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João Diniz da Costa

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1 Environmental mineralization of caffeine micro-pollutant by Fe-MFI zeolites

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10 **Key words:** Fe-MFI; zeolite; caffeine; micro-pollutant; mineralization; Fenton reaction.

11 **Abstract**

12 Environmentally emerging micro-pollutant, caffeine, was mineralized (i.e full degradation)  
13 by the isomorphic incorporation of Fe into silicalite-1 (MFI structure zeolite) through a  
14 microwave synthesis method. The Fe incorporation conferred mesopore formation that  
15 facilitated caffeine access and transport to the MFI zeolite structure. Increasing the Fe  
16 content favored the formation of Fe(O)<sub>4</sub> sites within the MFI structure. The catalytic activity  
17 for the degradation of caffeine increased as a function of Fe(O)<sub>4</sub> sites via a Fenton-like

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4 18 heterogeneous reaction, otherwise not attainable using Fe-free pure MFI zeolites.  
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6 19 Caffeine degradation reached 96% (TOC based) for zeolites containing 2.33% of Fe.  
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## 10 20 **1. Introduction**

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13 21 Caffeine is rapidly becoming a contemporary anthropogenic pollutant in natural waters.  
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15 22 It has been found in lakes in Switzerland (Buerge et al., 2003) and in the sea coast of  
16 23 Oregon (Rodriguez del Rey et al., 2012) in the USA. Caffeine pollution may be caused  
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18 24 by effluents from our current lifestyle, related to drinking coffee and many energy drinks  
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20 25 containing caffeine. Although the caffeine toxicity is of little concern for humans under  
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22 26 moderate conditions, a similar generalization for aquatic organisms cannot be made since  
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24 27 they are continuously exposed over a lifetime (Bruton et al., 2010). Hence, it is imperative  
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26 28 to avoid future detrimental environmental impacts if caffeine continues to accumulate in  
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28 29 natural waters. Caffeine can be degraded biochemically by *Pseudomonas* bacteria  
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30 30 (Gummadi et al., 2009), by photolysis (Bruton et al., 2010), or by using chemical  
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32 31 processes such as ozonation (Rosal et al., 2009). Advanced oxidation processes (AOPs)  
33  
34 32 are also attractive in tackling caffeine degradation, particularly due to the simplicity of  
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36 33 coupling catalysts and oxidants in a single unit operation. One of the most promising  
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38 34 AOPs is the heterogeneous Fenton reaction using iron oxide catalyst and hydrogen  
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40 35 peroxide ( $\text{H}_2\text{O}_2$ ) oxidant (Klamerth et al., 2012, Zeng et al., 2015). In this reaction, the  
41  
42 36 active sites ( $\equiv\text{Fe}^{2+}$ ) react with  $\text{H}_2\text{O}_2$  and generate  $\cdot\text{OH}$  radical, a powerful oxidant  
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44 37 extensively used in the degradation of organic compounds in wastewaters by AOPs  
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46 38 processes (Zubir et al., 2015, Mijangos et a., 2006). The Fenton reaction approach was  
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48 39 recently investigated for caffeine degradation using bio-based combined iron oxide photo  
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4 40 catalysts (Franzoso et al., 2017) and persulfated activated iron catalysts (S. Rodríguez  
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6 41 et al., 2017).

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9 42 Zeolites are efficient materials for separation (Rangnekar et al., 2015), adsorption  
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11 43 (Hoffmann et al., 1997) and catalysis (Vermeiren and Gilson, 2009 and Li et al., 2014)  
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14 44 applications, though they are generally used as adsorbents in water and wastewater  
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16 45 treatment (Kragovi et al., 2013, An, 2013 and Wingenfelder et al., 2005). They can be  
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19 46 prepared and used as either purely microporous or hierarchical micro/mesoporous  
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21 47 materials (Pérez-Ramírez et al., 2008) . The latter form decreases diffusion restrictions  
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24 48 and is widely applied in sorption (Meng et al., 2011) and catalysis (Christensen et al.,  
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26 49 2003). A large variety of functionalities, such as acid-base or redox centers, can be  
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29 50 introduced in zeolites (Moliner, 2012). Heteroatoms, such as Fe, can be incorporated in  
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31 51 zeolites through various methods such as cationic exchange, impregnation, or chemical  
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33 52 vapor deposition of metal precursors after zeolite crystallization (post-synthesis  
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35 53 treatment). Another strategy, called “one pot”, consists in the direct insertion of  
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38 54 heteroatoms during zeolite formation (Bordiga et al., 1996, Giordano et al., 2002); and is  
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41 55 an attractive option for lowering the manufacturing costs and ensuring uniform dispersion  
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43 56 of heteroatoms in either framework or extra-framework positions.

