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Heterogeneous Fenton oxidation using Fe-ZSM5 catalyst for removal of ibuprofen in wastewater

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ABSTRACT

Heterogeneous Fenton oxidation using Fe-zeolite catalyst (of ZSM5 type) was investigated for the removal of ibuprofen (20 mg/L) in water. In particular, the effects of catalyst concentration, oxidant dosage, temperature, solution pH, and water matrix on pollutant conversion and mineralization were evaluated. The activity of leached iron species in solution was also measured to determine the contribution of the homogeneous reaction.

Oxidation rate of ibuprofen obeyed a pseudo-first-order kinetics with respect to the pollutant concentration, and the apparent rate constant increased with catalyst and hydrogen peroxide concentrations in the investigated ranges (1-5 g/L of Fe-zeolite and 0.5-7 times the stoichiometric amount of oxidant). Energy activation of 53 kJ/mol was obtained from Arrhenius plot. However, the mineralization yield was not significantly improved by a too large excess of H2O2 or increase of temperature. In the selected conditions (25 °C, 4.8 g/L of catalyst, 2 times the stoichiometric amount of H2O2), 88% of ibuprofen and 27% of TOC were removed after 3 hours of reaction under “natural” pH conditions.

Very low leaching (up to 0.2 mg/L) and negligible activity of leached iron in solution indicated that Fenton reaction was mainly induced by iron species on the catalyst surface.

Degradation rate of ibuprofen was slower in wastewater effluent as compared to distilled water, mainly due to alkaline buffering and radical scavenging effects of organic and inorganic compounds present in the matrix.

Mono- and multi-hydroxylated ibuprofen adducts were found as main oxidation intermediates -in line with free-radical mechanism- as well as 4-isobutylacetophenone from decarboxylation route.

1. Introduction

Contaminated water is a world concern, and threatens both the quality of life and public health. With the increase of population, urbanization, industrialization and agriculture intensification, new types of pollutants have arisen such as fertilizers, pesticides and pharmaceuticals. Among organic pollutants, pharmaceutical products are of particular concern due their increasing consumption and unclear cumulative effect on environment and human health. Moreover, previous studies reported that pharmaceutical compounds are only partially degraded by conventional biological treatments [1,2] or may be only adsorbed on suspended solids and accumulated in settling tank [3,4]. Therefore, more efficient processes are needed to remove pharmaceuticals or convert them into innocuous compounds. In the last decades, numerous studies showed that advanced oxidation processes (AOPs) are effective for the degradation of refractory organic compounds, including drugs [5-8]. AOPs are based on the generation of powerful and non-selective oxidant species, such as hydroxyl radical (•OH), that are capable to degrade organic compounds, transforming them into water (H2O) and carbon dioxide (CO2) as ultimate products. Homogeneous Fenton oxidation is one of the most appealing AOPs owing to: (i) the utilization of environmental friendly reagents (Fe2+ and H2O2), (ii) its low energy consumption compared to other AOPs, (iii) its ability to destroy various organic compounds along with an improvement of biodegradability, and (iv) the simplicity of the required equipment allowing an easy scale up from laboratory reactor to large scale process [9-11].

It is generally accepted that homogeneous Fenton reaction follows a free radical mechanism [12,13], involving the reaction between ferrous ions (Fe2+) and hydrogen peroxide (H2O2) in acidic conditions (pH
between 2 and 4) to generate hydroxyl radicals (·OH) (Eq. (1)). For mation of stable ferric complexes (such as Fe OOH2+), Eq. (2) hinders the catalytic cycle due to their slow decomposition into Fe2+ (Eq. (3)).

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH} \quad \text{(k = 40 - 80 Lmol}^{-1}\text{s}^{-1} \quad \text{[14])} \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \leftrightarrow \text{Fe} \text{OOH}^2+ + \text{H}^+ \quad \text{(K = 3.1 \times 10^{-3} \quad [15])} \\
\text{Fe} \text{OOH}^2+ & \rightarrow \text{OOH} + \text{Fe}^{2+} \quad \text{(k = 2.7 \times 10^{-3} \quad s}^{-1} \quad \text{[15])}
\end{align*}
\]

(1) (2) (3)

Therefore, iron concentration (10-500 mg/L) much higher than the discharge limit (2 mg/L) is generally needed to obtain appreciable mineralization yield by homogeneous Fenton process [10,14]. Moreover, over as abovementioned, this reaction operates at low pH to avoid the precipitation of inactive iron oxyhydroxides [16]. Therefore subsequent treatments are required for catalyst separation and effluent neutralization, which often generate large volumes of iron containing sludge that are hardly disposable [9].

In order to overcome these disadvantages and reduce costs, application of heterogeneous iron based catalyst is a promising solution. Various solid catalysts have been studied including iron oxides, zero valent iron, iron (oxide) loaded materials, iron rich soils, etc [17,19]. Among these, iron loaded materials such as Fe ZSM5 zeolite are very interesting due to their affinity for various pollutants, activity at near neutral pH, and low leaching rate [17,20]. Concomitant adsorption on the catalyst can indeed help to concentrate the pollutant molecules in the vicinity of active species and to buffer variations in effluent loadings [21].

Fenton oxidation catalyzed by Fe ZSM5 zeolite has been reported for the degradation of carboxylic acids [22,23], gasoline additive [21,24] and dyes [25,28]. On the other hand, its application for the degradation of pharmaceuticals is still limited. Velichkova et al. [20] reported that Fe ZSM5 was active for Fenton oxidation of paracetamol and could maintain its catalytic activity in continuous process.

