



HAL
open science

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

Sandyanto Adityosulindro, Carine Julcour-Lebigue, Laurie Barthe

► **To cite this version:**

Sandyanto Adityosulindro, Carine Julcour-Lebigue, Laurie Barthe. Heterogeneous Fenton oxidation using Fe-ZSM5 catalyst for removal of ibuprofen in wastewater. *Journal of Environmental Chemical Engineering*, 2018, 6 (5), pp.5920-5928. 10.1016/j.jece.2018.09.007 . hal-01942287

HAL Id: hal-01942287

<https://hal.science/hal-01942287>

Submitted on 3 Dec 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Open Archive Toulouse Archive Ouverte

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible

This is an author's version published in: <http://oatao.univ-toulouse.fr/21070>

Official URL: <https://doi.org/10.1016/j.jece.2018.09.007>

To cite this version:

Adityosulindro, Sandyanto^{ORCID} and Julcour-Lebigue, Carine^{ORCID} and Barthe, Laurie^{ORCID} *Heterogeneous Fenton oxidation using Fe-ZSM5 catalyst for removal of ibuprofen in wastewater.* (2018) *Journal of Environmental Chemical Engineering*, 6 (5). 5920-5928. ISSN 2213-3437

Any correspondence concerning this service should be sent to the repository administrator: tech-oatao@listes-diff.inp-toulouse.fr

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

Sandyanto Adityosulindro^{a,b}, Carine Julcour^{a,*}, Laurie Barthe^a

^a *Laboratoire de Génie Chimique, Université de Toulouse, CNRS, Toulouse, France*

^b *Environmental Engineering Study Program, Civil Engineering Department, Universitas Indonesia, Depok, 16424, Indonesia*

A B S T R A C T

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.

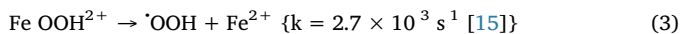
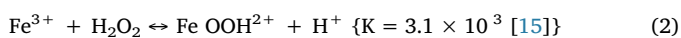
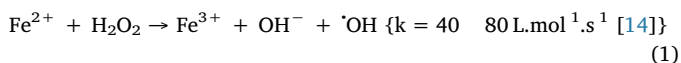
1. Introduction

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 ($\cdot\text{OH}$), 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 ($\cdot\text{OH}$) (Eq. (1)). Formation of stable ferric complexes (such as Fe OOH^{2+} , Eq. (2)) hinders the catalytic cycle due to their slow decomposition into Fe^{2+} (Eq. (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, 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 consumed pharmaceuticals worldwide. A recent study has reported that exposure to ibuprofen at high concentration (0.25 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 $\mu\text{g/L}$) 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, H_2O_2 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 $\text{C}_{13}\text{H}_{18}\text{O}_2$, purity 99.99%) was supplied by BASF Corporation and used as received. H_2O_2 solution 30% w/w, mono potassium phosphate (KH_2PO_4), sodium phosphate dibasic dehydrate ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$), potassium iodide (KI), titanium tetrachloride (TiCl_4), sodium sulfite (Na_2SO_3), sulfuric acid (H_2SO_4 , 1 M) and sodium

Table 1
Properties of Fe-MFI.

Properties	
Si/Al ratio	27 ^a
Fe content (wt. %)	3.4 ^b
Fe dispersion (%)	22 ^c
$d_{\text{c,CO}}$ (nm)	4 ^c
S_{BET} (m^2/g)	329 ^d
$V_{\text{Mesopores}}$ (cm^3/g)	0.05 ^d
$V_{\text{Micropores}}$ (cm^3/g)	0.13 ^d
V_{Porous} (cm^3/g)	0.18 ^d
d_{43} (μm)	7.9 ^e
pH_{pzc}	2.9 ^f

^a as given by the supplier.

^b Iron content from ICP-AES analysis of acid leachate.

^c Metal dispersion and mean diameter of metal crystallites calculated from CO chemisorption.

^d Specific surface area, mesoporous, microporous and total porous volumes measured by N_2 porosimetry.

^e Volume mean diameter of particles in suspension (laser diffraction method).

^f pH at the point of zero charge measured by mass titration.

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.

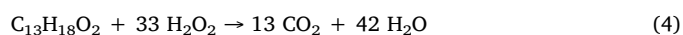
2.2. Experimental setup and protocols

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 H_2O_2 (without catalyst) at two or seven times the stoichiometric amount (cf. Eq. (4)) did not result in any measurable IBP and H_2O_2 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 Brønsted 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 H_2O_2 into the slurry (t_0). The stoichiometric amount of H_2O_2 required for IBP mineralization was calculated according to the following equation:



Aliquots samples (9 mL) were withdrawn throughout the oxidation step (at $t = 5, 10, 30, 60, 120, 180$ min) and filtered onto $0.45 \mu\text{m}$ regenerated cellulose (RC) syringe filter. To prevent further oxidation, the filtered samples were immediately treated by phosphate buffer (mixture of KH_2PO_4 0.05 M and $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ 0.05 M) or quenching solution (mixture of phosphate buffer, KI 0.1 M and Na_2SO_3 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 membrane filter with $0.22 \mu\text{m}$ pore size (GSWP, Merck Millipore) for further analyses of liquid and solid phases.

Effects of Fe MFI concentration (1–4.8 g/L), H_2O_2 concentration (1.6–22.4 mM, corresponding to 0.5–7 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, H_2O_2 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 the reproducibility 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 H_2O_2 concentrations.

2.3. Analytical methods

Concentration of IBP during reaction was measured by liquid chromatography (HPLC) with UV detection at $\lambda = 222 \text{ nm}$ (PDA detector, Thermo Finnigan). Separation was performed on a C18 reverse phase column (ProntoSIL C18 AQ $5 \mu\text{m}$, $250 \times 4 \text{ mm}$). 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 analysis (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 $0.45 \mu\text{m}$ RC syringe filter and diluted by twofold with ultrapure water before being analyzed (injection volume was set to 50 μL and 400 μL for TC and IC, respectively).

