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Heterogeneous Fenton oxidation of paracetamol using iron oxide (nano)particles

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ABSTRACT

100 mg L\(^{-1}\) paracetamol aqueous solutions were treated by heterogeneous Fenton oxidation at acidic pH (2.6). Three types of iron oxides – nano- and submicro-structured magnetite, nanostructured maghemite – were tested as catalysts for that purpose. For each system, the paracetamol conversion and mineralization yield (Total Organic Carbon removal) were evaluated, as well as the catalyst stability upon recycling.

The influence of reaction parameters such as temperature, iron amount, and hydrogen peroxide dosage was also investigated. Paracetamol mineralization was improved by high temperature and low oxidant dosage due to radical scavenging effects. In best conditions (two times the stoichiometric amount of H\(_2\)O\(_2\), a temperature of 60 °C, a catalyst concentration of 6 g L\(^{-1}\)), paracetamol was fully degraded after 5 h, but total mineralization was not yet achieved: TOC removal reached about 50% when magnetite powders were used as catalysts. All iron oxides exhibited low iron leaching (<1%) and stable catalytic activity upon first recycling.

Introduction

For more than a decade, the presence of pharmaceutical compounds in water resources has been considered as a worrying environmental issue. Due to their increasing input and persistence in the environment, they have been detected in surface water [1], groundwater [2] and even in drinking water [3]. Many of these substances are suspected to have adverse environmental and health effects, although still not clearly defined [3]. Beside, available data clearly indicate that some pharmaceutical compounds develop multi-resistant strains in microorganisms [4], exert toxic effects on algae and invertebrates [5] and affect the endocrine system of fishes [6].

The pharmaceutical compounds are designed to have a complex structure and as a consequence they are not completely removed by conventional wastewater treatment techniques. On the other hand, Advanced Oxidation Processes (AOPs) have proved to be efficient for the elimination of pharmaceuticals from water, either as an alternative or a complement to the conventional treatments [7,8]. With AOPs used as a pre-treatment step, the pollutants can be oxidized to by-products that are easily biodegradable and less toxic, preventing the death of microorganisms in the subsequent biological treatments [8].

Among these processes, Fenton and Fenton-like oxidations have retained attention of many researchers, as they use easy to handle reagents (Fe\(^{2+}\) or Fe\(^{3+}\) and H\(_2\)O\(_2\)), require very little energy compared to other oxidation technologies and are able to destroy a large number of organic compounds. They involve numerous parallel and consecutive reactions, but are generally described by the following dominant reactions [9]:

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \quad (1) \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{2+} + \cdot\text{OOH} + \text{H}^+ \quad (2)
\end{align*}
\]

in which reaction (2) is several orders of magnitude slower than reaction (1).

The generated hydroxyl radicals (\(\cdot\text{OH}\)) are powerful oxidant species, which exhibit a very high oxidation potential of 2.80 V, only being surpassed by fluorine [10].

However the homogeneous Fenton oxidation suffers from a few drawbacks [7,11]: (i) the recovery of dissolved iron ions from the treated solution requires additional treatments, (ii) Fenton catalytic cycle is restrained by the formation of stable iron complexes with phosphates anions or generated carboxylic acids and (iii) the process needs to be operated in a narrow pH range, between 2 and 4, to avoid the formation and subsequent precipitation of iron oxyhydroxides. To overcome these drawbacks an adequate solution seems to be the use of heterogeneous catalysts in the so-called heterogeneous Fenton-like oxidation, which also might avoid the initial acidification.

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Zero-valent iron nanoparticles [12,13], iron containing clays [14,15], iron oxide immobilized on zeolites [11,16] and activated carbons [17,18], iron oxide minerals [19–21] have been investigated as heterogeneous Fenton catalysts. The latter are especially interesting, because they are ubiquitous in the environment and can be easily applied in in-situ remediation processes [20].

Paracetamol or acetaminophen is a mild analgesic and anti-inflammatory, commonly used for humans and animals. Concentrations up to 6 μg L⁻¹ have been reported in European sewage treatment plant effluents [22], up to 10 μg L⁻¹ in natural waters in USA [23], and up to 61 μg L⁻¹ in a WWTP located in East Lansing, Michigan [24]. Moreover it is transformed into toxic compounds by chlorination process used in wastewater treatment plants [25].