In this paper, a commercial Fe ZSM5 was studied as catalyst for the heterogeneous Fenton oxidation of ibuprofen, one of the most common pharmaceuticals worldwide. A recent study has reported that exposure to ibuprofen at high concentration (0.25-1 mM) results in a significant reduction of the viability of bacteria (B. megaterium and P. atlantica) and algae (Chlorella sp.) [29]. Moreover, chronic exposure to ibuprofen at very low concentration (0.1 µg/L) affects several end points related to the reproduction of the fishes, including induction of vitellogenin in male fish, fewer broods per pair, and more eggs per brood [30].

This work more particularly evaluates the effects of several operating parameters - catalyst loading, H2O2 concentration, temperature, and solution pH - to optimize the degradation of the pollutant. In addition, activity of leached iron, influence of radical scavenger and water matrix were also addressed to give further insight into reaction mechanisms. Finally, main oxidation intermediates were identified and degradation pathways were proposed. Besides further assessing the activity of Fe ZSM5 catalyst for the remediation of emerging pollutants, the aim of this study was to evaluate the contribution of homogeneous and heterogeneous mechanisms, the role of pollutant adsorption and to elucidate the effects of wastewater properties on the oxidation performance.

2. Materials and methods

2.1. Chemicals and catalyst

Ibuprofen (IBP or C13H18O2, purity 99.99%) was supplied by BASF Corporation and used as received. H2O2 solution 30% w/w, mono potassium phosphate (KH2PO4), sodium phosphate dibasic dehydrate (Na2HPO4.2H2O), potassium iodide (KI), titanium tetrachloride (TiCl4), sodium sulfite (Na2SO3), sulfuric acid (H2SO4, 1 M) and sodium hydroxide (NaOH, 1 M) were purchased from Sigma Aldrich.

A commercial iron containing zeolite catalyst (Fe MFI) was obtained from Süd Chemie AG (ref. Fe MFI 27). Detailed characterization of the catalyst has been previously reported [20] and its main properties are summarized in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/Al ratio</td>
<td>27a</td>
</tr>
<tr>
<td>Fe content (wt. %)</td>
<td>3.4b</td>
</tr>
<tr>
<td>Fe dispersion (%)</td>
<td>22c</td>
</tr>
<tr>
<td>d_{50,CO} (nm)</td>
<td>4d</td>
</tr>
<tr>
<td>S_{micr} (m^2/g)</td>
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</tr>
<tr>
<td>V_{macro} (cm^3/g)</td>
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<tr>
<td>V_{meso} (cm^3/g)</td>
<td>0.13f</td>
</tr>
<tr>
<td>V_{micro} (cm^3/g)</td>
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</tr>
<tr>
<td>d_{50} (µm)</td>
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</tr>
<tr>
<td>pH_{spec}</td>
<td>2.9h</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Notes</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>as given by the supplier.</td>
</tr>
<tr>
<td>b</td>
<td>Iron content from ICP-AES analysis of acid leachate.</td>
</tr>
<tr>
<td>c</td>
<td>Metal dispersion and mean diameter of metal crystallites calculated from CO chemisorption.</td>
</tr>
<tr>
<td>d</td>
<td>Specific surface area, mesoporous, microporous and total porous volumes measured by N2 porosimetry.</td>
</tr>
<tr>
<td>e</td>
<td>Volume mean diameter of particles in suspension (laser diffraction method).</td>
</tr>
<tr>
<td>f</td>
<td>pH at the point of zero charge measured by mass titration.</td>
</tr>
</tbody>
</table>

2.2. Experimental setup and protocols

Experiments were conducted in a 1 L jacketed glass reactor equipped with a pitch blade impeller, temperature probe and several injection/sampling points. The working volume was 1 L. Ibuprofen (IBP) solution (20 mg/L) was prepared at room temperature by dissolving appropriate amount of powder in distilled water under vigorous stirring for 10 h.

It was checked in preliminary experiments that the sole addition of H2O2 (without catalyst) at two or seven times the stoichiometric amount (cf. Eq. (4)) did not result in any measurable IBP and H2O2 conversion within 3 hours, corresponding to the standard reaction time.

The assay started by a preliminary adsorption step, in which Fe MFI catalyst was contacted with IBP solution during 120 min up to equilibrium. It should be mentioned that since molecular size of IBP (1.3 nm x 0.6 nm) is larger than minor and major axes of the sinusoidal (0.51 nm x 0.55 nm) and straight channels (0.54 nm x 0.56 nm) of Fe MFI zeolite, the molecules may be only adsorbed at the intersection of these channels [31]. Furthermore, most of the experiments were carried out without any pH adjustment, but the pH of the IBP solution decreased from 4.3 to 3.3.3.7 (depending on Fe MFI concentration) by simple contact with Fe MFI due to its acidic surface. The acidity of Fe MFI could be ascribed by the presence of Bronsted and Lewis acid sites on zeolite framework [32].