Residual concentration of H_2O_2 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 TiCl_4 solution and 1 mL of 1 M H_2SO_4 to form a yellow pertitanic acid complex detected at $\lambda = 410 \text{ nm}$.

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 resolution 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 PFP2, $150 \text{ mm} \times 2 \text{ mm}$, $3 \mu\text{m}$). Mobile phases were: (A) Ultrapure water acidified with formic acid 0.1% (v/v) and (B) Acetonitrile. Elution was conducted at 40 °C in gradient mode: 3% B in 0–5 min, 3–95% B in 5–25 min, 95% 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 , respectively. 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

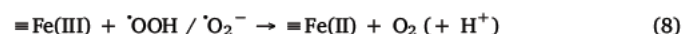
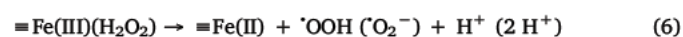
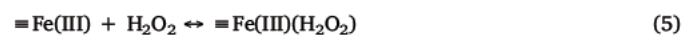
mass range between m/z 50 and 1000. Prediction of compound formula and noise reduction were realized by Xcalibur software (version 2, Thermo scientific Inc.) and MetAlign software (version 041011, Arjen Lommen).

3. Results and discussion

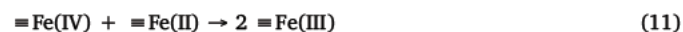
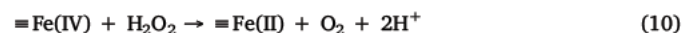
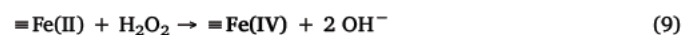
3.1. Mechanism of Fenton oxidation of IBP over Fe MFI

Compared to its homogeneous counterpart, the mechanism of heterogeneous Fenton reaction has been less investigated and is still subject 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 $\cdot\text{OH}$):



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



Where \equiv indicates species on catalyst surface

Using the same theoretical amount of accessible iron (1 g/L of Fe MFI $\sim 0.134 \text{ mM}$ of surface Fe), Fenton oxidation catalyzed by Fe MFI started at a much lower rate than the homogeneous reaction performed with ferrous salt (FeSO_4) (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 ($> 10 \text{ mg/L}$) [14]. Nonetheless, 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 H_2O_2 decomposition by Fe MFI catalyst, oxidant consumption was also monitored without IBP (using 1 g/L of Fe MFI). It resulted into 31% of H_2O_2 conversion after 180 min, which was similar to that measured during the oxidation of IBP (26%), indicating

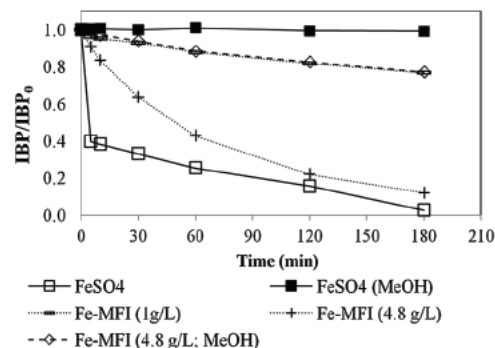


Fig. 1. Fenton oxidation of IBP over Fe-MFI and FeSO_4 catalysts ($[\text{IBP}]_0 = 20 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 6.4 \text{ mM}$, $T = 25 \text{ }^\circ\text{C}$, $[\text{MeOH}] = 50 \text{ mM}$; heterogeneous Fenton: $[\text{Fe-MFI}] = 1$ and 4.8 g/L , $\text{pH}_0 = 4.3$; homogeneous Fenton: $[\text{Fe}^{2+}] = 0.134 \text{ mM}$, $\text{pH}_0 = 2.6$).

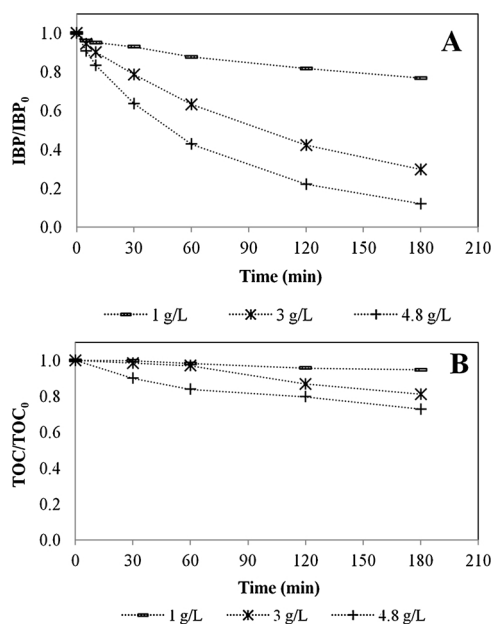


Fig. 2. Effect of Fe-MFI concentration on Fenton oxidation: evolution of (A) IBP and (B) TOC concentration ($[IBP]_0 = 20 \text{ mg/L}$, $[Fe\text{-MFI}] = 1\text{-}4.8 \text{ g/L}$, $[H_2O_2]_0 = 6.4 \text{ mM}$, $pH_0 = 4.3$, $T = 25 \text{ }^\circ\text{C}$).

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 $9.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ [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 led 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: $k_{1\text{g/L}} = 0.0014 \text{ min}^{-1}$ ($R^2 = 0.9741$), $k_{3\text{g/L}} = 0.0071 \text{ min}^{-1}$ ($R^2 = 0.9984$), $k_{4.8\text{g/L}} = 0.0139 \text{ min}^{-1}$ ($R^2 = 0.9976$). 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

