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# Influence of different activation strategies on the activity and stability of MIL-53(Fe) as a dark-Fenton heterogeneous catalyst



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### ABSTRACT

MIL-53(Fe) was synthesized using solvothermal method without HF. Three different activation methodologies were applied in order to remove N,N-dimethylformamide (DMF) from the inner pores of the material. The incidence of these treatments in the activity and stability as heterogeneous catalyst in a dark-Fenton reaction was evaluated for Rhodamine 6G (Rh6G) degradation. Important improvements in the catalytic performance of ML-53(Fe) were obtained after activation. Operational variables such as pH, reaction temperature,  $[H_2O_2]/[Fe^{3+}]$  molar ratio, and initial Rh6G concentration were evaluated. Likewise, catalyst reusability assays were also performed. The obtained results indicate that a partial removal of DMF affects not only the stability but also the catalytic activity of MIL-53(Fe) in the Fenton reaction. Different solid state characterization techniques, including PXRD, SEM, FTIR, elemental analysis, XPS, and Mössbauer spectroscopy, were applied to the as-synthesized and activated materials as well as post-reaction catalysts in order to understand the catalytic behavior.

### 1. Introduction

The textile industry is one of the most significant sectors of the global economy and its development represents a serious environmental problem that, on the one hand, requires large water consumption, and on the other hand, generates alkaline effluents containing high amounts of detergents, dyes, salts and/or other auxiliary agents with high chemical stability and low biodegradability. The latter fact makes this kind of effluent hard to treat effectively by traditional biological processes [1].

Faced with this situation, innovative technologies for the treatment of industrial effluents have been developed, among them, the advanced oxidation processes (AOPs) [2]. The AOPs are based on the generation of hydroxyl radicals (•OH), which are highly oxidant species capable of degrading a wide variety of organic pollutants [3,4]. Among the most studied AOPs for wastewater treatment are Fenton process and their derivations [5–7]. The traditional methodology in the homogeneous phase involves the use of ferrous salts (Fenton catalyst), which are highly efficient for the generation of the •OH radicals but also have serious disadvantages that limit their industrial applicability [8,9]. For this reason, the looking for new redox catalysts with activity in Fenton-type heterogeneous processes is currently a hot and demanding topic [10].

Up to now, progress has been made by studying solid catalysts consisting of an active phase (mainly iron compounds) immobilized on the surface of different supports such as alumina, mesoporous silica, zeolites, clays, ion exchange resins, nanodiamonds, magnetic materials, and porous carbons [11–14]. The great impact that materials known as Metal Organic Frameworks (MOFs) have experienced in catalysis [15] postulates them as good candidates to be tested as heterogeneous catalysts in AOPs [16,17]. MOFs are crystalline compounds formed by the assembly of metal ions (discrete, clusters or condensed secondary building units (SBUs) of different dimensions) and organic ligands, determining a periodic network characterized by the presence of

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channels or cavities [18]. The synergy resultant from the organic-inorganic composition and the characteristic pore architecture, place MOFs as singular materials for a new generation of catalysts [19].

One major problem of MOFs that has limited considerably their application in catalysis so far is their low structural stability [20]. This lack of stability of many MOFs is particularly severe when water, amine and even alcohol are the reaction medium [21,22]. Within the large number of MOFs reported in literature, some of them have demonstrated excellent stability as active catalysts for different chemical reactions, including the material known as MIL-53(Fe) [23,24]. This MOF has the peculiarity of presenting a flexible crystal structure, adopting different pore sizes depending on the solvent content or the gas pressure that it bears. Such dynamic behavior was named as *breathing effect* [25]. The structural stability of MIL-53(Fe) in aqueous media was demonstrated by several papers dealing with biomedical applications as a drug delivery carrier, suggesting that it could also be tested as Fenton catalyst for wastewater treatments [26–28].

Apart from the questionable structural stability of MOFs in some solvent media, another drawback of these materials is the fact that they rarely can be used in its as-synthesized form. In most cases, it is necessary to develop specific strategies to modify the starting material before it is used as a catalyst, removing the solvent molecules from the structural channels [29]. As often occurs with MOFs, the processes applied to eliminate the occluded solvent are not trivial, and conditions such as solvent exchange, heating method, atmosphere, among others, must be critically controlled in order to avoid total or partial collapse of the pores [30]. Differences in such procedures have been pointed out as causes of the wide discrepancies between properties such as specific surface area values or adsorption capacities for the same material synthesized in different laboratories [31].

MIL-53(Fe) is frequently synthesized in N,N-dimethylformamide (DMF) solvent and thus, DMF molecules are retained in the pores of the MOF structure blocking the access of substrates to the active catalytic sites. Considering this MOF as a suitable heterogeneous catalyst to be tested in a Fenton-like reaction, the exchange of DMF by water molecules is required, since aqueous effluents are the most common ones to be treated with Fenton technologies. For this reason, the main goal of this work is to evaluate the incidence of different activation methods of MIL-53(Fe) devoted fundamentally to remove DMF, preserving quantitatively the structural stability and tending to achieve the maximum efficiency as catalyst in a heterogeneous Fenton process for the degradation of Rhodamine 6G (Rh6G) dve in dark conditions. The interest in the use of dark conditions is due not only to the fact that they allow studying the catalytic behavior inherent to the material but also that they allow carrying out catalytic processes in which the use of light is not convenient or economically feasible. It should be noted that other works that involve the use of MIL-53(Fe) as a dark-Fenton catalyst for the degradation of this dye molecule have not been reported so far. Likewise, the influence of different activation strategies applied to MIL-53(Fe) on its catalytic activity and stability has not been studied. A deep catalytic study evaluating different operational variables such as pH, reaction temperature, [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>3+</sup>] ratio and Rh6G concentration, as well as catalyst reuse experiments, is performed here. A set of solid state characterization techniques including PXRD, FTIR, TGA, SEM, elemental analysis, XPS and Mössbauer spectroscopy are applied in order to understand the observed catalytic behavior.

### 2. Experimental

### 2.1. Materials

1,4-benzenedicarboxylic acid (Sigma-Aldrich,  $H_2BDC$ ), FeCl<sub>3</sub>·6H<sub>2</sub>O, *N*,*N*'-dimethylformamide (DMF),  $H_2O_2$  (30% v/v), methanol, Rhodamine 6G (Aldrich, Rh6G, 95%), titanium (IV) oxysulfate solution (15%, w/v), hydroxylamine hydrochloride, 1,10-phenanthroline, Na<sub>2</sub>SO<sub>3</sub>, NaOH, HCl,  $H_2SO_4$ ,  $HgSO_4$ ,  $K_2Cr_2O_7$  and  $Ag_2SO_4$ . All chemicals and solvents were obtained from commercial sources and used without further purification.

### 2.2. Synthesis of MIL-53(Fe)

MIL-53(Fe) was synthesized by a solvothermal process according to the literature [28,32] from a mixture of FeCl<sub>3</sub>·6H<sub>2</sub>O; 1,4-benzenedicarboxylic acid and DMF in a molar ratio of 1:1:130. The mixture was transferred to a Teflon-lined stainless steel autoclave (internal volume of 42 mL) and heated at 150 °C for 24 h. The resultant solid product, MIL-53(Fe)·(DMF), was recovered by filtration as a yellow polycrystalline powder, washed with DMF and dried under atmospheric conditions. The described solvothermal procedure allowed obtaining the desired compound with MIL-53 structure and a very good yield of 87%. The corresponding solid is named from now on as MIL-53(Fe)<sub>as</sub>.