During adsorption step, IBP concentration was only reduced by 25% at the highest catalyst amount (4.8 g/L) during adsorption step. As the contribution of adsorbed compounds thus remained low, the evolution of liquid phase concentrations was used to evaluate the performance of the heterogeneous processes. The oxidation step was then initiated by injection of H2O2 into the slurry (t0). The stoichiometric amount of H2O2 required for IBP mineralization was calculated according to the following equation:

\[
\text{C}_{13}\text{H}_{18}\text{O}_2 + 33 \text{H}_2\text{O}_2 \rightarrow 13 \text{CO}_2 + 42 \text{H}_2\text{O} \quad \text{(4)}
\]
Aliquots samples (9 mL) were withdrawn throughout the oxidation step (at t = 5, 10, 30, 60, 120, 180 min) and filtered onto 0.45 µm并不能 generated cellulose (RC) syringe filter. To prevent further oxidation, the filtered samples were immediately treated by phosphate buffer (mixture of KH₂PO₄ 0.05 M and Na₂HPO₄·2H₂O 0.05 M) or quenching solution (mixture of phosphate buffer, KOH 0.1 M and Na₂SO₃ 0.1 M) as described in the following section. At the end of experiment (after 180 min of oxidation) the whole suspension was filtered on a nitrocellulose mem brane filter with 0.22 µm pore size (GSWP, Merck Millipore) for further analyses of liquid and solid phases.

Effects of Fe MFI concentration (1-4.8 g/L), H₂O₂ concentration (1.6-22.4 mM, corresponding to 0.57 times the stoichiometric amount required for IBP mineralization), temperature (15-45°C) and solution pH (4.3-8.0) were evaluated separately. Unless otherwise stated, the parameters were set as follows: initial IBP concentration = 20 mg/L, Fe MFI concentration = 4.8 g/L, H₂O₂ concentration = 6.4 mM, temperature = 25°C and initial pH of the solution = 4.3 (pH of synthetic solution of IBP in distilled water).

Several experimental runs were duplicated to check for re producibility of concentration time profiles of ibuprofen and Total Organic Carbon (TOC). The experimental errors were estimated by pooled standard deviations. The observed deviation was less than 5% for ibuprofen, TOC and H₂O₂ concentrations.

2.3. Analytical methods

Concentration of IBP during reaction was measured by liquid chromatography (HPLC) with UV detection at λ = 228 nm (PDA de tector, Thermo Finnigan). Separation was performed on a C18 reverse phase column (ProntoSil C18 AQ 5µm, 250 x 4 mm). The column, maintained at 40°C, was eluted with an isocratic mixture of acetonitrile and water (acidified with phosphoric acid at 0.1% v/v) flowing at 1 mL/min. 1 mL of filtered samples was mixed with 1 mL of phosphate buffer and the mixture was again filtered before chromatography analy sis (Injection volume was 20 µL).

The extent of mineralization was calculated from the difference between Total Carbon (TC) and Inorganic Carbon (IC), measured by a Total Organic Carbon (TOC) analyzer (TOC L, Shimadzu Corp.). In this case, the rest of filtered sample (8 mL) was treated with 3 mL of quenching solution, filtered again on 0.45-µm RC syringe filter and diluted by twofold with ultrapure water before being analysed (Injection volume was set to 50 µL and 400 µL for TC and IC, respectively).

Residual concentration of H₂O₂ was measured spectrophotometrically by titanium tetrachloride method [33]. At the end of reaction, 5 mL of filtered sample was diluted to 25 mL with ultrapure water and mixed with 1 mL of 0.09 M TiCl₄ solution and 1 mL of 1 M H₂SO₄ to form a yellow perititanic acid complex detected at λ = 410 nm.

Iron leaching from the Fe MFI catalyst was also evaluated at the end of the reaction by inductively coupled plasma emission spectroscopy (ICP AES) (Ultima 2, HORIBA Jobin Yvon).

High Performance Liquid Chromatography coupled with high re solution Mass Spectrometry (HPLC HRMS) was used to identify the transformation products formed during the Fenton reaction. These analyses were carried out using a liquid chromatograph (ACCELA LC, Thermo scientific Inc.) working in tandem with a mass spectrometer (Exactive™ Plus Orbitrap Mass Spectrometer, Thermo scientific Inc.). Separation was achieved on a PFP column (Phenomenex Luna PFP, 150 mm x 2 mm, 3 µm). Mobile phases were: (A) Ultrapure water acid ifed with formic acid 0.1% (v/v) (B) Acetonitrile. Elution was conducted at 40°C in gradient mode: 3% B in 0 5 min, 3 5% B in 5 25 min, 55% B in 25 30 min, 95 3% B in 30 31 min, 3% B in 31 37 min. The flow rate and injection volume were 0.2 mL/min and 5 µL re spectively. The HRMS analysis was performed with electrospray ionization (ESI) interface in the positive and negative ion modes applying a capillary voltage of 3000 V at 350°C. The instrument operated with mass range between m/z 50 and 1000. Prediction of compound formula and noise reduction were realized by Xcalibur software (version 2, Thermo scientific Inc.) and MetaAlign software (version 041011, Arjen Lommen).

3. Results and discussion

3.1. Mechanism of Fenton oxidation of IBP over Fe MFI

Compared to its homogeneous counterpart, the mechanism of heterogenous Fenton reaction has been less investigated and is still sub ject of discussion. Namely, three possible mechanisms were reported: (i) free radical mechanism induced by surface iron species [34,35] (Eqs. (5) (8));(ii) non radical mechanism involving high valent iron species on the catalyst surface (Eqs. (9) (11)) [36,38]; and (iii) homogeneous pathway induced by leached iron in solution (Eqs. (1) (3)) [39,40].

