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.

Fe2+ + H2O2 → Fe3+ + OH· + OH− (1)

Recent efforts5–9 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. Fe3−xMxO4 (M = Mn or Co)10,11 and Fe8/Fe3O412,13 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.7–23 Electrospray ionization mass spectrometry (ESI-MS) has became 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.
EXPERIMENTAL

Magnetite was prepared by co-precipitation of its precursor ferric hydroxyacetate from an aqueous solution of FeCl₃ (1.65 mol L⁻¹, 85 mL), NH₄OH (28%, 100 mL) and CH₃COONH₄ (20%, 500 mL), followed by a thermal treatment at 430 °C in N₂ for 2 h. After preparation, the magnetite was kept under an atmosphere of N₂ to avoid long-term oxidation by air. Mechanically alloyed mixtures were prepared from α-Fe and Fe₃O₄ 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. 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% H₂O₂ and 30 mg of the Fe⁰/Fe₃O₄ 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 °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 μL 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 (N₂) flow rate, 20 units (ca. 0.50 L min⁻¹); spray voltage, 4.5 kV; capillary voltage, 25 V; and 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 Fe⁰/Fe₂O₄/H₂O₂ oxidation of phenol (I). At the beginning (zero reaction time, Fig. 1(a)), phenol is detected solely as [1 – 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 – H]⁻ of m/z 109, [4 – H]⁻ of m/z 123, [5 – H]⁻ of m/z 139, [6 – H]⁻ of m/z 155, [7 – H]⁻ of m/z 113, and [8 – H]⁻ of m/z 125.

Based on the ESI-MS data, we propose a reaction sequence for the oxidation of phenol by the Fe⁰/Fe₂O₄/H₂O₂ 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 hydroxylations to yield 4, 5, and 6. Finally, the acyclic carboxylic acid 7 is formed from the cyclic intermediate 4 via...
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 Fe(0)/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 Fe(0)/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
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 that heterogeneous Fenton systems based on Fe₃O₄, i.e. Fe⁶⁺/Fe₃O₄ and Fe₃₋ₓMₓO₄ (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 Fe⁶⁺/Fe₃O₄/\( \text{H}_2\text{O}_2 \) 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, 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 \( \text{HO}^- \). Isotopic labelling experiments with \(^{14}\text{C}-\text{formic acid} \) also suggested the participation of \( \text{HO}^- \) for a system based on FeOOh. In addition, the probable detection of the peroxide-type intermediate (Scheme 1) suggests that hydroperoxide radicals (\( \text{HOO}^- \)) are also formed under such reaction conditions.

In the heterogeneous system, \( \text{HO}^- \) are probably formed from reduced iron species on the solid surface, e.g. Fe⁶⁺surf, in a Fenton-like mechanism (Eqn. (2)). The strong effect of Fe⁶⁺ in the Fe⁶⁺/Fe₃O₄ mixtures can be attributed to the surface reaction of Fe⁶⁺ and the iron oxide during mechanical alloying. In these surface reactions, Fe⁶⁺ can reduce Fe³⁺surf species of FeO₃ or FeO₃ (an oxidized phase present on the magnetite surface) by a thermodynamically favoured process to produce a higher Fe²⁺surf concentration (Eqn. (2)).

\[
2\text{Fe}^{3+}_{\text{surf}} + \text{Fe}^{6+} \rightarrow 3\text{Fe}^{2+}_{\text{surf}} \quad \Delta E^\circ = 1.21\text{V} \quad (2)
\]

The higher concentration of Fe²⁺surf species should therefore generate from \( \text{H}_2\text{O}_2 \) higher amounts of \( \text{HO}^- \) which can then participate in two competing processes: (i) the oxidation of organics and (ii) the decomposition of \( \text{H}_2\text{O}_2 \) to \( \text{O}_2 \) (Scheme 2). \( \text{H}_2\text{O}_2 \) decomposition can occur via \( \text{HOO}^- \) formed by the reaction of \( \text{HO}^- \) with \( \text{H}_2\text{O}_2 \). The participation of \( \text{HOO}^- \) is indicated by the interception of the peroxide-type intermediate (Scheme 1). This radical can react with Fe²⁺surf on the oxide surface to produce \( \text{O}_2 \) and Fe³⁺surf (Scheme 2).

CONCLUSIONS

On-line ESI-MS(/MS) monitoring of the degradation of phenol in aqueous solution using the heterogeneous Fenton Fe⁶⁺/Fe₃O₄/\( \text{H}_2\text{O}_2 \) system reveals the participation of several hydroxylated intermediates. The detection of these intermediates suggests the participation of \( \text{HO}^- \) formed via the reaction of \( \text{H}_2\text{O}_2 \) with Fe²⁺surf, therefore providing evidence that the Fe⁶⁺/Fe₃O₄/\( \text{H}_2\text{O}_2 \) system acts via a classical Fenton mechanism. Remarkably, the formation of hydroperoxide radicals (\( \text{HOO}^- \)) under these reaction conditions is also suggested by the interception of a peroxide-type intermediate.
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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