Almost all past research pertaining to the removal of paracetamol by the Fenton process used soluble Fe²⁺ as catalyst [26–30]. A recent successful example can be found in the work of Almeida et al. [29] on paracetamol by the Fenton process using soluble Fe⁶⁺ in a WWTP located in East Lansing, Michigan [24]. Moreover it is transformed into toxic compounds by the chlorination process used in wastewater treatment plants [25].

The aim of the present work is to investigate the degradation of paracetamol by heterogeneous Fenton oxidation using three types of iron oxides as catalysts: nano- and submicro-structured magnetite powders (MGN1 and MGN2 respectively) and nano-structured maghemite powder (MGM). The influence of catalyst amount, H₂O₂ dosage, as well as temperature is also considered.

Materials and methods

Chemicals

Paracetamol (N-(4-hydroxyphenyl)acetamide) was supplied by BioXtra with a purity ≥99.0%.

Hydrogen peroxide (Ph Eur; 30% w/w) and magnetite or maghemite were used as Fenton’s reagents. These minerals have the same spinel structure and are ferromagnetic. This property makes them particularly interesting as they could be magnetically separated from the treated solution. Their main difference relies in the oxidation state of iron. Three catalyst powders supplied by Sigma-Aldrich were investigated here: MGN1 (Fe₃O₄ powder < 50 nm, purity ≥ 98%), MGN2 (Fe₂O₄ powder < 5 μm, purity of 95%) and MGM (γ-Fe₂O₃ powder < 50 nm).

During the Fenton experiments, samples of the reactant mixture were withdrawn at different reaction times and mixed with a quenching solution containing KI (0.1 mol L⁻¹), Na₂SO₃ (0.1 mol L⁻¹) and a phosphate buffer (mixture of KH₂PO₄, 0.05 mol L⁻¹ and Na₂HPO₄·2H₂O, 0.05 mol L⁻¹). KI and Na₂SO₃ reduce H₂O₂ while the phosphate buffer precipitates leached iron [35]. All these reagents were analytical grade and supplied by Sigma-Aldrich.

Experimental setup

The experimental setup used for Fenton oxidation consisted in a 650 mL stirred Pyrex reactor, equipped with a jacket to maintain the temperature of the solution. For all the experiments, 500 mL of paracetamol solution with an initial concentration of 100 mg L⁻¹ were used. Agitation speed was set to 350 rpm. The initial pH of the solution was adjusted to 2.6 with 10% H₂SO₄, after which the catalyst powder was added. The suspension was stirred during 90 min to ensure preliminary adsorption equilibrium, as confirmed by the chromatography analysis of samples withdrawn at different times (0, 30, 60 and 90 min). Then H₂O₂ was added to initiate the Fenton oxidation.

During the 5 h oxidation, 7 mL aliquots were withdrawn at selected time intervals (after 5, 10, 60, 180 and 300 min of oxidation process), treated with the quenching solution, filtered through 0.2 μm nylon membrane syringe filters and analyzed. Paracetamol conversion was monitored by liquid chromatography and the extent of mineralization by Total Organic Carbon (TOC) analyzer. The experimental runs were performed at different temperatures (30 °C and 60 °C). Concentrations of catalyst (1, 3 and 6 g L⁻¹) and H₂O₂ (28 and 153 mmol L⁻¹, corresponding to 2 and 11 times the stoichiometric amount of H₂O₂ required for complete mineralization, respectively) were also varied for the optimization of the degradation process. The stoichiometric amount of H₂O₂ required for the total oxidation of paracetamol was calculated based on the following equation:

\[
C₄H₈NO₂ + 2H₂O₂ = 8CO₂ + HNO₃ + 25H₂O
\]

Analytical methods

Analysis of aqueous solution samples

Prior to TOC analysis, 5 mL of the reacting solution were treated with 2 mL of the quenching solution (KI, 0.1 mol L⁻¹; Na₂SO₃, 0.1 mol L⁻¹; KH₂PO₄, 0.05 mol L⁻¹; Na₂HPO₄·2H₂O, 0.05 mol L⁻¹) to prevent any further oxidation by reducing remaining oxidant and precipitating dissolved iron. The sample was filtered and diluted with ultrapure water to 24 mL. The TOC concentration was obtained from the difference between Total Carbon and Inorganic Carbon concentrations measured with a Shimadzu TOC-VCSN analyzer.