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45 57 *In-situ* hydrothermal synthesis methods have been used to provide isomorphic  
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48 58 incorporation of Fe into MFI zeolite structure, although reports to date have limited the  
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50 59 Si/Fe molar ratio to 100 (1 at%Fe) (Kritchayanon et al., 2006; [Taniguchi et al., 2016](#)).  
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53 60 Further Fe incorporation can be carried out by post-synthesis methods, but they mostly  
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55 61 yield extra-framework iron oxide species (Maxwell et al., 2003; [Anizelli et al., 2016](#)). The  
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58 62 isomorphic incorporation of iron species into zeolites differs from conventional  
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4 63 immobilization of iron-based particles (e.g. Fe, Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub>) on substrates such as  
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6 64 graphene oxides (Zubir et al., 2014), silica shells (Liu et al, 2014), carbon aerogels (Wang  
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9 65 et al., 2013) or clays (Gao et al., 2015). The main advantage of inserting transition  
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11 66 elements in zeolites by direct synthesis is related to the possibility of achieving a high  
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14 67 dispersion of the metal in the zeolitic structure.

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16 68 Herein, we show the production of higher Fe content Fe-MFI zeolites **confers enhanced**  
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19 69 catalytic performance for the mineralization of caffeine **as compared to traditional pure**  
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21 70 **MFI zeolites**. The as-synthesized Fe-MFI zeolites **were** tested for the catalytic caffeine  
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24 71 removal from synthetic wastewaters under the conditions of the Fenton-like  
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26 72 heterogeneous reaction. **The catalytic testing was accompanied by the charactersition of**  
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29 73 **Fe-MFI zeolites. Of particular interest, the catalytic results are corelated to the role played**  
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31 74 **by Fe–O sites in the mesoporous zeolite structure, in order to** provided new insights into  
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34 75 the improved catalytic efficiency of Fe-MFI zeolites.

## 35 36 76 37 38 77 **2. Experimental**

### 39 78 40 79 **2.1. Materials Synthesis**

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43 80 The zeolite synthesis solutions were prepared by mixing TEOS (98%, Aldrich), ultrapure  
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46 81 water (18.2 MΩ), tetrapropyl ammonium hydroxide (TPAOH, 20 wt% aqueous solution,  
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48 82 Sigma) and iron (III) acetylacetonate (Fe(acac)<sub>3</sub>, 99.9%, Alfa Aesar). The sol molar  
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51 83 concentration was set at (x/2) Fe<sub>2</sub>O<sub>3</sub> :100 SiO<sub>2</sub> : 40 TPAOH : 1950 H<sub>2</sub>O : 400 C<sub>2</sub>H<sub>5</sub>OH  
52  
53 84 where x is the required atomic concentration of Fe in the MFI zeolite. Subsequently, the  
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56 85 sols were aged under stirring for 24 h at 25 °C. The aged sols were placed into autoclaves  
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58 86 in a commercial laboratory microwave oven (Milestone ETHOS 1600). The hydrothermal  
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4 87 treatment was conducted as one pot synthesis. **Initially**, the closed autoclaves were  
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6 88 irradiated for 90 min at 80 °C with a MW power of 250 W. **Subsequently**, the autoclaves  
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9 89 were heated to 180 °C and left for 60 min under MW irradiation of 400 W. Finally, the  
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11 90 autoclaves were cooled down to 50 °C before opening. The formed solid products were  
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14 91 separated by centrifugation at 9500 rpm (JOUAN B4i) and washed twice with distilled  
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16 92 water. A centrifugation step followed after each wash. The washed solids were dried for  
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19 93 4 h at 155 °C prior to calcination. The dried materials were then calcined in air at 550 °C  
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21 94 for 8 h with heating and cooling rates of 5 °C min<sup>-1</sup>.

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23 95 **Characterization.** A PANalytical X'Pert Pro X-ray diffractometer operating at 40 mA and  
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26 96 40 kV was used for measurement of X-ray diffraction patterns. PANalytical X'pert Pro  
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29 97 software was used to determine the crystal phase and calculate the lattice constants.  
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31 98 Morphological features of the samples were observed on a Hitachi S-4800 field emission  
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33 99 scanning electron microscope (FESEM), and a JEOL JMS-2010 high resolution  
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36 100 transmission electron microscope (HR-TEM). The elemental composition of samples was  
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38 101 assessed using a JEOL Model JSM-7001F SEM system equipped for energy-dispersive  
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41 102 X-ray spectroscopy (EDS). X-ray spectra were collected with a JEOL Minicup EDS  
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43 103 detector (Model EX-64175JMH), with a 133 eV resolution, 10 mm<sup>2</sup> effective area, polymer  
44  
45 104 ultrathin window (UTW) and using JEOL Analysis Station JED-2300 Series (v. 3.84)  
46  
47  
48 105 software. Microanalysis acquisition conditions were 20 keV at 10 mm working distance.  
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51 106 The descriptors (x%Fe-MFI) for the samples are based on the Fe content detected in  
52  
53 107 the solid ascertained by EDS, where x represents the atomic percentage of Fe in (Si+Fe)  
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56 108 mixture within the zeolite sample (i.e. x=0.34 (0.34%Fe-MFI)). A Renishaw inVia confocal  
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59 109 Raman Microscope Spectrometer operated with UV laser line (325 nm) was employed  
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110 for Raman measurements. The Raman spectra were deconvoluted using Origin 8.5  
111 software. Nitrogen sorption measurements were performed on a Micromeritics TriStar  
112 3020 analyzer after degassing at 300 °C for 24 h under vacuum on a VacPrep061  
113 degassing system. Specific surface area values were calculated by Brunauer-Emmett-  
114 Teller (BET) model, from adsorption data in the 0.05–0.20 relative pressure range ( $p/p_0$ ).  
115 Pore diameters were determined via the density functional theory (DFT) modeling of the  
116 entire adsorption branch ( $p/p_0 = 0.0005–0.95$ ) using a cylindrical pore model on metal  
117 oxide surface with a regularization factor of 0.40. The minimum size modeled by DFT  
118 ( $12\text{\AA}$ ) was limited by the lower limit value of the relative pressure ( $p/p_0 \sim 5 \times 10^{-4}$ ).