Radical mechanism (involving hydroxyl radical·OH):

\[
\text{Fe(III)} + H_2O_2 \rightarrow \text{Fe(II)}(H_2O_2) (5)
\]

\[
\text{Fe(III)}(H_2O_2) \rightarrow \text{Fe(II)} + \cdotOH (\cdotO_3^-) + H^+ (2 H^+) (6)
\]

\[
\text{Fe(II)} + H_2O_2 \rightarrow \text{Fe(III)} + \cdotOH + OH^- (7)
\]

\[
\text{Fe(III)} + \cdotOH + \cdotO_2^- \rightarrow \text{Fe(II)} + O_2 (+ H^+) (8)
\]

Non radical mechanism (involving high valent iron species Fe(IV)):

\[
\text{Fe(II)} + H_2O_2 \rightarrow \text{Fe(IV)} + 2 OH^- (9)
\]

\[
\text{Fe(IV)} + H_2O_2 \rightarrow \text{Fe(II)} + O_2 + 2H^+ (10)
\]

\[
\text{Fe(IV)} + \rightarrow \text{Fe(III)} (11)
\]

Where = indicates species on catalyst surface.

Using the same theoretical amount of accessible iron (1 g/L of Fe MFI - 0.134 mM of surface Fe), Fenton oxidation catalyzed by Fe MFI started at a much lower rate than the homogeneous reaction performed with ferrous salt (FeSO₄) (Fig. 1). This observation is consistent with previous studies [41,42]. Interestingly, after the five first minutes, the rate of the homogeneous reaction was very similar to that observed with Fe MFI, suggesting that the difference in initial activity could be due to iron speciation (ferrous vs. ferric iron). On the other hand, the concentration of leached iron from Fe MFI was very low (0.014 and 0.048 mg/L for 1 and 4.8 g/L Fe MFI, respectively) compared to that reported to initiate homogeneous pathway (> 10 mg/L) [14]. None theless, the activity of leached iron was further evaluated (see section 3.3). To check for a possible detrimental influence of the adsorbed pollutant on the H₂O₂ decomposition by Fe MFI catalyst, oxidant consumption was also monitored without IBP (using 1 g/L of Fe MFI). It resulted into 31% of H₂O₂ conversion after 180 min, which was similar to that measured during the oxidation of IBP (26%), indicating

![Fig. 1. Fenton oxidation of IBP over Fe-MFI and FeSO₄ catalysts (IBP₀ = 20 mg/L, H₂O₂₀ = 6.4 mM, T = 25°C, [FeO₄⁻·] = 50 mM): heterogeneous Fenton: [Fe-MFI] = 1 and 4.8 g/L, pH₀ = 4.3; homogeneous Fenton: [Fe²⁺] = 0.134 mM, pH₀ = 2.6.](image-url)
therefore negligible competition effect for the active catalytic sites.

In order to appreciate the contribution of free radicals with Fe MFI, a complementary experiment was carried out using methanol as radical scavenger (reaction rate constant with hydroxyl radical of 9.7 × 10^8 M^-1.s^-1 [43]). Methanol concentration was set to 50 mM corresponding to 500 times the molar concentration of IBP and high Fe MFI loading condition (4.8 g/L) was selected to highlight the scavenging effect. Methanol was introduced after adsorption step (at the same time as H_2O_2). From Fig. 1, it can be seen that this addition significantly reduced final IBP removal yield from 88% to 23% although similar H_2O_2 consumption of about 80% was still observed. This result pled for a main contribution of free radical mechanism. Note that complete inhibition of the reaction (no IBP removal) was observed in the homogeneous process.

3.2. Parametric study

3.2.1. Effect of solid catalyst concentration

Effect of catalyst concentration was first evaluated by varying Fe MFI loading between 1 and 4.8 g/L. In these conditions, increasing Fe MFI concentration was always found beneficial for both IBP and TOC removal (Figs. 2A and 2B). IBP degradation rate was fitted by a first order kinetic law, resulting in: k_{1g/L} = 0.0014 min^-1 (R^2 = 0.9741), k_{3g/L} = 0.0071 min^-1 (R^2 = 0.9984), k_{4.8g/L} = 0.0139 min^-1 (R^2 = 0.9976). Similarly, Olmos et al. [21] and Makhotkina et al. [44] reported that increasing catalyst concentration improved the oxidation of acetone and MTBE, even at very high loadings (5.25 and 5.70 g/L of Fe ZSM5, respectively). The fact that rate constants did not strictly increase proportionally with respect to Fe MFI concentration could make suspect a possible role of the pollutant adsorption inducing nonlinear effects.

The positive effect of solid catalyst concentration could be explained by a higher amount of active sites for H_2O_2 decomposition, as confirmed by the increased oxidant consumption: 26%, 65% and 79% at 1 g/L, 3 g/L and 4.8 g/L respectively. At the highest solid concentration, the mineralization yield reached 27% after 180 min, resulting into an oxidant utilization efficiency (according to Eq. (4)) of about 17%.

3.2.2. Effect of H_2O_2 concentration

Generally, the degradation rate of organic compounds is improved by an increase in initial H_2O_2 concentration until an optimum value is reached; then scavenging of ‘OH by excess H_2O_2 reduces the oxidation rate [23,27]. On the other hand, iron containing zeolite tends to decompose part of H_2O_2 into water and oxygen [22] that should shift this optimum to a higher value.

Three levels of H_2O_2 concentration were tested: 1.6, 6.4 and 22.4 mM (corresponding to 0.5, 2 and 7 times the stoichiometric amount needed for IBP mineralization) with catalyst loading set at the highest value.