Paracetamol concentration was measured by a high performance liquid phase chromatograph (HPLC) with UV detection (UV6000 diode array detector, Thermo Finnigan). The separation was achieved on a C18 reverse phase column (ProntoSil C18 AQ) using an isocratic mobile phase (10/90 mixture of acetonitrile and deionised water acidified at pH 2.0 with H₃PO₄) fed at 1 mL min⁻¹. The wavelength was set to 254 nm for paracetamol detection. Quantification was made from a calibration curve periodically updated with fresh standard solutions. In this case, only the phosphate buffer (0.5 mL) was added to the reaction solution (1 mL) in order to precipitate Fe²⁺ and avoid any interference of KI and Na₂SO₃. Samples were injected in the chromatograph immediately after the addition of the buffer solution.

At the end of the experiments, residual H₂O₂ was titrated with a 0.02 M permanganate solution (standardized with sodium oxalate prior to use).

To evaluate Fe leaching, the concentration of dissolved iron was measured in the final solution, after filtration through a 0.2 μm cellulose acetate membrane, by Inductively Coupled Plasma Atomic Emission Spectroscopy (Ultima 2, Horiba Jobin-Yvon).

Characterization of the iron oxide catalysts

X-ray diffraction (XRD) was used to check for the presence of crystalline impurities and calculate crystallite size from Scherrer method. XRD patterns were collected on a theta/theta powder X-ray diffraction MPD Pro system (PAAnalytical Company) equipped with a fast X'Celerator detector. The diffractiongrams were recorded in 5–70° 2θ range with a 0.017° step size.

Brunauer–Emmett–Teller (BET) surface area of the iron oxide catalysts was measured using nitrogen adsorption on a Micromeritics ASAP 2010 instrument. The solids were degassed 2 h at 60 °C prior to the measurement.

Scanning Electron Microscopy (SEM) was used to determine the morphology of the catalysts. The SEM images were obtained on a LEO 435 VP apparatus.

The particle size distribution of the iron oxide agglomerates in solution was analyzed by laser diffraction on a Mastersizer 2000 (Malvern Co) instrument.
The values of pH_{pzc}, pH at the point of zero charge, were measured by mass titration method [36].

Results and discussion

Characterization of iron oxide catalysts

The diffractograms of all iron oxides are shown in Fig. 1. The diffraction pattern of nano- and submicro-structured Fe_{3}O_{4} could be associated to magnetite (ICDD cards 00-001-1111 and 01-085-1436, respectively) and that of nanostructured Fe_{3}O_{4} to maghemite (ICDD card 00-039-1346). No peaks attributable to other phases were observed. Note that magnetite and maghemite cannot be easily differentiated from each other by XRD analysis.

Diffraction peaks of MGN1 are broader and lower in intensity as compared to MGN2, which results from smaller crystallites. Their average size (d_{c}) was calculated from the full width at half-maximum of the strong intensity peaks using Scherrer equation, giving a ratio of about 2 between the two magnetite powders.

The elemental particle diameter (d_{ep}) could be also calculated from BET surface area (S_{BET}) assuming spherical shape: 

\[ d_{ep} = \frac{6}{S_{BET} \rho} \]  

where \( \rho \) is the density of the oxide. All these properties are listed in Table 1. For MGN1 and MGM, DRX and BET size measurements were in good agreement, confirming that their elemental particles consist in nanosized single crystallites. Conversely it could be concluded that MGN2 is composed of submicronic polycrystalline grains.

This was confirmed by SEM analysis which shows that MGN2 is a homogeneous powder formed by small rounded grains of about 200 nm in size (Fig. 2B). MGN1 and MGM (Fig. 2A and C) are polydispersed powders consisting in porous agglomerates up to 100 and 50 \( \mu m \), respectively.

Suspension of MGN1 in osmosed water showed a broad monomodal distribution of particle sizes (2–300 \( \mu m \)), while MGN2 and MGM exhibited bimodal distributions, most of the agglomerates ranging between 1 and 10 \( \mu m \). Their apparent volume mean diameter (d_{s1}) is also given in Table 1.