### 2.3. Activation methodologies

Three activation strategies were tested. *Method 1*: 0.5 g of MIL-53 (Fe)<sub>as</sub> were heated at 150 °C in air atmosphere for 12 h, using heating and cooling rates of 1 °C ·min<sup>-1</sup>. Subsequently, the solid was suspended in 0.2 L of distilled water for 12 h. *Method 2*: 0.5 g of MIL-53(Fe)<sub>as</sub> were dispersed in an aqueous solution of  $H_2O_2$  (8.0 mmol·L<sup>-1</sup>) at pH 4.0, temperature = 50 °C, keeping the system under magnetic stirring during 4 h. *Method 3*: 0.5 g of the MIL-53(Fe)<sub>as</sub> were immersed in 0.1 L of methanol during 24 h at room temperature, subsequently the solvent was removed and replaced for the same fresh solvent volume in three consecutive exchange steps. By applying the described activation methods, the resultant MIL-53(Fe) phases were recovered by filtration, air dried and stored for subsequent characterization. Such activated solids are named from now on as solid 1–150/H<sub>2</sub>O, solid 2–50/H<sub>2</sub>O<sub>2</sub>, and solid 3–25/CH<sub>3</sub>OH, respectively.

### 2.4. Structural characterization

Powder X-Ray Diffraction (PXRD) patterns of solids were collected with a Rigaku Ultima IV type II diffractometer using Cu-K $\alpha$  ( $\lambda = 1.5418$ Å) radiation, in the 20 range of  $2^\circ\text{--}40^\circ\text{,}$  with increments of  $0.02^\circ$  and scan speed of 2°min<sup>-1</sup>. All solids were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) using a Nicolet Protégé 460 spectrometer applying the KBr pellet technique. SEM images were obtained with a LEO1450VP microscope. Thermogravimetric analysis of all solids was performed with a Shimadzu TGA-50H thermal analyzer from room temperature (RT) to 600 °C, applying a heating rate of 10 °C·min<sup>-1</sup> under air flow, at 50 mL·min<sup>-1</sup>. Elemental analysis of C, H and N was carried out using CHN628 LECO® Brand equipment. Mössbauer spectra were obtained in transmission geometry with a 512-channel constant acceleration spectrometer (WissEl, Germany), using a source of <sup>57</sup>Co in Rh matrix of nominally 50 mCi. The sample ideal thickness was evaluated considering the weight percentages of the different elements of each catalyst (about 100 mg of powder were used for a holder of 1.8 cm of diameter). Velocity calibration was performed using a 12-µm-thick  $\alpha\mbox{-Fe}$  foil as reference. Spectra were collected at 298 K and 13 K. Measurements at low temperatures were done working with a closed-cycle cryogenic system (ARS, Model DE-202, USA). Each spectrum was folded to minimize geometric effects and the experimental data were fitted using a commercial program with constraints named Recoil [33]. XPS spectra of the samples were collected using a VG Microtech ESCA spectrometer with a non-monochromatic Al Ka radiation source (300 W, 15 kV,  $h\nu = 1486.6$  eV), combined with a VG-100-AX hemispherical analyzer operating at 25 eV pass energy. The instrumental resolution was 0.1 eV. All the XPS spectra were calibrated with the C 1s peak at 284.6 eV as reference, to rule out any possible spectral shift due to charging effects. The chamber pressure was kept at  $<10^{-9}$  Torr during the measurements.

### 2.5. Dark-Fenton screening experiments

The dark-Fenton reactions were carried out in batch stirred-tank mode at 25  $\pm$  1 °C, in a Pyrex cylindrical reactor with an internal volume of 0.5 L. Firstly, 0.2 L of an aqueous solution of Rh6G dye (5 mg·L^{-1}) without pH adjust (pH = 6) was added to the reactor with 0.2 g of the catalysts (MIL-53(Fe)\_{as} or activated solids) under stirring conditions for 30 min to ensure suitable distribution of MOF in the solution. Afterwards, 160  $\mu$ L of 30% v/v H<sub>2</sub>O<sub>2</sub> were added to the system to obtain a [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>3+</sup>] = 2/1 M ratio. The reaction conditions applied in the catalytic activity screening tests were selected on the basis of criteria tending to reduce energetic and process costs; that is, by using the native pH of the Rh6G aqueous solution and operating at room temperature.

The progress of reaction was evaluated by extracting 1.0 mL aliquots periodically, which were filtered through 0.45  $\mu$ m membranes to separate the solid catalyst and immediately analyzed in a UV–Vis spectrophotometer to monitor the evolution of Rh6G absorption spectrum as a function of reaction time. H<sub>2</sub>O<sub>2</sub> consumption was measured by TiOSO<sub>4</sub> colorimetric technique [34,35]. After 6 h of reaction, the catalyst was separated by centrifugation, dried and stored for further analysis and reuse. The liquid phase was reserved to quantify the leached iron content by the 1,10-phenanthroline/hydroxylamine method [36]. In addition to these measurements, chemical oxygen demand (COD) reduction of the dye solution was determined by measuring initial and final COD (after 6 h reaction) by the 5220D SMWW method [37].

## 2.6. Catalytic activity and stability evaluation of activated solids under different reaction conditions

The catalytic activity and robustness of the activated solids were also tested using different reaction conditions: initial pH was varied from 4.0 to 10.0 by adding drops of HCl (0.1 M) or NaOH (0.1 M) to the reaction medium. The influence of temperature was evaluated from 25 °C to 45 °C; the  $[H_2O_2]/[Fe^{3+}]$  molar ratio was varied from 1.0 to 2.5 and the Rh6G initial concentration was modified from 5 to 25 mg·L<sup>-1</sup>.

### 2.7. Reuse experiment conditions

The recovered solid catalysts from the corresponding screening tests were separated from reaction medium by filtration and dried under atmospheric conditions. After that, the solids were reused in a subsequent reaction cycle, operating under the same experimental conditions as was described in 2.5. This procedure was repeated up to five times. After each reaction step the solids were characterized by PXRD, FTIR, and elemental analysis. All reaction tests were performed in three replicas in order to ensure recovery of enough amount of catalyst to fully characterize it after every reaction cycle.

### 3. Results and discussion

### 3.1. Characterization of MIL-53(Fe)as

The synthesized solid was evaluated by PXRD. The good agreement between the experimental and simulated diffraction profiles confirms that the [Fe(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)(OH)]•DMF phase, known as MIL-53(Fe), was obtained (Fig. S1a). It should be noted that the well-defined diffraction peaks and the absence of additional reflections in the diffraction pattern of the material demonstrate the high crystallinity and purity of the synthesized MOF. The FTIR spectrum of this material showed the characteristic vibrational modes reported for MIL-53(Fe) [23]. However, another set of signals was observed, including a typical absorption band at 1668 cm<sup>-1</sup> attributed to the stretching modes of carbonyl groups and bands at 865 and 663 cm<sup>-1</sup> consistent with C–N stretching and O–C–N bending vibrations, respectively (Fig. S1b). Considering that the stretching modes of OH and C=O groups are shifted to lower frequencies, it can be inferred that the MIL-53(Fe)<sub>as</sub> contains DMF molecules within their pores that are involved in H-bond interactions with the OH groups of MIL-53(Fe). Additionally, SEM images of this material show that its morphology is consistent with an elongated trigonal prism with a particle length of ~200  $\mu$ m and ~40–50  $\mu$ m in width (Fig. S1c). Similar morphology of rod-like prisms of 4–10  $\mu$ m in width and several tens of  $\mu$ m in length has been previously reported for this material [38,39]. However the crystal size seems to be much higher in the present case, consistent with a longer synthesis time employed. Elemental Analysis for [Fe(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)(OH)] • DMF is shown in Table 1.