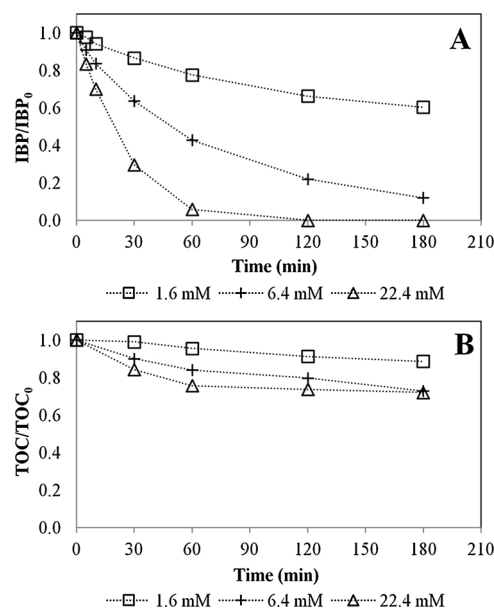
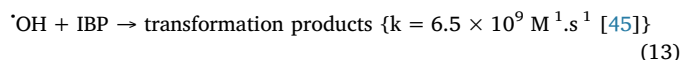
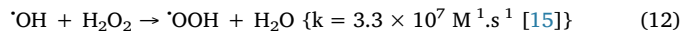


Fig. 3. Effect of H_2O_2 concentration on Fenton oxidation: evolution of (A) IBP and (B) TOC concentration ($[IBP]_0 = 20 \text{ mg/L}$, $[Fe\text{-MFI}] = 4.8 \text{ g/L}$, $[H_2O_2] = 1.6\text{-}22.4 \text{ mM}$, $pH_0 = 4.3$, $T = 25 \text{ }^\circ\text{C}$).

by an increase in initial H_2O_2 concentration until an optimum value is reached; then scavenging of $\cdot\text{OH}$ 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: $k_{1.6 \text{ mM}} = 0.0029 \text{ min}^{-1}$ ($R^2 = 0.9678$), $k_{6.4 \text{ mM}} = 0.0139 \text{ min}^{-1}$ ($R^2 = 0.9976$), $k_{22.4 \text{ mM}} = 0.0411 \text{ min}^{-1}$ ($R^2 = 0.9983$). According to the corresponding rate constants, reaction of $\cdot\text{OH}$ 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).



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.

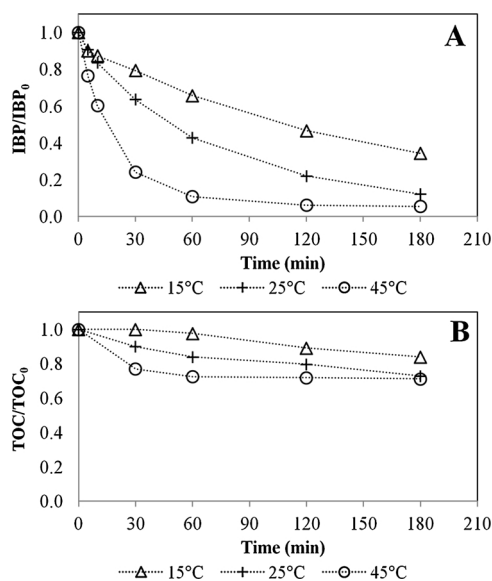


Fig. 4. Effect of temperature on Fenton oxidation: evolution of (A) IBP and (B) TOC concentration ($[IBP]_0 = 20 \text{ mg/L}$, $[Fe\text{-MFI}] = 4.8 \text{ g/L}$, $[H_2O_2]_0 = 6.4 \text{ mM}$, $pH_0 = 4.3$, $T = 15 - 45^\circ\text{C}$).

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 80°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: $k_{15^\circ\text{C}} = 0.0057 \text{ min}^{-1}$ ($R^2 = 0.9946$), $k_{25^\circ\text{C}} = 0.0139 \text{ min}^{-1}$ ($R^2 = 0.9976$), $k_{45^\circ\text{C}} = 0.0470 \text{ min}^{-1}$ ($R^2 = 0.9992$), 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_2O_2 concentration, the removal of TOC plateaued after 60 min for the experiment conducted performed at 45°C , so that mineralization yield still did not exceed 28%. Actually, in this case, all H_2O_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 benefice 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]. Velichkova et al. [20] observed that the oxidation rate of paracetamol over Fe MFI was similar with or without preliminary acidification of the solution (at $pH_0 = 2.8$), 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_2O_2 (6.4 mM) was stable after 5 hours at pH 8, because self decomposition of H_2O_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 towards 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 ($k = 0.0012 \text{ min}^{-1}$) than under non controlled pH, and final TOC abatement decreased from 27% to 7% (with similar H_2O_2 consumption of 80%). Under this condition, IBP ($pK_a = 3.97$) was in ionic form and zeolite surface ($pH_{PZC} = 2.9$) was negatively charged, thus leading to electrostatic repulsion. This observation would provide support for the hypothesis that $\cdot\text{OH}$ 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_2O_2 decomposition (50 and $17 \text{ kJ}\cdot\text{mol}^{-1}$ 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 $\cdot\text{OH}$ 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 ($0.048 - 0.21 \text{ mg/L}$ 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 ($0.040 - 0.4 \text{ mg/L}$ 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 = $48 \mu\text{g/L}$) and 45°C ($[Fe]$ leached = $210 \mu\text{g/L}$) both with 4.8 g/L Fe MFI and 6.4 mM H_2O_2 were filtered on $0.2 \mu\text{m}$ pore size membrane. Then the leachates were complemented with IBP and H_2O_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 ($210 \mu\text{g/L}$ of Fe at 45°C). In line with this result, only marginal H_2O_2 consumptions were measured ($< 10\%$), indicating that the

Table 2
Experimental conditions for pH effect.

Experiment	pH ₀	pH _i	pH _f	pH setting method
pH 4.3	4.3	3.3	3.2	Experiment was conducted with synthetic IBP solution without pH adjustment
pH 6.0	6.0	3.3	3.2	pH of the solution was set to 6.0 using NaOH 1 M before contact with solid catalyst
pH 8.0	8.0	3.6	3.5	pH of the solution was set to 8.0 using NaOH 1 M before contact with solid catalyst
pH 7.0 (controlled)	7.0	7.0	7.0	pH of the solution was adjusted to 7.0 (± 0.2) using NaOH 1 M during the experiment

pH₀: initial pH of the solution, pH_i: pH of the solution after adsorption step, pH_f: pH of the solution at the end of reaction.