As depicted in Fig. 3A, IBP oxidation rate increased with H_2O_2 dosage on the whole investigated range and the first order rate constant was proportional to the concentration of oxidant: k_{1.6 mM} = 0.0029 min^-1 (R^2 = 0.9678), k_{6.4 mM} = 0.0139 min^-1 (R^2 = 0.9976), k_{22.4 mM} = 0.0411 min^-1 (R^2 = 0.9983). According to the corresponding rate constants, reaction of ‘OH with H_2O_2 (Eq. (12)) should occur at similar rate than that with IBP (Eq. (13)) at 22.4 mM of H_2O_2. On the other hand, if a significant residual amount of H_2O_2 (15.9 mM, corresponding to 29% of oxidant use) was measured under the highest oxidant concentration, it was almost all consumed below (95% of consumption when starting with 1.6 mM).

\[ \cdot \text{OH} + \text{H}_2\text{O}_2 \rightarrow \cdot \text{OOH} + \text{H}_2\text{O} \quad (k = 3.3 \times 10^7 \text{ M}^{-1}\text{s}^{-1} [15]) \]  
\[ \cdot \text{OH} + \text{IBP} \rightarrow \text{transformation products} \quad (k = 6.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1} [45]) \]

Effect of H_2O_2 was however somewhat different regarding TOC removal. Increasing H_2O_2 concentration from 1.6 mM to 6.4 mM enhanced TOC conversion from 11% to 27%, but further increase to 22.4 mM resulted in only a slight positive effect (28% of mineralization), mainly due to some levelling off after 60 min (Fig. 3B). This kind of plateau in TOC removal profile was also observed in previous studies [20,25,26]. It might result from the complexation of iron active sites by oxidation intermediates, that hampered Fenton cycle [26], or to the formation of intermediates exhibiting slower rate constants for radical attack (especially small organic compounds, such as carboxylic acids [46]). Moreover, under excess of H_2O_2 higher iron leaching concentration was observed (0.1 mg/L of Fe at 22.4 mM H_2O_2 vs. 0.048 mg/L at 6.4 mM H_2O_2) which might be the result of higher complexation of surface iron.
3.2.3. Effect of temperature

Based on Arrhenius law, it is expected that an increase in temperature leads to a faster generation of hydroxyl radicals by the Fenton reaction. On the other hand, it also increases the rate of wasteful reactions, and temperature effect thus depends on the respective activation energies. Previous studies in heterogeneous Fenton oxidation using Fe ZSM5 catalyst reported that catalytic activity was improved by increasing temperature from 10 °C to 50 °C and no optimum value was observed [22,23,27,44].

Three levels of temperature, i.e., 15 °C, 25 °C and 45 °C, were investigated here, that only marginally affected IBP adsorption. Conversely, increasing temperature resulted in a clear enhancement of IBP oxidation rate constant: $k_{15°C} = 0.0057$ min$^{-1}$ ($R^2 = 0.9946$), $k_{25°C} = 0.0139$ min$^{-1}$ ($R^2 = 0.9976$), $k_{45°C} = 0.0470$ min$^{-1}$ ($R^2 = 0.9992$), leading to an apparent activation energy of 53 kJ/mol. TOC conversion was also improved at higher temperature, but to a lesser extent than IBP conversion (Fig. 4). As observed previously at the highest H$_2$O$_2$ concentration, the removal of TOC plateaued after 60 min for the experiment conducted at 45 °C, so that mineralization yield still did not exceed 28%. Actually, in this case, all H$_2$O$_2$ was consumed at the end of the experiment.

On the other hand, iron leaching was significantly higher at 45 °C (0.21 mg/L of Fe) than at 25 °C (0.048 mg/L) and 15 °C (0.046 mg/L), and possible contribution of homogeneous Fenton reaction was thus evaluated (see section 3.3).

Accounting for the moderate benefit and increased metal loss, room temperature was only considered for subsequent experiments.

3.2.4. pH effect

Heterogenization of the Fenton system usually overcomes the classical problems of loss of iron catalyst and narrow pH range (pH = 2-4). However, several studies using Fe ZSM5 catalyst reported that acidic conditions (pH = 3-4) were still necessary to obtain appreciable catalytic activity [23,27,44], while others indicated that this type of catalyst could work well under near neutral pH (pH = 4-6) [20,22,25,26]. Ve Šmejkalova et al. [20] observed that the oxidation rate of paracetamol over Fe MFI was similar with or without preliminary acidification of the solution (at pH 4, 2.8), probably due to the zeolite ability to significantly lower the pH. The acidity of Fe MFI could be ascribed to the presence of Brønsted and Lewis acid sites on zeolite framework [32].

Investigation of pH effect was here carried out close to neutral conditions (pH = 4.8) with or without pH control. This range was also chosen to mimic the pH of effluents from wastewater treatment plants which are usually buffered at circumneutral or slightly alkaline value [18,47,49]. Details of experimental conditions are given in Table 2.

A blank experiment confirmed that the mixture of IBP and H$_2$O$_2$ (6.4 mM) was stable after 5 hours at pH 8, because self decomposition of H$_2$O$_2$ occurs at pH > 10 [50].

Increasing the initial pH of the solution to 6 or 8 had negligible influence on IBP adsorption and oxidation: IBP concentration time profile, Fig. 5A, was almost superimposed to that obtained without pH adjustment. Regarding TOC removal, a moderate decrease in conversion was observed at the highest pH value (Fig. 5B). These results could be explained by the ability of Fe MFI to acidify all these solutions to wards almost a single pH value (pH$_i$ = 3.3-3.6) during the adsorption step (Table 2).