### 3.2. Characterization of activated solids

PXRD patterns of the three activated solids were consistent with the simulated profile obtained from single crystal XRD data of MIL-53(Fe)-H<sub>2</sub>O phase (Fig. 1a) [40], suggesting that in all cases the DMF molecules were quantitatively exchanged by water. This fact indicates that the applied activation methodologies induce the recognized breathing effect resultant from the solvent exchange. As it was reported [41,42], the change in cell parameters in MIL-53(Fe) when the DMF is replaced by H<sub>2</sub>O is accompanied by a decrease in cell volume of approximately 26%. whereas the framework topology is maintained unaltered. According to FTIR analysis, the spectra of activated solids show the stretching modes characteristic of OH and/or  $H_2O$  in the 3592 - 3295 cm<sup>-1</sup> spectral range, in addition to the H–O–H bending mode at 1625  $\text{cm}^{-1}$ . The band at 1668 cm<sup>-1</sup> assigned to the C=O stretching mode of DMF molecule completely disappears (solids 2-50/H<sub>2</sub>O<sub>2</sub> and 3-25/CH<sub>3</sub>OH) or notably decrease its intensity (solid 1-150/H2O); while the O-C-N bending mode at  $663 \text{ cm}^{-1}$  is absent in the spectra of all activated solids (Fig. 1b). Thermogravimetric analysis performed on MIL-53(Fe)<sub>as</sub> and activated solids (Fig. 1c and Table S1) evidenced the different thermal behaviors observed for the hydrated forms (activated solids) in comparison with the as synthesized one. The mass decays of these processes were interpreted taking into account the corresponding formulae proposed on the basis of elemental analysis displayed in Table 1. Based on the characterization results, it is possible to confirm that the activation strategies carried out were able to remove the occluded DMF from the MIL-53  $(Fe)_{as}$  and replace it with H<sub>2</sub>O in 88, 95 and 97% for solids 1–150/H<sub>2</sub>O, 2-50/H<sub>2</sub>O<sub>2</sub> and 3-25/CH<sub>3</sub>OH, respectively.

### 3.3. Dark-Fenton screening experiments

Rh6G decolorization and  $H_2O_2$  consumption was followed by UV–Vis spectroscopy throughout the dark-Fenton reaction, using MIL-53(Fe)<sub>as</sub> and activated solids as catalysts. Firstly, reference tests were performed by analyzing independently the effect of catalyst and  $H_2O_2$  in contact with Rh6G dye solution. As can be seen in Fig. 2a, the presence of the catalysts alone (MIL-53(Fe)<sub>as</sub> or activated solids) produced a decrease in Rh6G concentration of 14–38%, a fact that is probably due to an adsorption process occurring mainly in the external particle surface. According to different experimental and computational investigations dealing with the adsorption of drug molecules on MIL-53(Fe) [28,43], pore sizes of this MOF were reported as 7.4–8.6 Å in diameter. Even though the structure of MIL-53 is flexible due to its recognized *breathing* 

Solids	Experiment	al (calculate	d) %	Experimental formulas		
	C N H					
MIL-53	41.88	4.56	3.90	[Fe(C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> )(OH)]·(C <sub>3</sub> H <sub>7</sub> NO)		
(Fe) <sub>as</sub>	(42.60)	(4.52)	(3.91)			
1-150/	37.82	0.64	2.99	[Fe(C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> )(OH)]·		
H <sub>2</sub> O	(38.32)	(0.64)	(2.94)	(C <sub>3</sub> H <sub>7</sub> NO) <sub>0.12</sub> (H <sub>2</sub> O) <sub>0.90</sub>		
2-50/	36.95	0.26	2.95	[Fe(C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> )(OH)]·		
$H_2O_2$	(37.32)	(0.26)	(2.98)	(C <sub>3</sub> H <sub>7</sub> NO) <sub>0.05</sub> (H <sub>2</sub> O) <sub>1.20</sub>		
3-25/	37.16	0.16	3.01	[Fe(C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> )(OH)]·		
CH <sub>3</sub> OH	(37.06)	(0.16)	(3.00)	(C <sub>3</sub> H <sub>7</sub> NO) <sub>0.03</sub> (H <sub>2</sub> O) <sub>1.29</sub>		



Fig. 1. (a) Comparison between simulated PXRD profile of MIL-53(Fe)·H<sub>2</sub>O [23] and the PXRD patterns of activated solids, (b) FTIR spectra and (c) TGA curves of MIL-53(Fe)<sub>as</sub> and activated solids.

effect, the adsorption of drug molecules of considerable size; such as CDV, AZT-TP and DOXO, could not be achieved using this material [27]. This fact suggests that the apparent maximum pore size (ca. 8.6 Å) would allow the entry of molecules as large as ibuprofen or busulfan, but not bigger. Considering the crystal structure of MIL-53(Fe) in aqueous media [41] and in order to evaluate the possibility of entrance of Rh6G into inner pores of the MOF, we calculated the Connolly surface of this phase (see Supporting Information, Figs. S2 and S3) as a tool to estimate an approximated effective pore diameter of MIL-53(Fe) phase containing water; such a value being about  $\sim$ 6.5 Å. Taking this into account and the corresponding dimensions of the optimized geometry of Rh6G molecule (see Fig. S3, ca.  $14.12 \times 7.19 \times 7.38 \text{ Å}^3$ ), it is possible to infer that the adsorption of this dye in the inner pores of the MOF would hardly occur. On the basis of this analysis, we explain the observed tendency in Rh6G adsorption in terms of the particle size decrease and the increase of surface defects resulting from the application of different activation procedures. As can be seen in Fig. 3, the activation methodologies modified the morphology and size of the MOF crystals in comparison with the ones of the as synthesized material described above (see Fig. S1). For solids  $1-150/H_2O$  and  $2-50/H_2O_2$ , rod-type crystals of  $\sim 50$ and  $\sim$ 37 µm in length and  $\sim$ 12 and  $\sim$ 10 µm in width were observed, respectively. For solid 3-25/CH<sub>3</sub>OH, smaller and irregular microparticles of approximately 7 µm in diameter without a defined morphology were obtained. Such decrease in particle size from MIL-53(Fe)as, solid 1-150/H<sub>2</sub>O, 2-50/H<sub>2</sub>O<sub>2</sub> to 3-25/CH<sub>3</sub>OH coincides with the adsorption tendency obtained with these materials (Fig. 2a).

On the other hand, the presence of  $H_2O_2$  without catalyst caused a Rh6G decolorization of  $5 \pm 1\%$ , while the combined use of MIL-53(Fe)<sub>as</sub> and  $H_2O_2$  prompted a decrease in Rh6G concentration of  $48 \pm 3\%$ . As it is displayed in Table 2, the degradation of Rh6G is improved with the use of activated solids in the presence of  $H_2O_2$ . Likewise, the activation methodologies also improved the ability of this MOF to decrease COD;

the corresponding values achieved after 6 h of reaction are shown in Table 2 and Fig. S4. The results obtained here indicate that different activation methodologies lead to obtaining materials (activated solids) more efficient in the degradation of Rh6G compared to the use of the assynthesized material (Fig. 2b). This relative enhancement in the catalytic performance seems to be related to the replace of the bulky DMF molecules by smaller H<sub>2</sub>O molecules. Apparently, the accessibility of H<sub>2</sub>O<sub>2</sub> to the metal sites of the MOF was favored with the decrease of DMF content (Table 1). This fact can be understood in terms of a faster intrapore diffusivity of H<sub>2</sub>O<sub>2</sub> in a structure with H<sub>2</sub>O molecules than in the assynthesized material. When the internal pores are filled with DMF, such molecules could play the role of obstacles for the oxidant molecules.