Selection of iron oxides as catalysts in Fenton oxidation

Decomposition of hydrogen peroxide over iron oxides

In order to investigate the capacity of the different iron oxides to produce hydroxyl radicals, decomposition of \( H_{2}O_{2} \) (without pollutant) was first investigated. All the experiments were conducted at 60 \(^{\circ}\)C with 6 g L\(^{-1}\) of catalyst and an initial pH set to 2.6. The corresponding results are presented in Fig. 3. No \( H_{2}O_{2} \) consumption was observed in absence of catalyst. In the heterogeneous Fenton type process, the reaction between ferrous or ferric ions and hydrogen peroxide takes place at the surface of the solid catalyst and then depends on the specific surface area (SSA) of the catalyst [14]. As expected MGN2 which exhibits the lowest SSA also yielded the lowest \( H_{2}O_{2} \) decomposition rate. Surprisingly MGN1 and MGM nanopowders showed very similar activities despite their different oxidation states. One reason could be the fast conversion of magnetite into maghemite by oxidation with \( H_{2}O_{2} \) [37]. The catalytic reaction obeyed first-order kinetics with respect to \( H_{2}O_{2} \) concentration and Table 2 gives the corresponding kinetic constants both on a weight basis and on a surface basis. When referring to the constant per surface area unit MGN2 appears in fact more active than MGN1. It might be explained by the presence of a surfactant on the surface of the nanostructured oxide inhibiting its activity (carbon being detected by EDX analysis), or by some diffusional limitations as MGN1 agglomerates are much larger than those of MGN2 (Table 1).

Effect of iron oxide type and concentration on the degradation of paracetamol

Before oxidation was started by addition of \( H_{2}O_{2} \), adsorption equilibrium was achieved by 90 min of equilibration. No significant adsorption of paracetamol was observed for any of the catalysts (with less than 10% paracetamol uptake from the aqueous phase for a catalyst concentration of 6 g L\(^{-1}\)).

The effect of iron catalyst concentration on the evolution of paracetamol and TOC concentrations is depicted in Figs. 4 and 5, respectively. The conditions were: temperature of 60 \(^{\circ}\)C, \( H_{2}O_{2} \) concentration of 153 mmol L\(^{-1}\), and initial pH of 2.6.

The experiments with 6 g L\(^{-1}\) of each catalyst were duplicated, showing mean deviations of less than 10% for paracetamol and TOC concentrations as a function of time. Without iron oxide, paracetamol was not significantly oxidized by \( H_{2}O_{2} \) (less than 1% conversion after 5 h). For all the catalysts, a complete degradation of paracetamol was achieved after 5 h of oxidation with 6 g L\(^{-1}\) of iron oxide, while mineralization yield reached 43%, 34% and 39% with MGN1, MGN2 and MGM, respectively. The conversion of TOC leveled off after long reaction times as the result of surface passivation or formation of refractory oxidation intermediates.

Table 1

<table>
<thead>
<tr>
<th>Label</th>
<th>Chemical formula</th>
<th>d_{c} [\mu m]</th>
<th>S_{BET} [m^{2}/g]</th>
<th>d_{ep} [\mu m]</th>
<th>d_{s1} [\mu m]</th>
<th>%\text{Fe [%wt]}</th>
<th>pH_{pzc}</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGN1</td>
<td>Fe_{3}O_{4}</td>
<td>29</td>
<td>39.6 (±0.1)</td>
<td>29</td>
<td>90.0</td>
<td>67.5</td>
<td>6.2 (±0.1)</td>
</tr>
<tr>
<td>MGN2</td>
<td>Fe_{3}O_{4}</td>
<td>67</td>
<td>5.84 (±0.07)</td>
<td>208</td>
<td>12.9</td>
<td>69.7</td>
<td>7.4 (±0.1)</td>
</tr>
<tr>
<td>MGM</td>
<td>Fe_{3}O_{4}</td>
<td>48</td>
<td>35.2 (±0.3)</td>
<td>35</td>
<td>4.8</td>
<td>69.2</td>
<td>4.6 (±0.1)</td>
</tr>
<tr>
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</tbody>
</table>

\(^{a}\) Mean diameter of crystallites calculated from XRD pattern using Scherrer’s equation.

\(^{b}\) Mean diameter of elemental particles calculated from S_{BET} assuming spherical shape.

\(^{c}\) Volume mean diameter of agglomerates in solution from laser diffraction measurement.

\(^{d}\) As given by the supplier (from titration with Na_{2}S_{2}O_{3}) – theoretical values for magnetite and maghemite: 72.4% and 69.9%, respectively.
As previously found for $\text{H}_2\text{O}_2$ decomposition, MGN1 exhibited a better performance than MGN2 at the same concentration. However comparing paracetamol conversion obtained with MGN1 at 1 g L$^{-1}$ and MGN2 at 6 g L$^{-1}$ (see small chart in Fig. 4B), MGN1 seemed again less active on surface area basis.