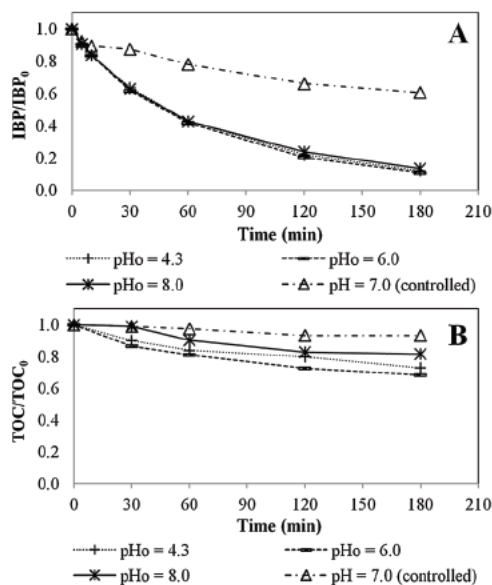


Fig. 5. Effect of pH on Fenton oxidation: evolution of (A) IBP and (B) TOC concentration ([IBP]₀ = 20 mg/L; [Fe-MFI] = 4.8 g/L, [H₂O₂]₀ = 6.4 mM, pH₀ = 4.3-8.0 or pH controlled at 7.0, T = 25 °C).

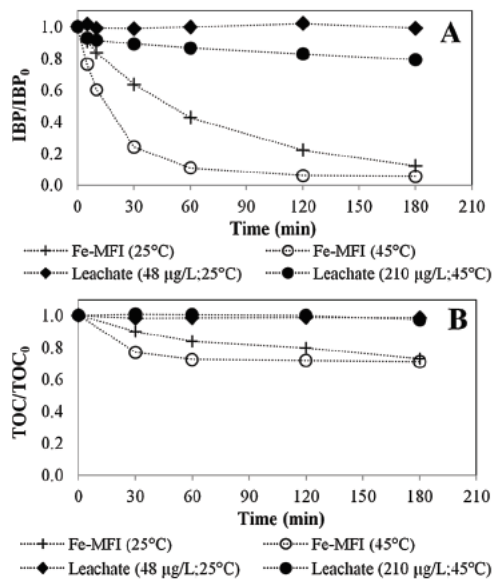


Fig. 6. Activity of leachate for Fenton oxidation: evolution of (A) IBP and (B) TOC concentration ([IBP]₀ = 20 mg/L, [Fe-MFI] = 4.8 g/L, [Fe]_{leachate} = 48 µg/L (25 °C) and 210 µg/L (45 °C), [H₂O₂]₀ = 6.4 mM, pH_{0 Fe MFI} = 4.3, pH_{0 leachate} = 3.2, T = 25 °C and 45 °C) (*before contact). Results of heterogeneous Fenton oxidations are recalled for comparison.

amount of dissolved iron was too small to yield appreciable decomposition 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.

3.4. Catalyst evolution

SEM/EDX analysis showed no major modification of the catalyst morphology and surface iron content after Fenton reaction ($3.3 \pm 1.0\%$), 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 H₂O₂ decomposition by the catalyst, no significant deactivation is expected.

3.5. IBP degradation pathways

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 intermediates were detected, up to 4 in our case referred to as TP1(A, D), among which those classically mentioned: 1 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 di hydroxylated IBP (TP2(A, C)) and tri hydroxylated IBP (TP3(A, C)). They are consistent with a free radical mechanism.

In parallel to hydroxylation route, decarboxylation of hydroxylated IBP yields 4 isobutylacetophenone (TP4) [51,52,55]. Isomer of TP4 was also observed, referred to as TP5. Next, TP6 (C₉H₈O₃) could be formed by successive hydroxylation and loss of terminal propyl group from TP4 [53]. TP8 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 (C₅H₁₀O₃). In addition, an alternative degradation pathway of IBP might go through the cleavage of isobutyl moiety from IBP, forming TP7 (C₉H₁₀O₂) [55].

Table 3
Identified compounds from HPLC-HRMS.

Abbreviation	Molecule	t _R (min)	Ion mode	m/z	Fe-MFI	FeSO ₄
TP1A	C ₁₃ H ₁₈ O ₃ (1-hydroxy-IBP) ^a	19.75	Neg	221.118	D	ND
TP1B	C ₁₃ H ₁₈ O ₃ (2-hydroxy-IBP) ^a	18.70	Neg	221.118	D	ND
TP1C ^b	C ₁₃ H ₁₈ O ₃	21.15	Neg	221.118	D	D
TP1D ^b	C ₁₃ H ₁₈ O ₃	22.15	Neg	221.118	D	D
TP2A	C ₁₃ H ₁₈ O ₄	19.8	Neg	237.113	ND	D
TP2B ^c	C ₁₃ H ₁₈ O ₄	20.05	Neg	237.113	D	ND
TP2C ^c	C ₁₃ H ₁₈ O ₄	20.50	Neg	237.113	ND	D
TP3A	C ₁₃ H ₁₈ O ₅	18.35	Neg	253.108	D	D
TP3B ^d	C ₁₃ H ₁₈ O ₅	18.65	Neg	253.108	D	D
TP3C ^d	C ₁₃ H ₁₈ O ₅	19.15	Neg	253.108	D	D
TP4	C ₁₂ H ₁₆ O 4-isobutylacetophenone ^a	25.1	Pos	177.127	D	ND
TP5 ^e	C ₁₂ H ₁₆ O	20.95	Neg	175.111	D	D
TP6	C ₉ H ₈ O ₃	16.75	Neg	163.040	D	D
TP7	C ₉ H ₁₀ O ₂	16.8	Neg	149.061	D	D
TP8	C ₉ H ₁₀ O	17.7	Neg	133.066	D	D
TP9	C ₅ H ₁₀ O ₃	~4.0	Neg	117.056	D	D

^a confirmed by standard.

^b isomer of TP1A.

^c isomer of TP2A.

^d isomer of TP3A.

^e isomer of TP4, D: detected, ND: not detected, Fe-MFI: heterogeneous Fenton oxidation, FeSO₄: homogeneous Fenton oxidation.