H<sub>2</sub>O<sub>2</sub> consumption during the reaction was also evaluated and the resultant curves are displayed in Fig. 2c. As it is shown, the H<sub>2</sub>O<sub>2</sub> consumption was 3  $\pm$  1% when the catalyst was not present in the reaction system. Then, MIL-53(Fe)<sub>as</sub> and the activated solids were incorporated as catalysts and this value was around 10-19% for MIL-53(Fe)<sub>as</sub> or the solids 1–150/H<sub>2</sub>O and 2–50/H<sub>2</sub>O<sub>2</sub>, while it achieved 98  $\pm$  1% for solid 3–25/CH<sub>3</sub>OH. The marked difference in H<sub>2</sub>O<sub>2</sub> consumption when solid 3-25/CH<sub>3</sub>OH is used as catalyst suggests a significant change in the reaction system. The amount of iron leached into the solution can shed light on this singular behavior of solid 3-25/CH<sub>3</sub>OH. As can be seen in Table 2 and Fig. S4, the solids 1-150/H<sub>2</sub>O and 2-50/H<sub>2</sub>O<sub>2</sub> leached approximately the same amount of iron as the non-activated material, while this value was seven times higher for solid 3–25/CH<sub>3</sub>OH. With this iron concentration in solution, a homogeneous reaction is probably prevailing over the heterogeneous one. To confirm this assumption, homogeneous phase reaction assays were carried out using FeCl<sub>3</sub> as the source of ferric ions. In Fig. S5, the obtained Rh6G decolorization curves are presented. It is interesting to note that the decolorization of Rh6G is negligible when  $3 \text{ mg} \cdot \text{L}^{-1}$  Fe are used (amount of iron leached from MIL- $53(Fe)_{as}$  and solids  $1-150/H_2O$  and  $2-50/H_2O_2$ ). These results confirm



Fig. 2. (a) Rh6G adsorption curves, (b) Rh6G decolorization curves, (c)  $H_2O_2$  consumption obtained with MIL-53(Fe)<sub>as</sub>, and the activated solids. Reaction conditions:  $pH_0 = 6.0$ ,  $[H_2O_2] = 8 \text{ mmol}\cdot L^{-1}$ ,  $[catalyst] = 1 \text{ g}\cdot L^{-1}$ ,  $[Rh6G] = 5 \text{ mg}\cdot L^{-1}$  and  $T = 25 \degree C$ .



Fig. 3. SEM images of MIL-53(Fe)\_{as} (a) and the solids  $1-150/H_2O$  (b),  $2-50/H_2O_2$  (c) and  $3-25/CH_3OH$  (d).

Table 2
Effect of activation on the activity and stability of MIL-53(Fe) after 6 h of reaction.

Solids	Decolorization (%)	1	H <sub>2</sub> O <sub>2</sub> Consumption (%)	COD Reduction (%)	Leached Iron (mg $\cdot$ L <sup>-1</sup> )
	Adsorption	Fenton			
MIL-53(Fe) <sub>as</sub>	$14\pm2$	$48\pm3$	$10\pm3$	$17 \pm 4$	$2.7\pm0.3$
$1-150/H_2O$	$22\pm3$	$71\pm3$	$14\pm2$	$43\pm3$	$2.6\pm0.2$
$2-50/H_2O_2$	$30\pm2$	$83\pm4$	$19\pm3$	$48\pm3$	$2.7\pm0.4$
3-25/CH <sub>3</sub> OH	$38\pm2$	$97\pm3$	$98\pm3$	$80\pm3$	$21.0\pm0.7$

that the catalytic activity observed with MIL-53(Fe)<sub>as</sub> and solids 1–150/ H<sub>2</sub>O and 2–50/H<sub>2</sub>O<sub>2</sub> is mainly due to their heterogeneous phase contribution. In contrast, the Rh6G decolorization is total in 60 min when 22 mg·L<sup>-1</sup> Fe<sup>3+</sup> is employed. Thus, the existence of a homogeneous contribution is confirmed using solid 3–25/CH<sub>3</sub>OH as catalyst. However, it is important to note that such contribution seems to begin after an induction period in which solid 3–25/CH<sub>3</sub>OH degrades Rh6G by heterogeneous reaction.

Contributions by reaction in homogeneous and heterogeneous phase using the different catalysts can be deduced from the comparison of the kinetic constants (k). In the literature [44], pseudo-first order kinetics were assumed for a Fenton reaction using MIL-53(Fe) as catalyst, then in this work the kinetic constants were calculated taking into account this consideration. To obtain an acceptable fit  $(R^2 > 0.98)$  it was necessary to consider different regions of each discoloration curves derived from the use of solids 1–150/H<sub>2</sub>O, 2–50/H<sub>2</sub>O<sub>2</sub> or 3–25/CH<sub>3</sub>OH. On the contrary, for MIL-53(Fe)<sub>as</sub> catalyst the whole reaction curve could be adjusted as a unique set of data (Fig. S6). The *k* values obtained for all solid catalysts are displayed in Table 3. Additionally, the k values for homogeneous experiments are also included. As can be seen, the k value for MIL-53  $(Fe)_{as}$  is in the same order than the k values for the region I of activated solids. When the reaction progresses, an increase of the kinetic constants is observed using the activated solids. For the solid  $3-25/CH_3OH$  the k value is three times higher than those of solids 1-150/H<sub>2</sub>O and 2-50/H<sub>2</sub>O<sub>2</sub>, which can be ascribed to the homogeneous reaction contribution.

Regarding the mainly heterogeneous contributions demonstrated for the activated solids 1-150/H<sub>2</sub>O and 2-50/H<sub>2</sub>O<sub>2</sub>, the analysis of MIL-53 (Fe) crystallographic data helps to understand how the Fenton reaction could occur mediated by this framework. MIL-53(Fe) · H<sub>2</sub>O, whose formula is Fe<sup>III</sup>(OH){O<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>-CO<sub>2</sub>}·H<sub>2</sub>O, exhibit a three-dimensional structure built up of corner-sharing trans chains of octahedral Fe(III) linked by benzenedicarboxylate (BDC) moieties, creating an open framework with one-dimensional channels running parallel to the *c*-axis. These corner-sharing iron octahedra are linked by  $\mu_2(OH)$  bridging groups, with the distances between two nearest iron (III) cations along the c-axis (small diagonal of the lozenge) equal to  $Fe_1$ - $Fe_1$  = 7.353 Å and  $Fe_1$ - $Fe_1$  = 7.702 Å in the largest diamond-shaped tunnel while the distances are  $Fe_2$ - $Fe_3 = 7.518$  Å in the smallest cannel [40]. The careful inspection of MIL-53(Fe)·H<sub>2</sub>O crystallographic data allowed us to identify the existence of a highly asymmetric OH bridging (Fe1-OH-Fe1, see Fig. 4). Such stressed geometry could propitiate that the most elongated Fe-OH bond breaks down when the activated solid is in contact with H<sub>2</sub>O<sub>2</sub>; thus generating an intermediate species with a coordinatively unsaturated site, which can be active for starting the Fenton reaction.

In summary, on the basis of the observed noticeable differences in decolorization,  $H_2O_2$  consumption, COD reduction percentages, and leached iron concentrations obtained with all solids under study, it is

### Table 3

Kinetic constants of heterogeneous reaction with MIL-53(Fe)\_{as} and the activated solids as well as homogeneous reaction with ferric ions.