A higher concentration of catalyst insures a higher number of active sites which decompose $\text{H}_2\text{O}_2$, but also a higher concentration of leached iron, promoting homogeneous Fenton reaction. However above 3 g L$^{-1}$ the effect of catalyst content tended to vanish for MGN1 and MGM nanopowders (cf. Figs. 4A, 5A and 4C, 5C, respectively). Such behavior or even a reaction inhibition at high iron oxide concentration has been already reported [19,37] and attributed to radical scavenging by the oxide surface.

**Leaching tests**

Iron leaching can occur due to two main mechanisms: “standard” dissolution by protons at low pH and promoted dissolution with the help of complexing agents, such as oxalic acid formed as oxidation intermediate. It is a surface mechanism in which the oxalate ion binds to one or two iron atoms, which weakens the Fe–O bond more efficiently than water alone, thereby increasing dissolution kinetics [38,39]. Whether it is free or as a complex, dissolved iron will play a different role in the oxidation process efficiency.

At the end of the experiments, the total amount of iron in solution was measured by ICP/AES. Moreover homogeneous Fenton oxidation was performed using the final solutions obtained after the heterogeneous reactions, as believed to be more representative than synthetic Fe$^{2+}$ or Fe$^{3+}$ solutions with the same iron content (see also Section “Comparison to the homogeneous system”). To account for the effect of dissolved iron only, the oxides were filtered off and the solution passed through a membrane with 0.2 μm pore size. In all cases, the pH of the filtrate was found almost equal to 2.6. Paracetamol and $\text{H}_2\text{O}_2$ concentrations were titrated and readjusted to match previous initial conditions.

Recycling tests were performed in order to evaluate the stability of the iron oxides during successive Fenton reactions and the possibility of their use in a continuous membrane coupling process. The catalysts from 6 g L$^{-1}$ experiments were filtered off, washed with distilled water several times and dried at 70 °C for 24 h. Then aliquots of these spent catalysts (equivalent to 3 g L$^{-1}$) were recycled. Fig. 7 compares the activity of recycled catalysts to that of fresh ones. All the catalysts show a good stability upon recycling. Yet MGM was found slightly less active in the second run (with a final TOC conversion of 34% against 43% in the first run, Fig. 7B). This could be surprising as this oxide should be more chemically stable. As shown in Table 3, a slightly lower concentration of leached iron was found in the second solution. This might result in a lower contribution of the homogeneous Fenton reaction that proved to be significant (cf. Section “Leaching tests”). It can be also concluded that MGN1 and MGN2 did not exhibit significant surface passivation as shown by an unchanged – or even improved – initial rate of paracetamol oxidation on recycled magnetites (Fig. 7A).

**Table 2**

First-order kinetic constants of $\text{H}_2\text{O}_2$ decomposition over the three oxides (same operating conditions as for Fig. 3).

<table>
<thead>
<tr>
<th>Label</th>
<th>$k$ (L g$^{-1}$ min$^{-1}$)</th>
<th>$k'$ (L m$^{-2}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGN1</td>
<td>$2.2 \times 10^{-4}$</td>
<td>$5.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>MGN2</td>
<td>$7.2 \times 10^{-5}$</td>
<td>$1.2 \times 10^{-6}$</td>
</tr>
<tr>
<td>MGM</td>
<td>$1.9 \times 10^{-4}$</td>
<td>$5.4 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
Analysis of reaction parameters for paracetamol degradation using nano- and submicro-structured magnetite powders as catalysts

According to previous results, maghemite was not selected for further investigation of reaction parameter due to the significant contribution of the homogeneous reaction and the slight loss of activity upon recycling.

Effect of temperature

The influence of reaction temperature on the degradation of paracetamol and its mineralization is shown in Fig. 8 for both magnetite powders. Two sets of data are displayed for each catalyst at a given temperature, corresponding to almost the same ratio of catalyst to \( \text{H}_2\text{O}_2 \) concentration. They correspond to two different initial concentrations of \( \text{H}_2\text{O}_2 \), 28 and 153 mmol L\(^{-1}\), equivalent to 2 and 11 times the stoichiometric amount for complete mineralization, respectively. Previous works on homogeneous Fenton reaction showed that this ratio is a critical parameter for
optimizing the process efficiency when the Fenton's reagent is in sufficient amount [41,42].