On the contrary, IBP adsorption was reduced from 25% to 5% (data not shown) and degradation kinetics was significantly hampered, if the reaction was performed under a controlled pH of 7 by continuous addition of NaOH during the experiment. IBP removal rate was found 12 times slower (k = 0.0012 min$^{-1}$) than under non controlled pH, and final TOC abatement decreased from 27% to 7% (with similar H$_2$O$_2$ consumption of 80%). Under this condition, IBP (pK$_a$ = 3.97) was in ionic form and zeolite surface (pH$_{ZSM}$ = 2.9) was negatively charged, thus leading to electrostatic repulsion. This observation would provide support for the hypothesis that OH attack of IBP mainly occurred on Fe MFI surface.

Similar trends were reported by Makhotkina et al. [44] for the wet peroxide oxidation of 1,1 dimethylhydrazine over Fe ZSM5 catalyst: the molecule abatement was lower at alkaline pH (pH = 8-10) compared to acidic pH (pH = 2-5). From measured activation energy of H$_2$O$_2$ decomposition (50 and 17 kJ mol$^{-1}$ in acidic and alkaline media, respectively), the authors concluded that high pH conditions favored non radical route. Reaction mechanism mediated by high valent iron species at neutral or alkaline pH was also proposed by other researchers [37,38].

An alternative explanation for this lower performance at pH 7 could lie in the reduction of OH oxidation potential at neutral pH (2.8 V at pH 3 vs 1.9 V at pH 7 [27]). Regarding iron leaching, increasing pH toward alkaline condition (pH controlled at 7) reduced the concentration of dissolved iron from 0.048 mg/L to 0.024 mg/L.

3.3. Activity of leached iron

Metal loss into the solution could initiate homogeneous Fenton reaction, whose contribution should depend not only on the concentration of dissolved iron, but also on the nature of the corresponding species (for instance free or as complexes).

It should be mentioned first that the concentration of leached iron measured in the present study (0.048 0.21 mg/L) corresponding to 0.03 0.13% of total iron content in Fe ZSM5) was in the lower range of that reported in previous works with Fe ZSM5 catalyst (0.040 4 mg/L or 0.4 7% of initial catalyst content) [20,22,25,26,28].

Nonetheless, to evaluate possible contribution of homogeneous Fenton reaction due to dissolved iron, activity of the leachates was also examined. The suspensions collected after heterogeneous oxidation experiment operated at 25 °C ([Fe] leached = 48 μg/L) and 45 °C ([Fe] leached = 210 μg/L) both with 4.8 g/L Fe MFI and 6.4 mM H$_2$O$_2$ were filtered on 0.2 μm pore size membrane. Then the leachates were complemented with IBP and H$_2$O$_2$ to match previous initial conditions. Fig. 6A and Fig. 6B compare the evolution of IBP and TOC concentrations during the reaction with Fe MFI catalyst and corresponding filtrate.

The leachate at 25 °C resulted in negligible IBP and TOC degradation, while only 21% conversion of IBP was observed for the other solution (210 μg/L of Fe at 45 °C). In line with this result, only marginal H$_2$O$_2$ consumptions were measured (< 10%), indicating that the
Table 2
Experimental conditions for pH effect.

<table>
<thead>
<tr>
<th>pH</th>
<th>( pHi_0 )</th>
<th>( pHi_1 )</th>
<th>( pHi_2 )</th>
<th>pH setting method</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3</td>
<td>4.3</td>
<td>3.3</td>
<td>3.2</td>
<td>Experiment was conducted with synthetic IBP solution without pH adjustment</td>
</tr>
<tr>
<td>6.0</td>
<td>6.0</td>
<td>3.3</td>
<td>3.2</td>
<td>pH of the solution was set to 6.0 using NaOH 1 M before contact with solid catalyst</td>
</tr>
<tr>
<td>8.0</td>
<td>8.0</td>
<td>3.6</td>
<td>3.5</td>
<td>pH of the solution was set to 8.0 using NaOH 1 M before contact with solid catalyst</td>
</tr>
<tr>
<td>7.0 (control 0)</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>pH of the solution was adjusted to 7.0 (± 0.2) using NaOH 1 M during the experiment</td>
</tr>
</tbody>
</table>

pHi: initial pH of the solution, pHi: pH of the solution after adsorption step, pHi: pH of the solution at the end of reaction.

3.4. Catalyst evolution

SEM/EDX analysis showed no major modification of the catalyst morphology and surface iron content after Fenton reaction (3.3 ± 1.0%), which is consistent with the very low iron leaching measured in the final solutions. For the 1 g/L experiment, carbon content on Fe MFI decreased from 0.35% after preliminary adsorption (in rather good agreement with IBP adsorbed amount) to 0.28% after 3 hours of Fenton oxidation. It is accordance with the corresponding limited TOC removal (about 5%) measured in solution. Note that it was not possible to determine the residual carbon content for the experiments with 4.8 g/L of catalyst, because the carbon content after adsorption was below the detection limit (0.1%). In this case, BET surface area and microporous volume of the catalyst were only slightly reduced after use (by 10% maximum).

In Velichkova et al. [20] Fe MFI stability was assessed by catalyst recycling, as well as over 40 h of continuous operation mode where the solid was retained by a microfiltration membrane. In both cases, Fe MFI exhibited almost unchanged activity. Given that iron leaching was about one order of magnitude lower in the present study and pollutant adsorption did not modify \( \text{H}_2\text{O}_2 \) decomposition by the catalyst, no significant deactivation is expected.