Systems		Kinetic constants (k, min <sup><math>-1</math></sup> ) x 10 <sup><math>-3</math></sup>				
		Region I	Region II	Region III		
Catalyst	MIL-53	1.1				
	(Fe) <sub>as</sub>					
	1-150/	1.2 (<210	3.7 (210-330	10.5 (300-360		
	H <sub>2</sub> O	min)	min)	min)		
	2-50/	1.4 (<150	3.8 (150-270	10.8 (270-360		
	$H_2O_2$	min)	min)	min)		
	3-25/	2.3 (≤120	34.2 (>	120 min)		
	CH <sub>3</sub> OH	min)				
Fe <sup>3+</sup>	3	0.4				
$(mg \cdot L^{-1})$	6	0.9				
-	22	122.1				

suggested that in each case, the catalytic behavior involve two different processes: *i*) a mainly heterogeneous Fenton-like reaction when MIL-53 (Fe)<sub>as</sub>, solid 1–150/H<sub>2</sub>O and solid 2–50/H<sub>2</sub>O<sub>2</sub> are incorporated as catalysts, and *ii*) a dominantly homogeneous Fenton reaction after 2 h of reaction, due to the iron leached from solid 3–25/CH<sub>3</sub>OH as catalyst. According to the exposed results, the activation strategies performed to obtain solids 1–150/H<sub>2</sub>O and 2–50/H<sub>2</sub>O<sub>2</sub> prompted to improve almost three times the catalytic capacity of the MOF MIL-53(Fe)<sub>as</sub> while for solid 3–25/CH<sub>3</sub>OH a deterioration of the MOF structure is induced, making it more fragile and sensitive to the reaction conditions. This fact is also evidenced in the lower intensity of the PXRD pattern of this solid (Fig. 1a).

Making a comparison of the catalytic results with data reported in the literature is not straightforward, since different reaction conditions are used and/or insufficient information is presented. For instance, in the case of Rhodamine B degradation by using MIL-53(Fe) as catalyst [44], the obtained kinetic constants were one order of magnitude higher than in this work (Table 3), but the iron leaching associated with that process is not mentioned; therefore, a deeper comparative analysis cannot be performed.

### 3.4. Catalytic and stability evaluation of activated solids under different reaction conditions

Considering the degradation efficiency obtained by the screened activated MIL-53(Fe) phases and taking also into account the iron leaching in each system, solid 2–50/H<sub>2</sub>O<sub>2</sub> was selected as the catalyst to further study the influence of variations in initial pH (pH<sub>o</sub>), reaction temperature,  $[H_2O_2]/[Fe^{3+}]$  ratio and initial concentration of Rh6G, tending to evaluate the catalyst tolerance and activity under different experimental conditions.

### 3.4.1. Influence of pH on the catalytic degradation of Rh6G

Four reaction runs were performed adjusting the pH<sub>0</sub> value to 4.0, 6.0, 8.0 and 10.0, keeping the remaining variables constant as in the previous screening tests. Additionally, the pH value was measured along the reaction progress in order to evaluate the effective pH window in which the catalyst is working and how this parameter influences its catalytic activity. The decrease in Rh6G concentrations for these pH<sub>0</sub> values were 41  $\pm$  2, 83  $\pm$  4, 41  $\pm$  2 and 49  $\pm$  2%, respectively (Fig. 5a). The variations in pH ranges and iron leached concentrations are shown in Table S2.

The change in pH along the reaction suggests that pH and catalytic performance were affected by the formation of by-products from the partial degradation of Rh6G. These pH variations played a key role during each test that prompted the emergence of three processes: i) stabilization of  $H_2O_2$  as  $H_3O_2^+$  [45] when pH decreased from 4.0 to 2.3, reducing the catalyst reactivity; ii) the decrease of pH from 6.0 to 3.2, allowed obtaining a pH value close to the optimum one reported for Fenton reaction [46]; and iii) the formation and deposition of amorphous ferric oxide or oxyhydroxide (FeOOH) on the catalyst surface for experiments at pHo values of 8.0 and 10.0 [47]. XPS spectra of catalysts before and after the catalytic tests at the different pH values were analyzed in order to verify the fact described in iii) (Fig. 6). The O 1s signal showed two main contributions at  $\sim$ 531.5 and  $\sim$ 529.9 eV, that were assigned to hydroxyl oxygen ( $OH^-$ ) and lattice oxygen ( $O^{2-}$ ), respectively [48]. Hydroxyl oxygen seems to be the main oxygen specie at the surface of solid  $2-50/H_2O_2$ , whereas contribution of  $O^{2-}$ , which is assigned to the formation of surface ferric oxide or oxyhydroxide, increases in the samples tested at pH<sub>0</sub> of 8.0 and 10.0. The formation of these phases in the catalysts surface also explains the lower leached iron concentrations detected in the solutions of  $pH_0 = 8.0$  and 10.0(Table S2).



Fig. 4. Projection of MIL-53(Fe) structure along c-axis and details of the Fe1-Fe1 corner sharing inorganic SBU with selected bond distances.



Fig. 5. Rh6G degradation curves at different (a) initial pH, (b) reaction temperature, (c)  $[H_2O_2]/[Fe^{3+}]$  ratio and (d) initial Rh6G concentration.

3.4.2. Influence of reaction temperature on the catalytic degradation of Rh6G

and promoting a higher stability of the catalyst.

The effect of reaction temperature on the activity and stability of solid 2–50/H<sub>2</sub>O<sub>2</sub> as heterogeneous Fenton catalyst was also evaluated in the 25–45 °C range. As shown in Fig. 5b and Table S2, the increase of temperature intensified decolorization and iron leaching. The latter fact indicates that the observed degradation of Rh6G at 35 °C and 45 °C had a significant contribution of a homogeneous process. As a result, the lower temperature is the preferred one in order to avoid the solid dissolution, keeping the heterogeneous catalytic activity as the dominant process,

### 3.4.3. Effect of $[H_2O_2]/[Fe^{3+}]$ ratio

The effect of  $[H_2O_2]/[Fe^{3+}]$  ratio was another operational parameter evaluated. As can be seen in Fig. 5c and Table S2, the efficiency of the catalytic process is directly proportional to the  $[H_2O_2]/[Fe^{3+}]$  ratio at values between 1 and 2. This behavior could be explained by the fact that the Fenton process with Fe<sup>3+</sup> involves the consumption of 2 mol of  $H_2O_2$ : 1 mol to reduce Fe<sup>3+</sup> to Fe<sup>2+</sup> and the other one to oxidize Fe<sup>2+</sup> to Fe<sup>3+</sup>, producing the hydroxyl radicals. Interestingly, when  $[H_2O_2]/$ 



Fig. 6. O1s XPS spectra of solid 2–50/H $_2O_2$  and the materials recovered after reaction at different  $pH_0.$ 

 $[Fe^{3+}]$  ratio increased to 2.5, a decay in the kinetic of degradation was observed, which is associated to the appearance of scavenger reactions of •OH radicals [4,49].

3.4.4. Influence of Rh6G initial concentration on its catalytic degradation The ability of solid  $2-50/H_2O_2$  to catalyze the degradation of solutions containing three different concentrations of Rh6G: 5, 15 and 25 mg·L<sup>-1</sup> was determined. The resultant degradation performances are shown in Fig. 5d and Table S2. As can be seen, the increase of the initial concentration of Rh6G leads to a decrease in activity, as reported in literature for other target molecules [50,51]. This fact could be understood by considering the formation of Rh6G degradation by-products that also consume •OH radicals.

### 3.5. Catalysts reusability experiments

Catalyst reusability test were performed with five consecutive reaction runs. Since the catalytic activity and iron leaching obtained with solids  $1-150/H_2O$  and  $2-50/H_2O_2$  were similar (Table 2), these catalysts were selected to perform the reuse tests. Solid  $3-25/CH_3OH$  was not included in these tests due to its poor stability (Table 2).