A higher temperature increases the rate of *OH formation as per Arrhenius law, but it also promotes the decomposition of hydrogen peroxide into oxygen and water, reducing the efficiency of its utilization [43]. The increase of temperature from 30 °C to 60 °C showed here a beneficial effect for all the investigated conditions.
Effect of initial H$_2$O$_2$ concentration

Fig. 8C confirms that, at a given temperature and pH, the ratio [MO]/[H$_2$O$_2$]$_0$ is the key parameter that controls the mineralization yield, no matter of the H$_2$O$_2$ excess amount. Nevertheless it seems from Fig. 9A and B that the initial degradation rate of paracetamol is improved by a low amount of both reagents.

Fig. 9 illustrates the effect of H$_2$O$_2$ concentration (28 or 153 mmol L$^{-1}$) at a given magnetite concentration (1 or 6 g L$^{-1}$). In all cases, using 153 mmol L$^{-1}$ of H$_2$O$_2$ resulted in a decrease of both paracetamol degradation rate (Fig. 9A and B) and final TOC conversion (Fig. 9C). It was especially observed at low iron oxide concentration. This behavior may be explained by the parallel and undesired reaction between H$_2$O$_2$ and hydroxyl radicals [44]:

*OH $+\ H_2O_2 \rightarrow H_2O + *OOH$  \hspace{1cm} (4)

The produced *OOH radicals have an oxidation potential significantly lower than that of *OH. As a consequence of this scavenging effect an excess of H$_2$O$_2$ led to a less efficient degradation. Eq. (4) has a reference rate constant of 2.7 $\times$ 10$^7$ L mol$^{-1}$ s$^{-1}$ [45], while the reaction between hydroxyl radicals and paracetamol exhibits a rate constant of 1.9 $\times$ 10$^8$ L mol$^{-1}$ s$^{-1}$ [46]: therefore at the highest H$_2$O$_2$ concentration the scavenging of *OH by H$_2$O$_2$ becomes predominant to the detriment of pollutant oxidation.

As expected, the consumption of H$_2$O$_2$ when in large excess (153 mmol L$^{-1}$) was similar with or without pollutant (cf. Figs. 3 and 9D). Logically, it increased upon decreasing initial H$_2$O$_2$ concentration or increasing magnetite concentration.

Comparison to the homogeneous system

A few homogeneous experiments were conducted to assess the efficiency of the heterogeneous process. For nanosized magnetite such as MGN1 the main surface plane is (1 1 1) face associated with an iron density of 9.8 Fe atom/nm$^2$ [47]. Therefore 1 g L$^{-1}$ of iron oxide should correspond to 0.6 mmol L$^{-1}$ of accessible iron on the magnetite surface. Fig. 10 compares the degradation of paracetamol for both systems at two temperatures: 45 $^\circ$C and 60 $^\circ$C. The homogeneous tests were performed using either FeSO$_4$$\cdot$7H$_2$O (Fe$^{2+}$) or FeCl$_3$$\cdot$6H$_2$O (Fe$^{3+}$) with an initial pH of 2.6. No iron precipitate was observed in these conditions. As already reported, H$_2$O$_2$ being in large excess with respect of iron species, similar rates were obtained in both cases no matter the oxidation state of iron ion in solution [48]. It is striking that, despite MGN1 yielded much lower initial rates of paracetamol and TOC degradation, similar TOC concentrations were reached after 5 h of oxidation. MGN1 seems to exhibit an induction period that may be caused by the organic stabilizer coating the particle surface. This organic matter may need to be (partially) oxidized before surface iron can be available for paracetamol degradation.

Finally two experiments were performed using 2 and 10 mg L$^{-1}$ of Fe$^{3+}$ (0.035 mmol L$^{-1}$ and 0.18 mmol L$^{-1}$, respectively), which correspond to the lowest and highest bound of leached iron measured with magnetites. At these concentrations, iron ion proved to be already active, resulting in paracetamol depletion within about 10 min, a much lower time than observed with MGN1. Yet the final mineralization yield was lower than in case of MGN1. Therefore it confirms that Fenton oxidation over MGN1 should mainly proceed through heterogeneous mechanism.
Low cation leaching and good catalytic stability are essential parameters for the process economy and its environmental impact: magnetite powders showed promising results as their activity was maintained upon first recycling while exhibiting iron loss of much less than 1%.

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References


Conclusions

Catalytic wet peroxide oxidation of paracetamol could be successively performed using three types of iron oxides, leading to a complete conversion of paracetamol within 5 h and a TOC removal of about 50% with nano- and submicro-structured magnetite. This process was positively influenced by a rise in temperature from 30 °C to 60 °C. A small excess of oxidant should be preferred because of the occurrence of scavenging effect. The homogeneous contribution proved to be significant with magnetite only.