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 (iron 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 Nailloux village (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 distilled 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 nc) to 0.0016 min⁻¹ (WW pH nc). Among possible adverse effects, that of pH was evidenced by

Table 4
Physicochemical properties of the wastewater effluent.

Parameters	
pH	8.0
Turbidity (FNU)	1
BOD (mg/L)	< 2
COD (mg/L)	< 30
TC (mg/L)	39.2
IC (mg/L)	29.4
TOC (mg/L)	9.8
Total Fe (mg/L)	< 0.05

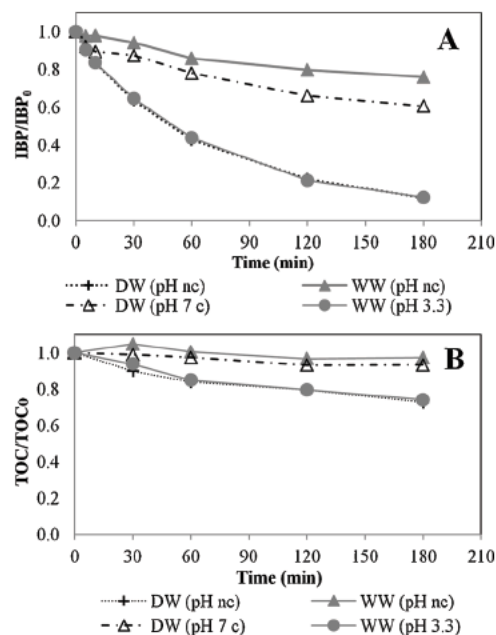


Fig. 7. Effect of wastewater effluent (WW) matrix on heterogeneous Fenton oxidation: evolution of (A) IBP and (B) TOC concentration ([IBP]₀ = 20 mg/L, [Fe-MFI] = 4.8 g/L, [H₂O₂]₀ = 6.4 mM, c: controlled, nc: not controlled, T = 25 °C). Results of Fenton oxidations performed in distilled water (DW) are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

comparison to the results obtained in DW with pH controlled to 7 (DW pH 7 c) (Fig. 7). As described previously in § 3.2.4, alkaline pH solution can affect heterogeneous Fenton oxidation by (i) limiting the interaction between ibuprofen and catalyst (repulsion between ionic form of IBP and negatively charged Fe MFI surface), (ii) by reducing the oxidation potential of hydroxyl radical, or (iii) by changing the reaction mechanism from radical to non radical one.

Nonetheless, IBP oxidation was still slower in WW matrix than in DW at pH 7. One possible explanation is catalyst fouling or poisoning. Actually, TOC adsorption on Fe FMI was very similar in WW and

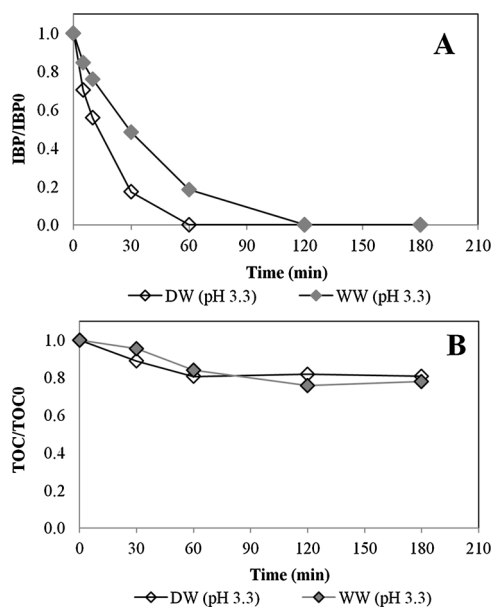


Fig. 8. Effect of wastewater effluent (WW) matrix on heterogeneous Fenton oxidation of IBP at low concentration: evolution of (A) IBP and (B) TOC concentration. ($[IBP]_0 = 5 \text{ mg/L}$, $[Fe\text{-MFI}] = 4.8 \text{ g/L}$, $[H_2O_2]_0 = 6.4 \text{ mM}$, $T = 25 \text{ }^\circ\text{C}$). Results of Fenton oxidation performed in distilled water (DW) are given for comparison.

alkalinized DW (about 4 mg/L adsorbed) and same H_2O_2 consumption (79%) was also observed in both matrixes excluding catalyst inactivation 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 H_2SO_4 , denoted as WW pH 3.3). This pH value matched the value reached in DW after contact with Fe MFI. Such acidification eliminated most of inorganic carbon content (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.

Similar role of pH was observed for mineralization yield. Under non controlled pH, TOC removal by Fenton oxidation was reduced from 27% (DW pH nc) to 3% (WW pH nc), but the efficacy of the process could be normalized by acid addition (WW pH 3.3) (Fig. 7B). Moreover, it should be mentioned that the acidification step caused more iron leaching (0.081 mg/L for WW pH nc vs. 0.250 mg/L for WW pH 3.3), but below values for significant effect (cf. § 3.3).

The effect of initial concentration of IBP was also addressed: IBP solution at 5 mg/L (accounting for 3.8 mg/L of TOC) was prepared with either WW or DW and oxidation tests were performed at acidic pH (set at 3.3 with 1 M H_2SO_4) to eliminate alkaline buffering and radical scavenging effects. Under these conditions, both adsorption yield and oxidation rate constant of IBP (Fig. 8A) were lower in WW: they respectively varied from 30% and 0.0579 min^{-1} in DW to 23% and 0.0236 min^{-1} in WW. This indicates that compounds from WW also competed with IBP for Fe MFI surface sites, but this effect contributed to a limited extent to the performance reduction in WW. On the other hand, TOC conversion was relatively similar in DW and WW (Fig. 8B). In addition, IBP degradation rate increased with a decrease in initial IBP concentration (Fig. 7A and Fig. 8A), which is typical for free radical based processes [10,14,23].

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 induced by iron surface species and probably implying adsorbed IBP. The formation of hydroxylated species, similar to the homogeneous reaction, was also consistent with $\cdot OH$ 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 pharmaceutical contaminants in real water matrix, which usually involve low drug concentrations and neutral buffered pH conditions.