Reusability tests of solid 1–150/H<sub>2</sub>O showed a marked increase in the catalytic activity and H<sub>2</sub>O<sub>2</sub> consumption after the first use in reaction. Thereafter, the catalytic performance was maintained at the achieved top-level (Fig. 7a and b). Interestingly, the concentration of leached iron remained constant after each reaction cycle at  $\leq 5 \text{ mg} \cdot \text{L}^{-1}$  (Table S3). To rule out the contribution of leached iron to the catalytic degradation of Rh6G, reaction tests using a solution of 6 mg  $\cdot \text{L}^{-1}$  of Fe<sup>3+</sup> instead solid 1–150/H<sub>2</sub>O were performed, finding a dye degradation value of 27  $\pm$  3% (Fig. S5), which is significantly lower than the 97–100% achieved with this catalyst. This result indicates that Rh6G is degraded by a catalytic process mediated by MIL-53(Fe), in a reaction scenario essentially heterogeneous in nature.

Reusability tests for solid 2–50/H<sub>2</sub>O<sub>2</sub> showed a marked increase in the catalytic activity from the first to the second reaction cycles as well. However, in this case, along with the marked increase in Rh6G decolorization and H<sub>2</sub>O<sub>2</sub> consumption, a high concentration of leached iron  $(43 \pm 3.1 \text{ mg} \cdot \text{L}^{-1})$  was observed (Table S3). This fact suggests that the improvement in the Rh6G degradation rate achieved in the second cycle can be attributed to a significant contribution of Fe<sup>3+</sup> in homogeneous phase instead of a process governed by a heterogeneous catalytic pathway. Solid 2–50/H<sub>2</sub>O<sub>2</sub> was not suitable to be reused in a third



Fig. 7. Reusability studies: Rh6G degradation curves (a,c) and H<sub>2</sub>O<sub>2</sub> consumption (b,d) using solids 1–150/H<sub>2</sub>O (a,b), and 2–50/H<sub>2</sub>O<sub>2</sub> (c,d).

degradation process, since a low structural stability was evident at the end of the second cycle (Fig. 7c and d).

Up to this point, two interesting facts arise from the catalysts reusability studies: i) the increase in the catalytic performance of solid 1-150/H<sub>2</sub>O during the reuse process (i.e. 69 to 98%), and *ii*) the influence of the activation treatments on the stability and reusability of MIL-53(Fe). Regarding *i*), in order to understand the increase in the catalytic efficiency of solid 1-150/H2O after the first reaction cycle, the recovered material from the reuse process was analyzed by PXRD and FTIR spectroscopy, after each catalytic test. The X-ray diffraction profiles showed a progressive decrease in crystallinity linked to the number of reuse cycles performed (Fig. 8a), but the whole crystal structure remains unchanged. This fact is also evident from the FTIR spectra that do not show significant changes, except for a successive decrease in the intensity of the band located at 1668 cm<sup>-1</sup>, associated to the C=O stretching of DMF (Fig. 8b). This change suggests that a likely cause of the increase in the catalytic activity could be related to the additional loss of the bulky DMF. However, the notable activity increase observed after the first use indicates that an additional phenomenon would exist. A modification of the iron oxidation state or a segregation of iron oxide nanoparticles appear as probable causes. However, it is important to remark that no changes in the spectral zone related to [FeO<sub>6</sub>] polyhedra are observed.

To shed light on analysis of the obtained results, solid 1-150/H<sub>2</sub>O, before and after the first catalytic run, was studied by Mössbauer spectroscopy at 298 and 13 K. All spectra exhibit two central peaks of similar intensity, which were adequately fitted using two doublets (Fig. 9). For both samples, the doublets have isomeric shifts ( $\delta$ ) assignable to highspin Fe<sup>3+</sup> ions in octahedral coordination [52], which is consistent with the structure of MIL-53(Fe) [53]. In addition, these doublets show different values of quadrupole splitting ( $\Delta$ ). The values of this hyperfine parameter are related with the surrounding symmetry of the iron nucleus: greater values of  $\Delta$  indicates the existence of a higher asymmetry of the site. Besides, high spin ferric ions have relatively small quadrupole splittings, typically 0.3-0.7 mm/s [52]. However, as it can been in Table 4, the  $\Delta$  values for both doublets in fresh and used catalyst are considerably larger than these values. Therefore, the paramagnetic Fe<sup>3+</sup> ions are in two highly distorted sites, one of them (with larger  $\Delta$  value) more asymmetric than the other one. These different environments are consistent with the existence of different types of interactions between the [FeO<sub>6</sub>] units and the DMF/H<sub>2</sub>O occluded inside of MIL-53(Fe) pores [40]. Considering that the isomer shift values of  $Fe^{2+}$  species are of about 1 mm/s, the existence of these species can be ruled out [54]. On the other hand, the presence of superparamagnetic iron oxide nanoparticles ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) can be discarded too. When the measurement temperature of the Mössbauer spectra is lowered, the magnetic relaxation processes are slowed. Consequently, if a complete magnetic blocking is reached, a doublet is transformed in a sextuplet. But, if extremely small nanoparticles would be present, a temperature as low as

13 K is not enough to complete the blocking of the superparamagnetic relaxation. Notwithstanding, at 13 K a partial blocking is reached and, depending on the degree of this blocking, at least a curved background should be undoubtedly observed. None of these phenomena are present in the spectra at 13 K of solid 1–150/H<sub>2</sub>O recovered after the first reaction cycle; therefore we can discard the presence of iron oxide nanoparticles in the used catalyst. Consequently, the increase of the catalytic activity in the first reaction cycle cannot be attributed to these species. An interesting detail is that both doublets in the spectrum of the catalyst after the first catalytic use show a decrease of quadrupole splitting ( $\Delta$ ) with respect to that one of the fresh catalyst. This result is detected in the spectra measured at 298 and 13 K. A possible explanation for this result is that changes in the second sphere of coordination of Fe<sup>3+</sup> ions occur during the catalytic reaction. This modification could be due to DMF removal, in agreement with the FTIR results.

Another remarkable aspect is related to the increase of Mössbauer effect when the measuring temperature is lowered from 298 K to 13 K. In the case of the fresh catalyst, Mössbauer effect increases 80% lowering the temperature. This indicates that the material is extremely flexible at 298 K and it becomes rigid at 13 K. This observation is coherent with the *breathing effect* characteristic of MIL-53(Fe) [25] and, as far as we know, this is the first time that this property is evidenced by Mössbauer spectroscopy. In the case of the catalyst after the first catalytic use, the increase of Mössbauer effect is around 150%. This extraordinary increase indicates that the catalyst structure becomes yet more flexible after reaction, in line with the lower crystallinity observed by XRD.

On the basis of these results, it is possible to attribute the increase in catalytic activity of solid  $1-150/H_2O$  after the first reaction run to the removal of DMF molecules remaining inside the structure when the activation method 1 is applied. The removal of DMF molecules would favor the reaction process by facilitating the accessibility of  $H_2O_2$  to the catalytic sites.

Concerning the influence of the activation treatment in the reusability and stability of the catalysts, it is important to remark that the main difference between solids  $1-150/H_2O$  and  $2-50/H_2O_2$  is their DMF and water contents (Table 1). However, as it was evidenced in reuse tests (Fig. 7), such difference would determine the stabilizing effect on the structure of the catalysts. Evolution of the DMF content of these solids during the reuse experiments is shown in Table 5. As can be seen, solid  $1-150/H_2O$  experienced a loss of DMF during the first reaction cycle that was subsequently stabilized at 0.06 mol; whereas, solid  $2-50/H_2O_2$  had an initial lower DMF content (0.05 mol of DMF per mole of [Fe(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>) (OH)]) which decreased to 0.03 after the two catalytic tests performed.

