O₂ heterogeneous system after 5 min reaction time.

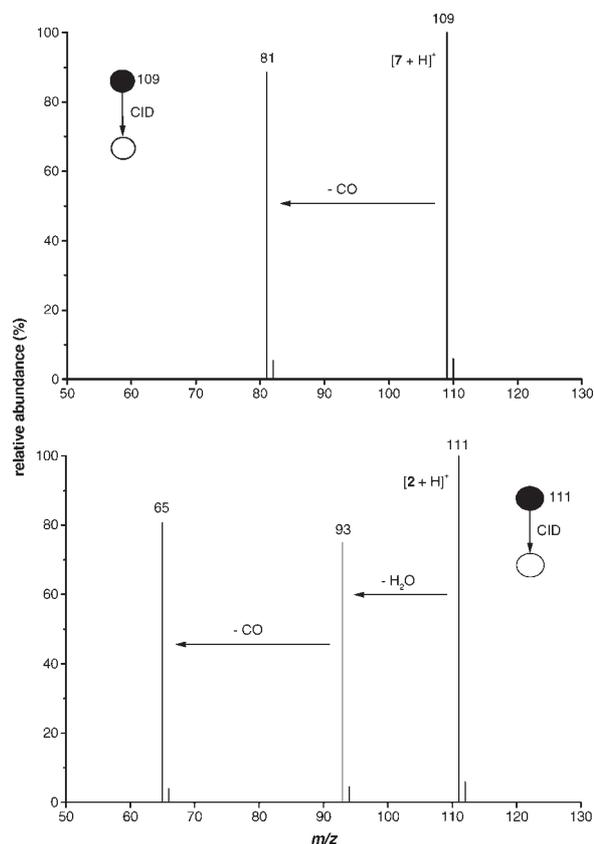


Figure 5. ESI(+)-MS/MS spectra of (a) $[7 + H]^+$ of m/z 109 and (b) $[2 + H]^+$ of m/z 111 intercepted during the $Fe^0/Fe_3O_4/H_2O_2$ oxidation of phenol in water.

losses are consistent with their postulated hydroquinone and benzoquinone structures, respectively.

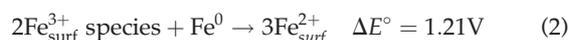
ESI-MS(/MS) monitoring of the oxidation of two other model aromatic compounds, benzene and chlorobenzene (not discussed in detail herein), indicates the participation of analogous intermediates.

DISCUSSION

Although we have shown^{8–11} that heterogeneous Fenton systems based on Fe_3O_4 , i.e. Fe^0/Fe_3O_4 and $Fe_{3-x}M_xO_4$ ($M = Fe, Mn$ and Co), are highly active, no direct evidence on their degradation mechanism has been reported. The present results offer therefore the first insights into the $Fe^0/Fe_3O_4/$

H_2O_2 oxidation mechanism, and the ESI-MS(/MS) interception and characterization of several hydroxylated intermediates confirm the participation of hydroxyl radicals. Previously, using membrane introduction mass spectrometry,¹⁷ we showed that analogous hydroxylated intermediates are involved in the oxidation of simple aromatic compounds by the classical Fenton system, which is well known to be promoted by HO^\cdot . Isotopic labelling experiments with ^{14}C -formic acid also suggested the participation of HO^\cdot for a system based on $FeOOH$.^{14,15} In addition, the probable detection of the peroxide-type intermediate **8** (Scheme 1) suggests that hydroperoxide radicals (HOO^\cdot) are also formed under such reaction conditions.

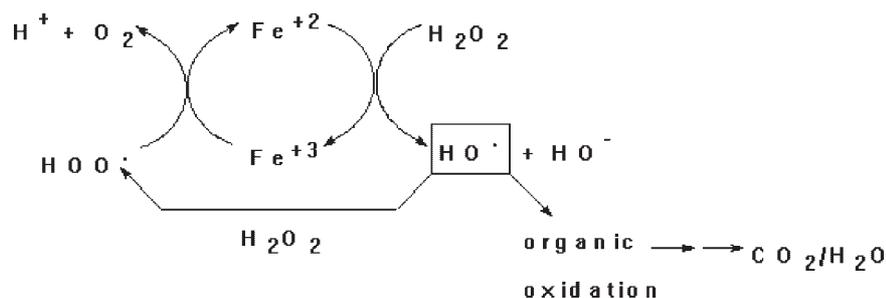
In the heterogeneous system, HO^\cdot are probably formed from reduced iron species on the solid surface, e.g. Fe_{surf}^{2+} , in a Fenton-like mechanism (Eqn. (2)). The strong effect of Fe^0 in the Fe^0/Fe_3O_4 mixtures can be attributed to the surface reaction of Fe^0 and the iron oxide during mechanical alloying. In these surface reactions, Fe^0 can reduce Fe_{surf}^{3+} species of Fe_3O_4 or Fe_2O_3 (an oxidized phase present on the magnetite surface) by a thermodynamically favoured process to produce a higher Fe_{surf}^{2+} concentration (Eqn. (2)).



The higher concentration of Fe_{surf}^{2+} species should therefore generate from H_2O_2 higher amounts of HO^\cdot , which can then participate in two competing processes: (i) the oxidation of organics and (ii) the decomposition of H_2O_2 to O_2 (Scheme 2). H_2O_2 decomposition can occur via HOO^\cdot formed by the reaction of HO^\cdot with H_2O_2 . The participation of HOO^\cdot is indicated by the interception of the peroxide-type intermediate **8** (Scheme 1). This radical can react with Fe_{surf}^{3+} on the oxide surface to produce O_2 and Fe_{surf}^{2+} (Scheme 2).

CONCLUSIONS

On-line ESI-MS(/MS) monitoring of the degradation of phenol in aqueous solution using the heterogeneous Fenton $Fe^0/Fe_3O_4/H_2O_2$ system reveals the participation of several hydroxylated intermediates. The detection of these intermediates suggests the participation of HO^\cdot formed via the reaction of H_2O_2 with Fe_{surf}^{2+} , therefore providing evidence that the $Fe^0/Fe_3O_4/H_2O_2$ system acts via a classical Fenton mechanism. Remarkably, the formation of hydroperoxide radicals (HOO^\cdot) under these reaction conditions is also suggested by the interception of a peroxide-type intermediate.



Scheme 2.

The improved knowledge provided by on-line ESI-MS(/MS) monitoring, of the oxidation mechanisms of this heterogeneous but efficient Fenton processes should allow further progress in establishing it as a time- and cost-effective process for the treatment of organics in wastewaters.

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