Acknowledgement

Financial support by ANR (French National Research Agency) through ANR project "SOFENCoMEM" (ANR 14 CE04 0006) and RISTEKDIKTI (Ministry of Research, Technology and Higher Education of Indonesia) for the scholarship of S. Adityosulindro (No. 2017/E4.4/K/2013) are gratefully acknowledged. The authors also thank A. Tişler (Süd Chemie AG, Clariant) for providing the zeolite, D. Riboul, G. Guittier, M.L. Pern and M.L. de Solan Bethmale (LGC Toulouse) for their help and expert advice on the analytical techniques, J.L. Labat (LGC Toulouse) for the implementation of the experimental set up and P. Calvet from Nailloux WWTP for wastewater samples.

References

- [1] C. Miège, J.M. Choubert, L. Ribeiro, M. Eusèbe, M. Coquery, Fate of pharmaceuticals and personal care products in wastewater treatment plants – Conception of a database and first results, *Environ. Pollut.* 157 (2009) 1721–1726, <https://doi.org/10.1016/j.envpol.2008.11.045>.
- [2] T. Deblonde, C. Cossu-Leguille, P. Hartemann, Emerging pollutants in wastewater: a review of the literature, *Int. J. Hyg. Environ. Health* 214 (2011) 442–448, <https://doi.org/10.1016/j.ijheh.2011.08.002>.
- [3] L. Berthod, D.C. Whitley, G. Roberts, A. Sharpe, R. Greenwood, G.A. Mills, Quantitative structure-property relationships for predicting sorption of pharmaceuticals to sewage sludge during waste water treatment processes, *Sci. Total Environ.* 579 (2017) 1512–1520, <https://doi.org/10.1016/j.scitotenv.2016.11.156>.
- [4] M. Carballa, F. Omil, J.M. Lema, Removal of cosmetic ingredients and pharmaceuticals in sewage primary treatment, *Water Res.* 39 (2005) 4790–4796, <https://doi.org/10.1016/j.watres.2005.09.018>.
- [5] A. Ziyilan, N.H. Ince, The occurrence and fate of anti-inflammatory and analgesic pharmaceuticals in sewage and fresh water: Treatability by conventional and non-conventional processes, *J. Hazard. Mater.* 187 (2011) 24–36.
- [6] J. Rivera-Utrilla, M. Sánchez-Polo, M.Á. Ferro-García, G. Prados-Joya, R. Ocampo-Pérez, Pharmaceuticals as emerging contaminants and their removal from water. A review, *Chemosphere.* 93 (2013) 1268–1287.
- [7] Y. Deng, R. Zhao, Advanced Oxidation Processes (AOPs) in Wastewater Treatment, *Curr. Pollut. Reports.* 1 (2015) 167–176, <https://doi.org/10.1007/s40726-015-0015-z>.
- [8] O.M. Rodriguez-Narvaez, J.M. Peralta-Hernandez, A. Goonetilleke, E.R. Bandala, Treatment technologies for emerging contaminants in water: A review, *Chem. Eng. J.* 323 (2017) 361–380, <https://doi.org/10.1016/j.cej.2017.04.106>.
- [9] V. Kavitha, K. Palanivelu, The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol, *Chemosphere.* 55 (2004) 1235–1243, <https://doi.org/10.1016/j.chemosphere.2003.12.022>.
- [10] A. Mirzaei, Z. Chen, F. Haghight, L. Yerushalmi, Removal of pharmaceuticals from water by homo/heterogeneous Fenton-type processes – A review, *Chemosphere* 174 (2017) 665–688, <https://doi.org/10.1016/j.chemosphere.2017.02.019>.