In summary, the results suggest a dual effect of DMF molecules in the MIL-53(Fe) structure, since the DMF content affects both the stability and the activity of MIL-53(Fe) as catalyst. Based on our results, a critical remaining DMF amount of 0.06 mol per [Fe(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)(OH)] unit in the MIL-53(Fe) structure seems to maximize the performance of the material



Fig. 8. (a) XRD profiles and (b) FTIR spectra of solid 1–150/H<sub>2</sub>O recovered after the reuse process.



Fig. 9. Mössbauer spectra of solid 1–150/H<sub>2</sub>O before and after the first catalytic cycle measured at (a) 298 K and (b) 13 K.

## Table 4 Mössbauer parameters of solid $1-150/H_2O$ before and after the first catalytic cycle.

Species	Parameters	298 K	298 K		
		Fresh	1 <sup>st</sup> cycle	Fresh	1 <sup>st</sup> cycle
Fe <sup>3+</sup> paramagnetic in distorted octahedral	$\Delta$ (mm/s)	$\begin{array}{c} 1.02 \pm \\ 0.01 \end{array}$	$\begin{array}{c} 0.85 \\ \pm \ 0.01 \end{array}$	$\begin{array}{c} 0.93 \pm \\ 0.01 \end{array}$	$\begin{array}{c} 0.88 \\ \pm \ 0.02 \end{array}$
site	δ (mm/s) %	$\begin{array}{l} 0.41 \pm \\ 0.01 \\ 80 \pm 3 \end{array}$	$\begin{array}{c} 0.42 \\ \pm \; 0.01 \\ 80 \pm 3 \end{array}$	$\begin{array}{c} 0.54 \pm \\ 0.01 \ 70 \pm 2 \end{array}$	$\begin{array}{c} 0.54 \\ \pm \ 0.01 \\ 77 \pm 1 \end{array}$
Fe <sup>3+</sup> paramagnetic in more distorted	Δ (mm/s)	$\begin{array}{c} 1.13 \pm \\ 0.05 \end{array}$	$\begin{array}{c} 0.92 \\ \pm \ 0.02 \end{array}$	$\begin{array}{c} 1.02 \pm \\ 0.01 \end{array}$	$\begin{array}{c} 0.98 \\ \pm \ 0.07 \end{array}$
octahedral site	δ (mm/s)	$\begin{array}{c} 0.36 \pm \\ 0.02 \end{array}$	0.35 (*)	$\begin{array}{c}\textbf{0.48} \pm \\ \textbf{0.01} \end{array}$	$\begin{array}{c} 0.49 \\ \pm \ 0.04 \end{array}$
	%	$20\pm3$	$20\pm3$	$30\pm2$	$23\pm1$

 $\Delta :$  quadrupole splitting,  $\delta :$  isomer shift (all isomer shifts are referred to  $\alpha \text{-} Fe$  at 298 K).

(\*): parameter held fixed in fitting.

in the heterogeneous catalytic reaction. This fact can be associated with the ability of DMF to act as a charge-neutral coordinating species [25, 55] allowing to stabilize the framework during Fenton reaction. Additionally, it could be related to the fact that at higher DMF contents the metal sites might be partially blocked while at lower contents the material loses stability, increasing iron leaching.

### 3.6. Comparison with other catalysts for Rh6G degradation

In order to discuss our results in a broader state-of-the-art context, examples of literature in which Rh6G dye was degraded by using different Fenton heterogeneous catalysts is also presented. The

Tai	ble	5

Elemental analysis and formulas of solids recovered from the reuse process.

corresponding experimental conditions and resultant dye degradation are summarized in Table 6.

By analyzing our catalysts in this context some interesting points emerge as conclusion: the activation strategies applied to MIL-53(Fe)<sub>as</sub> allowed to improve its catalytic activity under conditions reducing energy and process demands. Thus, working on the natural pH of the dye in aqueous solution and operating at room temperature appears as the most significant advantages. In addition, regarding other catalysts reported in the literature [56–58] it was also possible to reduce the H<sub>2</sub>O<sub>2</sub> requirement and optimize its consumption efficiency, which contributes to further decrease operational costs.

Considering the reaction kinetics, the catalysts tested in this work exhibit longer times to degrade the Rhodamine 6G dye than the catalysts found in literature [57–59], which is a disadvantage. However, it should be noted that in some of these works the leached iron concentrations during the reaction is not reported, being thus difficult to define clearly whether the obtained percentages of decolorization and degradation of the dye are exclusively resultant from a heterogeneous catalytic process. In such cases, the existence of homogeneous contribution derived from iron in solution cannot be ruled out.

Finally, in this work we show how to obtain a MOF material (MIL-53 (Fe) activated  $1-150/H_2O$ ) capable of being reused for at least five catalytic cycles without loss of activity and without requirements of additional treatments between reaction runs. This fact is undoubtedly another significant advantage over the heterogeneous catalysts reported in the literature [56–59].

### 4. Conclusions

In this work, the experimental evidence provided by: *i*) the screening of different activated MIL-53(Fe) phases, *ii*) the reuse assays of the catalysts named as solids  $1-150/H_2O$  and  $2-50/H_2O_2$  and *iii*) the

Solids	Use cycles	Experimental (calcula	ited) %	Experimental formulas					
		С	Ν	Н					
$1-150/H_2O$	Initial	37.82 (38.32)	0.64 (0.64)	2.99 (2.94)	[Fe(C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> )(OH)]·(C <sub>3</sub> H <sub>7</sub> NO) <sub>0.12</sub> (H <sub>2</sub> O) <sub>0.90</sub>				
	I	37.27 (37.37)	0.36 (0.36)	2.91 (2.93)	[Fe(C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> )(OH)]·(C <sub>3</sub> H <sub>7</sub> NO) <sub>0.07</sub> (H <sub>2</sub> O) <sub>1.01</sub>				
	III	37.12 (36.58)	0.31 (0.32)	3.12 (3.09)	[Fe(C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> )(OH)]·(C <sub>3</sub> H <sub>7</sub> NO) <sub>0.06</sub> (H <sub>2</sub> O) <sub>1.32</sub>				
	v	36.99 (36.58)	0.31 (0.32)	3.07 (3.09)	$[Fe(C_8H_4O_4)(OH)] \cdot (C3H7NO)_{0.06}(H_2O)_{1.27}$				
$2-50/H_2O_2$	Initial	36.95 (37.32)	0.26 (0.26)	2.95 (2.98)	[Fe(C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> )(OH)]·(C3H7NO) <sub>0.05</sub> (H <sub>2</sub> O) <sub>1.20</sub>				
	I	36.09 (36.05)	0.20 (0.21)	3.18 (3.19)	[Fe(C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> )(OH)]·(C <sub>3</sub> H <sub>7</sub> NO) <sub>0.04</sub> (H <sub>2</sub> O) <sub>1.57</sub>				
	п	37.40 (35.05)	0.18 (0.18)	3.32 (3.40)	$[Fe(C_8H_4O_4)(OH)] \cdot (C_3H_7NO)_{0.03}(H_2O)_{2.00}$				

### Table 6

Experimental conditions for degradation of Rhodamine 6G using different heterogeneous and homogeneous catalysts in dark-Fenton reactions.