3.5. IBP degradation pathways

Fig. 6. Activity of leachate for Fenton oxidation: evolution of (A) IBP and (B) TOC concentration ([IBP] = 20 mg/L, [Fe-MFI] = 4.8 g/L, \( [\text{Fe}^{2+}] \) = 48 μg/L, \( [\text{Fe}^{3+}] \) = 210 μg/L, \( [\text{H}_2\text{O}_2] \) = 6.4 mM, \( [\text{H}_2\text{O}] \) = 4.3, \( T = 25^\circ \text{C} \) and \( 45^\circ \text{C} \) (control contacts). Results of heterogeneous Fenton oxidations are recalled for comparison.

amount of dissolved iron was too small to yield appreciable decom position rate and/or the corresponding species exhibited negligible activity. This confirms that Fenton oxidation of IBP over Fe MFI was mainly induced by surface iron species.

Up to 14 transformation products of IBP (including several isomers) were detected during Fenton oxidation on Fe MFI (Table 3). Among them, three could be unequivocally identified thanks to available standards: 1 hydroxy IBP (referred to as TP1A), 2 hydroxy IBP (TP1B) and 4 isobutylacetophenone (TP4). Table 3 also shows that most of these intermediates were present in the homogeneous reaction, confirming analogous mechanisms.

In agreement with the literature [51-55], mono hydroxylated in termediates were detected, as depicted in our case referred to as TP1A (D), among which those classically mentioned: 2 hydroxy IBP (TP1A) and 2 hydroxy IBP (TP1B). These products can be formed by hydroxylation of IBP, taking place either on the side chains (methylpropyl moiety or phenylpropionic moiety) [51,53] or on the aromatic ring [54,55]. These hydroxylated adducts can undergo further hydroxylation yielding dihydroxylated IBP (TP2A) and tri hydroxylated IBP (TP3A). They are consistent with a free radical mechanism.

In parallel to hydroxylation route, dehydroxylation of hydroxylated IBP yields 4 isobutylacetophenone (TP4) [51,52,55]. Isomer of TP4 was also observed, referred to as TP5. Next, TP6 (CH\(_3\)OH) could be formed by successive hydroxylation and loss of terminal propyl group from TP4 [53]. TP6 was an isomer of 4 ethylbenzaldehyde, but in the absence of structural information its formation pathway could not be clearly derived. It was probably similar to that of TP6. Finally, ring opening could lead to the formation of small aliphatic molecules, such as TP9 (CH\(_2\)OH) in addition, as an alternative degradation pathway of IBP might go through the cleavage of isobutyl moiety from IBP, forming TP7 (CH\(_3\)OH) [55].
Table 3
Identified compounds from HPLC-HRMS.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Molecule</th>
<th>tₘ (min)</th>
<th>Ion mode</th>
<th>m/z</th>
<th>Fe-MFI</th>
<th>FeSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP1A</td>
<td>C₂₂H₂₄O₃</td>
<td>19.75</td>
<td>Neg</td>
<td>221.118</td>
<td>D</td>
<td>ND</td>
</tr>
<tr>
<td>TP1B</td>
<td>C₂₂H₂₄O₃</td>
<td>18.70</td>
<td>Neg</td>
<td>221.118</td>
<td>D</td>
<td>ND</td>
</tr>
<tr>
<td>TP1C</td>
<td>C₂₂H₂₄O₃</td>
<td>21.15</td>
<td>Neg</td>
<td>221.118</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>TP1D</td>
<td>C₂₂H₂₄O₃</td>
<td>22.15</td>
<td>Neg</td>
<td>221.118</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>TP2A</td>
<td>C₂₂H₂₄O₃</td>
<td>19.8</td>
<td>Neg</td>
<td>237.113</td>
<td>ND</td>
<td>D</td>
</tr>
<tr>
<td>TP2B</td>
<td>C₂₂H₂₄O₃</td>
<td>20.05</td>
<td>Neg</td>
<td>237.113</td>
<td>D</td>
<td>ND</td>
</tr>
<tr>
<td>TP2C</td>
<td>C₂₂H₂₄O₃</td>
<td>20.50</td>
<td>Neg</td>
<td>237.113</td>
<td>D</td>
<td>ND</td>
</tr>
<tr>
<td>TP2D</td>
<td>C₂₂H₂₄O₃</td>
<td>18.35</td>
<td>Neg</td>
<td>253.108</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>TP3A</td>
<td>C₂₂H₂₄O₃</td>
<td>18.65</td>
<td>Neg</td>
<td>253.108</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>TP3B</td>
<td>C₂₂H₂₄O₃</td>
<td>19.15</td>
<td>Neg</td>
<td>253.108</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>TP3C</td>
<td>C₂₂H₂₄O₃</td>
<td>25.1</td>
<td>Pos</td>
<td>177.127</td>
<td>D</td>
<td>ND</td>
</tr>
<tr>
<td>TP4</td>
<td>C₂₂H₂₄O₃</td>
<td>20.95</td>
<td>Neg</td>
<td>175.111</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>TP5</td>
<td>C₂₂H₂₄O₃</td>
<td>16.75</td>
<td>Neg</td>
<td>163.040</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>TP6</td>
<td>C₂₂H₂₄O₃</td>
<td>16.8</td>
<td>Neg</td>
<td>140.061</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>TP7</td>
<td>C₂₂H₂₄O₃</td>
<td>17.7</td>
<td>Neg</td>
<td>133.066</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>TP8</td>
<td>C₂₂H₂₄O₃</td>
<td>~4.0</td>
<td>Neg</td>
<td>117.056</td>
<td>D</td>
<td>D</td>
</tr>
</tbody>
</table>

* confirmed by standard.
* isomer of TP1A.
* isomer of TP2A.
* isomer of TP3A.