- [11] S. Foteinis, J.M. Monteagudo, A. Durán, E. Chatzisympson, Environmental sustainability of the solar photo-Fenton process for wastewater treatment and pharmaceuticals mineralization at semi-industrial scale, *Sci. Total Environ.* 612 (2018) 605–612, <https://doi.org/10.1016/j.scitotenv.2017.08.277>.
- [12] A.Y. Sychev, V.G. Isak, Iron compounds and the mechanisms of the homogeneous catalysis of the activation of O₂ and H₂O₂ and of the oxidation of organic substrates, *Russ. Chem. Rev.* 64 (1995) 1105–1129.
- [13] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, *J. Hazard. Mater.* 98 (2003) 33–50.
- [14] A. Babuponnusami, K. Muthukumar, A review on Fenton and improvements to the Fenton process for wastewater treatment, *J. Environ. Chem. Eng.* 2 (2014) 557–572, <https://doi.org/10.1016/j.jece.2013.10.011>.
- [15] J. De Laat, H. Gallard, Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: mechanism and kinetic modeling, *Environ. Sci. Technol.* 33 (1999) 2726–2732.
- [16] M. Klavarioti, D. Mantzavinos, D. Kassinos, Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, *Environ. Int.* 35 (2009) 402–417, <https://doi.org/10.1016/j.envint.2008.07.009>.
- [17] P.V. Nidheesh, Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution: a review, *RSC Adv.* 5 (2015) 40552–40577, <https://doi.org/10.1039/C5RA02023A>.
- [18] Y. Segura, F. Martínez, J.A. Melero, J.L.G. Fierro, Zero valent iron (ZVI) mediated Fenton degradation of industrial wastewater: Treatment performance and characterization of final composites, *Chem. Eng. J.* 269 (2015) 298–305, <https://doi.org/10.1016/j.cej.2015.01.102>.
- [19] R.R. Kalantary, M. Farzadkia, M. Kermani, M. Rahmatinia, Heterogeneous electro-Fenton process by Nano-Fe₃O₄ for catalytic degradation of amoxicillin: Process optimization using response surface methodology, *J. Environ. Chem. Eng.* 6 (2018) 4644–4652, <https://doi.org/10.1016/j.jece.2018.06.043>.
- [20] F. Velichkova, H. Delmas, C. Julcour, B. Koumanova, Heterogeneous Fenton and photo-Fenton oxidation for paracetamol removal using iron containing ZSM-5 zeolite as catalyst, *AIChE J.* 63 (2016) 669–679, <https://doi.org/10.1002/aic.15369>.
- [21] R. Gonzalez-Olmos, U. Roland, H. Toufar, F.-D. Kopinke, A. Georgi, Fe-zeolites as catalysts for chemical oxidation of MTBE in water with H₂O₂, *Appl. Catal. B Environ.* 89 (2009) 356–364, <https://doi.org/10.1016/j.apcatb.2008.12.014>.
- [22] G. Centi, S. Perathoner, T. Torre, M.G. Verduna, Catalytic wet oxidation with H₂O₂ of carboxylic acids on homogeneous and heterogeneous Fenton-type catalysts, *Catal. Today.* 55 (2000) 61–69, [https://doi.org/10.1016/S0920-5861\(99\)00226-6](https://doi.org/10.1016/S0920-5861(99)00226-6).
- [23] A. Cihanoglu, G. Gunduz, M. Dukkanci, Degradation of acetic acid by heterogeneous Fenton-like oxidation over iron-containing ZSM-5 zeolites, *Appl. Catal. B Environ.* 165 (2015) 687–699, <https://doi.org/10.1016/j.apcatb.2014.10.073>.
- [24] R. Gonzalez-Olmos, F.-D. Kopinke, K. Mackenzie, A. Georgi, Hydrophobic Fe-Zeolites for Removal of MTBE from Water by Combination of Adsorption and Oxidation, *Environ. Sci. Technol.* 47 (2013) 2353–2360, <https://doi.org/10.1021/es303885y>.
- [25] F. Duarte, L.M. Madeira, Fenton- and Photo-Fenton-Like Degradation of a Textile Dye by Heterogeneous Processes with Fe/ZSM-5 Zeolite, *Sep. Sci. Technol.* 45 (2010) 1512–1520, <https://doi.org/10.1080/01496395.2010.487452>.
- [26] M. Aleksic, H. Kusic, N. Koprivanac, D. Leszczynska, A.L. Bozic, Heterogeneous Fenton type processes for the degradation of organic dye pollutant in water — The application of zeolite assisted AOPs, *Desalination.* 257 (2010) 22–29, <https://doi.org/10.1016/j.desal.2010.03.016>.
- [27] S. Queiros, V. Morais, C.S.D. Rodrigues, F.J. Maldonado-Hódar, L.M. Madeira, Heterogeneous Fenton's oxidation using Fe/ZSM-5 as catalyst in a continuous stirred tank reactor, *Sep. Purif. Technol.* 141 (2015) 235–245, <https://doi.org/10.1016/j.seppur.2014.11.046>.
- [28] M.B. Kasiri, H. Aleboeyh, A. Aleboeyh, Degradation of Acid Blue 74 using Fe-ZSM5 zeolite as a heterogeneous photo-Fenton catalyst, *Appl. Catal. B Environ.* 84 (2008) 9–15, <https://doi.org/10.1016/j.apcatb.2008.02.024>.
- [29] G. Rubasinghege, R. Gurung, H. Rijal, S. Maldonado-Torres, A. Chan, S. Acharya, S. Rogelj, M. Piyasena, Abiotic degradation and environmental toxicity of ibuprofen: Roles of mineral particles and solar radiation, *Water Res.* 131 (2018) 22–32, <https://doi.org/10.1016/j.watres.2017.12.016>.
- [30] S. Han, K. Choi, J. Kim, K. Ji, S. Kim, B. Ahn, J. Yun, K. Choi, J.S. Khim, X. Zhang, J.P. Giesy, Endocrine disruption and consequences of chronic exposure to ibuprofen in Japanese medaka (*Oryzias latipes*) and freshwater cladocerans *Daphnia magna* and *Moina macrocopa*, *Aquat. Toxicol.* 98 (2010) 256–264, <https://doi.org/10.1016/j.aquatox.2010.02.013>.
- [31] A.O. Yazaydin, R.W. Thompson, Molecular simulation of the adsorption of mtbe in silicalite, mordenite, and zeolite beta, *J. Phys. Chem. B.* 110 (2006) 14458–14462.
- [32] J. Weitkamp, Zeolite and catalysis, *Solid State Ionics.* 131 (2000) 175–188, [https://doi.org/10.1016/S0167-2738\(00\)00632-9](https://doi.org/10.1016/S0167-2738(00)00632-9).
- [33] D.W. O'Sullivan, M. Tyree, The kinetics of complex formation between Ti(IV) and hydrogen peroxide, *Int. J. Chem. Kinet.* 39 (2007) 457–461.
- [34] S. Lin, M.D. Gurol, Catalytic Decomposition of Hydrogen Peroxide on Iron Oxide: Kinetics, Mechanism, and Implications, *Environ. Sci. Technol.* 32 (1998) 1417–1423, <https://doi.org/10.1021/es970648k>.