Entry	Catalysts	Reaction conditions	Time (min)	Decolorization (%)	Degradation (%)	H <sub>2</sub> O <sub>2</sub> Consumption (%)	Leached ions $(mg \cdot L^{-1})$	Catalysts reusability	Reference
1	MIL-53(Fe) activated 1-150/H <sub>2</sub> O	$[Rh6G] = 5 \\ mg \cdot L^{-1} \\ [Catalyst] = 1 \\ g \cdot L^{-1} \\ [H_2O_2] = 8 \\ mm0 \cdot L^{-1} \\ Initial pH = 6.0$	360	71	43 (COD)	14	Iron: 2.6	Five consecutive reaction runs. No significant loss of catalytic activity. No pretreatment	This work
2	MIL-53(Fe) activated 2-50/H <sub>2</sub> O <sub>2</sub>	$\begin{split} T &= 25 \ ^{\circ}\text{C} \\ & [Rh6G] = 5 \\ & \text{mg} \cdot L^{-1} \\ & [Catalyst] = 1 \\ & \textbf{g} \cdot L^{-1} \\ & [H_2O_2] = 8 \\ & \text{mmol} \cdot L^{-1} \\ & \text{Initial pH} = 6.0 \end{split}$	360	83	48 (COD)	19	Iron: 2.7	One reaction run	This work
3	CuFeZSM-5 Zeolite	$\begin{split} T &= 25 \ ^{\circ}\text{C} \\ [\text{Rh6G}] &= \\ 100 \ \text{mg} \cdot \text{L}^{-1} \\ [\text{Catalyst}] &= 1 \\ \text{g} \cdot \text{L}^{-1} \\ [\text{H}_2\text{O}_2] &= 267 \\ \text{mmol} \cdot \text{L}^{-1} \\ \text{Initial pH} &= \\ 3.4 \end{split}$	120	65	0 (TOC)	No data	Iron: 0.8 Copper: 2.1 Total: 2.9	Two consecutive reaction runs 26% decrease in catalytic activity	[56]
4	Fe-USY Zeolite	T = 25 °C  [Rh6G] =  100 mg · L-1  [Catalyst] = 1  g · L-1  [H2O2] = 160  mmol · L-1  Initial pH =  6.0  T = 50 °C	150	70	58 (TOC)	Not reported	Not reported	No data	[59]
5	FeZSM-5 (CE) Zeolite	[Rh6G] = [Rh6G] = $100 \text{ mg} \cdot L^{-1}$ [Catalyst] = 1 $g \cdot L^{-1}$ $[H_2O_2] = 160$ $mmol \cdot L^{-1}$ Initial pH = 4.9 T = 25 °C	150	90	80 (TOC)	Not reported	Not reported	No data	
6	Fe/Fe3C@ Fe/N- Graphene	$ \begin{array}{l} {\rm [Rh6G]} = 5 \\ {\rm [Rh6G]} = 5 \\ {\rm mg} \cdot {\rm L}^{-1} \\ {\rm [Catalyst]} = \\ {\rm 0.5 \ g} \cdot {\rm L}^{-1} \\ {\rm [H_2O_2]} = 50 \\ {\rm mmol} \cdot {\rm L}^{-1} \\ {\rm Initial \ pH} = \\ {\rm 3.0} \\ {\rm T} = {\rm Not} \\ {\rm specified} \end{array} $	40	96	62 (180 min) (TOC)	Not reported	Not reported	Thirteen reaction runs. No significant loss of catalytic activity. Requires pretreatment	[57]
7	α-FeOOH	specified $[Rh6G] = 5$ $mg \cdot L^{-1}$ $[Catalyst] = 1$ $g \cdot L^{-1}$ $[H_2O_2] = 33$ $mmol \cdot L^{-1}$ Initial pH = 7.0 T = Not specified	60	23	Not reported	Not reported	Not reported	Not reported	[58]
8	FeCl <sub>3</sub> ·6H <sub>2</sub> O Homogenous	[Rh6G] = 5 $mg \cdot L^{-1}$ [Catalyst] = 3 $mg \cdot L^{-1}$ $[H_2O_2] = 8$ $mmol \cdot L^{-1}$ Initial pH =	360	14	No data	Not reported	3	Non-reusable	This work (ESI)

(continued on next page)

#### Table 6 (continued)

Entry	Catalysts	Reaction conditions	Time (min)	Decolorization (%)	Degradation (%)	H <sub>2</sub> O <sub>2</sub> Consumption	Leached ions $(mg \cdot L^{-1})$	Catalysts reusability	Reference
9	FeCl <sub>3</sub> .6H <sub>2</sub> O Homogenous	$\begin{array}{l} 6.0 \\ T = 25 \ ^{\circ}\text{C} \\ [\text{Rh6G}] = 5 \\ \text{mg} \cdot \text{L}^{-1} \\ [\text{Catalyst}] = \\ 22 \ \text{mg} \cdot \text{L}^{-1} \\ [\text{H}_2\text{O}_2] = 8 \\ \text{mmol} \cdot \text{L}^{-1} \\ \text{Initial pH} = \\ 6.0 \\ T = 25 \ ^{\circ}\text{C} \end{array}$	70	98	80 (COD)	98	22	Non-reusable	

characterization (PXRD, FTIR, TGA, elemental analysis, XPS and Mössbauer spectroscopy) of all catalysts under study, demonstrated a dual role of DMF molecules in the structural stability as well as in the performance of MIL-53(Fe) as a dark-Fenton heterogeneous catalyst. As it was described above, by the application of different activation strategies it was possible to obtain different percentages of exchange of DMF by H<sub>2</sub>O molecules, increasing the activity of the catalyst when the DMF removal was highest. However, this fact was also adverse for the catalyst stability, and the highest iron leaching was observed as well. The presence of DMF in the MOF structure is necessary to get a balance between catalytic efficiency and stability. The present study allows us to conclude that it is essential to achieve a delicate tuning in the initial DMF content in order to get an optimal catalytic performance when MIL-53(Fe) is used as a dark-Fenton heterogeneous catalyst.

The incidence of different operational variables such as pH, temperature,  $[H_2O_2]/[Fe^{3+}]$  ratio and Rh6G concentration was also investigated in order to evaluate the catalyst tolerance and the better working windows. Through this study we found that MIL-53(Fe) exhibits the best catalytic performance in compromise with optimum structural stability when the DMF content is (not fully) eliminated by a thermal treatment followed by soaking of the solid in water. The Rh6G dye is more efficiently degraded by adjusting the initial pH value to 6.0, operating at 25 °C and fixing the  $[H_2O_2]/[Fe^{3+}]$  ratio in 2.

From a more general perspective, this work also demonstrated that the evacuation of DMF from a flexible MOF as MIL-53(Fe), whose internal porosity cannot be measured in the usual manner by N<sub>2</sub> adsorption, is indeed a challenge and it was never studied before in the context of its role in heterogeneous catalysis. The activation methods proposed by us could also be applied for other MOFs whose synthesis also involves DMF. Examples of these materials are: several members of the MILs family (including MIL-100, MIL-101, MIL-88 A, among others), MOF-74-M/CPO-27-M, UiO-66, IRMOFs, among the most famous archetypical MOFs that are synthesized using DMF as solvent. In the mentioned materials, not only their adsorption properties have been studied but also their catalytic activity. Thus, our activation methods would be suitable to be tested, in order to determine if they produce changes in their catalytic performances.

The conclusions of this work represent a significant contribution to the potential application of MOFs as heterogeneous catalysts, demonstrating particularly that MIL-53(Fe) is a suitable candidate to be employed in wastewater treatment.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### CRediT authorship contribution statement

Gabriela A. Ortega Moreno: Methodology, Formal analysis,

Writing - original draft. **María C. Bernini:** Conceptualization, Formal analysis, Supervision, Writing - original draft. **Andrés A. García Blanco:** Methodology, Formal analysis, Writing - original draft. **Sergio G. Marchetti:** Methodology, Formal analysis, Writing - original draft, Funding acquisition. **Bibiana P. Barbero:** Conceptualization, Formal analysis, Supervision, Writing - original draft, Funding acquisition. **Griselda E. Narda:** Conceptualization, Writing - original draft, Funding acquisition.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.micromeso.2020.110267.

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