3.6. Effect of water matrix

According to the literature [56,57], organic and inorganic compounds in wastewater may affect the heterogeneous reaction by (i) fouling the catalyst pores, (ii) poisoning the catalyst active sites (from active sites forming complexes with organic and/or inorganic compounds), (iii) scavenging hydroxyl radicals and (iv) increasing the pH value. Therefore, the catalytic activity of Fe MFI catalyst was also evaluated in the presence of wastewater (WW) matrix.

Effluent from a municipal wastewater treatment plant located in Nantux (France) was used to prepare the IBP solution. The physicochemical characteristics of this effluent are shown in Table 4. First, IBP concentration was set to 20 mg/L as usual, which resulted in an initial TOC concentration of 25 mg/L for the solution (with IBP as major organic compound, contributing to 60% of TOC). It is worth noting that during preliminary adsorption step, Fe MFI catalyst was not able to reduce the pH to acidic value (as observed in experiments carried out in distillated water) due to the presence of natural buffer in WW matrix. In this matrix, pH value was only reduced from 8.0 to 7.0 after contact with Fe MFI.

By comparing the oxidation performance to that observed in distilled water (DW), it is clear that IBP degradation rate was significantly lowered in wastewater matrix (WW) (Fig. 7): first order rate constant varied from 0.0139 min⁻¹ (DW pH 7.0) to 0.0016 min⁻¹ (WW pH 7.0). Among possible adverse effects, that of pH was evidenced by

Fig. 7. Effect of wastewater effluent (WW) matrix on heterogeneous Fenton oxidation: evolution of (A) IBP and (B) TOC concentration ([IBP]₀ = 20 mg/L, [Fe-MFI] = 4.8 g/L, [H₂O₂]₀ = 6.4 mM, c controlled, nc: not controlled, T = 25°C). Results of Fenton oxidations performed in distilled water (DW) are recalled for comparison.

Table 4
Physicochemical properties of the wastewater effluent.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.0</td>
</tr>
<tr>
<td>Turbidity (FNU)</td>
<td>1</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>TC (mg/L)</td>
<td>39.2</td>
</tr>
<tr>
<td>IC (mg/L)</td>
<td>29.4</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>9.8</td>
</tr>
<tr>
<td>Total Fe (mg/L)</td>
<td>&lt; 0.05</td>
</tr>
</tbody>
</table>
alkalinized DW (about 4 mg/L adsorbed) and same H₂O₂ consumption (79%) was also observed in both matrices excluding catalyst in activation by compounds from WW. Despite its IC content was reduced by almost 40% by contacting with Fe MFI, scavenging effect of residual carbonate and bicarbonate ions might explain slightly lower IBP removal in WW as compared to DW at pH 7.

In order to confirm the dominant role of pH in WW matrix, a supplementary experiment was conducted in WW matrix whose initial pH was set to 3.3 (adjusted with 1 M H₂SO₄, denoted as WW pH 3.3). This pH value matched the value reached in DW after contact with Fe MFI.

Similar role of pH was observed for mineralization yield. Under non-controlled pH, TOC removal by Fenton oxidation was reduced from 29.0 to 5.6 mg/L) and maintained the catalytic activity of the heterogeneous catalysis. As shown in Fig. 7A, same IBP removal was indeed obtained in DW and acidified WW matrix.

Iron containing zeolite of ZSM5 type was found to efficiently catalyze wet peroxide oxidation of IBP at acidic pH values driven by the zeolite surface, as the result of dominant free radical mechanism in doused by iron surface species and probably implying adsorbed IBP. The formation of hydroxylated species, similar to the homogeneous reaction, was also consistent with OH mediated mechanism.

In the investigated ranges, the reaction followed a pseudo first order kinetics with respect to IBP and the rate constant increased almost proportionally with catalyst loading and hydrogen peroxide concentration. Temperature rise was also beneficial, resulting in activation energy of 53 kJ/mol.

However, both adsorption capacity and catalytic activity of the Fe zeolite were significantly hindered in neutral to alkaline buffered solutions, which mainly explained its reduced performance in wastewater matrix. Radical scavenging and competition for active sites by inorganic and organic compounds present in the effluent were also evidenced.

Therefore, preliminary acidification and pre-concentration steps should be considered for the heterogeneous Fenton oxidation of pharmaceuticals in real water matrix, which usually involve low drug concentrations and neutral buffered pH conditions.

Acknowledgement

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References


4. Conclusion

Iron containing zeolite of ZSM5 type was found to efficiently catalyze wet peroxide oxidation of IBP at acidic pH values driven by the zeolite surface, as the result of dominant free radical mechanism in doused by iron surface species and probably implying adsorbed IBP. The formation of hydroxylated species, similar to the homogeneous reaction, was also consistent with OH mediated mechanism.

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Therefore, preliminary acidification and pre-concentration steps should be considered for the heterogeneous Fenton oxidation of pharmaceuticals in real water matrix, which usually involve low drug concentrations and neutral buffered pH conditions.