- [35] K. Rusevova, R. Köferstein, M. Rosell, H.H. Richnow, F.-D. Kopinke, A. Georgi, LaFeO₃ and BiFeO₃ perovskites as nanocatalysts for contaminant degradation in heterogeneous Fenton-like reactions, *Chem. Eng. J.* 239 (2014) 322–331, <https://doi.org/10.1016/j.cej.2013.11.025>.
- [36] A.L.-T. Pham, C. Lee, F.M. Doyle, D.L. Sedlak, A Silica-Supported Iron Oxide Catalyst Capable of Activating Hydrogen Peroxide at Neutral pH Values, *Environ. Sci. Technol.* 43 (2009) 8930–8935, <https://doi.org/10.1021/es902296k>.
- [37] R. Gonzalez-Olmos, F. Holzer, F.-D. Kopinke, A. Georgi, Indications of the reactive species in a heterogeneous Fenton-like reaction using Fe-containing zeolites, *Appl. Catal. A Gen.* 398 (2011) 44–53, <https://doi.org/10.1016/j.apcata.2011.03.005>.
- [38] J. He, X. Yang, B. Men, D. Wang, Interfacial mechanisms of heterogeneous Fenton reactions catalyzed by iron-based materials: A review, *J. Environ. Sci.* 39 (2016) 97–109, <https://doi.org/10.1016/j.jes.2015.12.003>.
- [39] X. Zeng, A.T. Lemley, Fenton Degradation of 4,6-Dinitro-o-cresol with Fe₂+ -Substituted Ion-Exchange Resin, *J. Agric. Food Chem.* 57 (2009) 3689–3694, <https://doi.org/10.1021/jf900764q>.
- [40] S. Zha, Y. Cheng, Y. Gao, Z. Chen, M. Megharaj, R. Naidu, Nanoscale zero-valent iron as a catalyst for heterogeneous Fenton oxidation of amoxicillin, *Chem. Eng. J.* 255 (2014) 141–148, <https://doi.org/10.1016/j.cej.2014.06.057>.
- [41] H. Kusić, N. Koprivanac, I. Selanec, Fe-exchanged zeolite as the effective heterogeneous Fenton-type catalyst for the organic pollutant minimization: UV irradiation assistance, *Chemosphere.* 65 (2006) 65–73, <https://doi.org/10.1016/j.chemosphere.2006.02.053>.
- [42] K.A. Sashkina, E.V. Parkhomchuk, N.A. Rudina, V.N. Parmon, The role of zeolite Fe-ZSM-5 porous structure for heterogeneous Fenton catalyst activity and stability, *Microporous Mesoporous Mater.* 189 (2014) 181–188, <https://doi.org/10.1016/j.micromeso.2013.11.033>.
- [43] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH/O⁻) in Aqueous Solution, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886, <https://doi.org/10.1063/1.555805>.
- [44] O.A. Makhotkina, E.V. Kuznetsova, S.V. Preis, Catalytic detoxification of 1,1-dimethylhydrazine aqueous solutions in heterogeneous Fenton system, *Appl. Catal. B Environ.* 68 (2006) 85–91, <https://doi.org/10.1016/j.apcatb.2006.07.008>.
- [45] R. Xiao, M. Noerpel, H. Ling Luk, Z. Wei, R. Spinney, Thermodynamic and kinetic study of ibuprofen with hydroxyl radical: A density functional theory approach, *Int. J. Quantum Chem.* 114 (2014) 74–83, <https://doi.org/10.1002/qua.24518>.
- [46] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Giménez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, *Appl. Catal. B Environ.* 47 (2004) 219–256, <https://doi.org/10.1016/j.apcatb.2003.09.010>.
- [47] L. Sanchez-Prado, R. Barro, C. Garcia-Jares, M. Llompарт, M. Lores, C. Petrakis, N. Kalogerakis, D. Mantzavinos, E. Psillakis, Sonochemical degradation of triclosan in water and wastewater, *Ultrason. Sonochem.* 15 (2008) 689–694, <https://doi.org/10.1016/j.ultrsonch.2008.01.007>.
- [48] R. Gonzalez-Olmos, M.J. Martin, A. Georgi, F.-D. Kopinke, I. Oller, S. Malato, Fe-zeolites as heterogeneous catalysts in solar Fenton-like reactions at neutral pH, *Appl. Catal. B Environ.* 125 (2012) 51–58, <https://doi.org/10.1016/j.apcatb.2012.05.022>.
- [49] S. Rahim Pouran, A.R. Abdul Aziz, W.M.A. Wan Daud, Review on the main advances in photo-Fenton oxidation system for recalcitrant wastewaters, *J. Ind. Eng. Chem.* 21 (2015) 53–69, <https://doi.org/10.1016/j.jiec.2014.05.005>.
- [50] E. Yazici, H. Deveci, Factors affecting decomposition of hydrogen peroxide, *Proc. XII Th Int. Miner. Process. Symp.* (2010) 609–616, <https://doi.org/10.13140/RG.2.1.1530.0648>.
- [51] F. Méndez-Arriaga, S. Esplugas, J. Giménez, Degradation of the emerging contaminant ibuprofen in water by photo-Fenton, *Water Res.* 44 (2010) 589–595.
- [52] S.-P. Sun, X. Zeng, A.T. Lemley, Nano-magnetite catalyzed heterogeneous Fenton-like degradation of emerging contaminants carbamazepine and ibuprofen in aqueous suspensions and montmorillonite clay slurries at neutral pH, *J. Mol. Catal. A Chem.* 371 (2013) 94–103, <https://doi.org/10.1016/j.molcata.2013.01.027>.
- [53] J.C.C. da Silva, J.A.R. Teodoro, R.J. de, C.F. Afonso, S.F. Aquino, R. Augusti, Photolysis and photocatalysis of ibuprofen in aqueous medium: characterization of by-products via liquid chromatography coupled to high-resolution mass spectrometry and assessment of their toxicities against *Artemia salina*, *J. Mass Spectrom.* 49 (2014) 145–153, <https://doi.org/10.1002/jms.3320>.
- [54] M. Marković, M. Jović, D. Stanković, V. Kovačević, G. Roglič, G. Gojčić-Cvijović, D. Manojlović, Application of non-thermal plasma reactor and Fenton reaction for degradation of ibuprofen, *Sci. Total Environ.* 505 (2015) 1148–1155.
- [55] I. Michael, A. Achilleos, D. Lambropoulou, V.O. Torrens, S. Pérez, M. Petrović, D. Barceló, D. Fatta-Kassinos, Proposed transformation pathway and evolution profile of diclofenac and ibuprofen transformation products during (sono)photocatalysis, *Appl. Catal. B Environ.* 147 (2014) 1015–1027.
- [56] M. Tokumura, A. Sugawara, M. Raknuzzaman, M. Habibullah-Al-Mamun, S. Masunaga, Comprehensive study on effects of water matrices on removal of pharmaceuticals by three different kinds of advanced oxidation processes, *Chemosphere.* 159 (2016) 317–325, <https://doi.org/10.1016/j.chemosphere.2016.06.019>.
- [57] P. Forzatti, Catalytic deactivation, *Catal. Today.* 52 (1999) 165–181, [https://doi.org/10.1016/S0920-5861\(99\)00074-7](https://doi.org/10.1016/S0920-5861(99)00074-7).