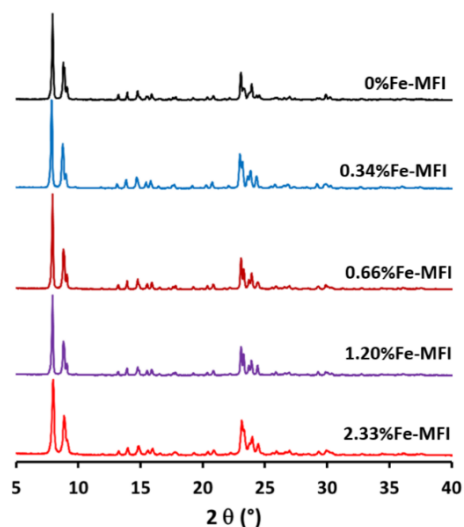
## 119 **2.2. Catalysis experiments**

120 The catalytic activity of materials was tested using  $0.33 \text{ g L}^{-1}$  zeolite and a commercial  
121  $\text{Fe}_3\text{O}_4$  (98%, Sigma-Aldrich), deionized water at pH of 3 (adjusted by HCl, 36%wt, Chem-  
122 supply Pty Ltd) and 22 mM hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%, Chem-supply Pty Ltd.). The  
123 caffeine concentration was varied from 10 to 20 and 50 ppm in solution at 25 °C. The  
124 oxidative degradation of caffeine was carried out using a fresh catalyst for each test.  
125 Liquid samples were taken after 1 h of dark adsorption, and 1, 3, 7 and 22 h after  $\text{H}_2\text{O}_2$   
126 was added. The concentration of caffeine in the solution was determined by measuring  
127 the absorbance of the filtered solution at 484 nm on an Evolution 220 UV–Vis  
128 spectrophotometer (Thermo Fisher Sci.). Experimental variation for the concentration of  
129 caffeine in the solution was  $\pm 0.8$  ppm. Total organic carbon (TOC) analysis was  
130 undertaken on a Shimadzu TOC analyzer with an Agilent Eclipse XDB-C8  $4.6 \times 150$  mm  
131 column with  $5 \mu\text{m}$  packing. The TOC analysis was carried out on a  $150 \mu\text{L}$  sample, and

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4 132 the organic carbon content was an average value calculated from four measurements for  
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7 133 each tested catalyst and tested condition.  
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### 9 134 3. Results and discussion

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11 135 The incorporation of Fe in MFI zeolites was carried out during zeolite formation, by a  
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14 136 two-steps microwave-assisted hydrothermal synthesis method. Fe-MFI was produced  
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17 137 from solutions with Si/Fe atomic ratios equal to  $\infty$  (0 %Fe), 400 (0.25 %Fe), 200 (0.5  
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19 138 %Fe), 100 (1 %Fe) and 50 (2 %Fe), though the 25 (4%Fe) samples failed due to direct  
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21 139 gelation of the sol. The Fe concentration in the produced powders, determined by EDS,  
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24 140 generally showed a good transfer of Fe ions from the sol (0.25, 0.5, 1 and 2%) to the  
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27 141 synthesized bulk materials resulting in measured Fe concentrations of 0.34, 0.66, 1.20  
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29 142 and 2.33 % in the solids, respectively. A wide angle XRD analysis was also conducted as  
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31 143 displayed in Fig. 1 in order to determine the crystal structure of the materials. The  
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34 144 measured patterns were compared to the reported in a PDF2 data basis and were  
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36 145 attributed to reference pattern 01-070-4744. These XRD patterns confirm that all formed  
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39 146 materials hold the monoclinic crystal structure (#14, P21/n1), characteristic for calcined  
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41 147 MFI structure.  
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4 149 Fig. 1 XRD patterns of pure MFI (silicalite-1) and Fe-MFI powders (FeS-1) series calcined  
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6 150 at 550 °C.  
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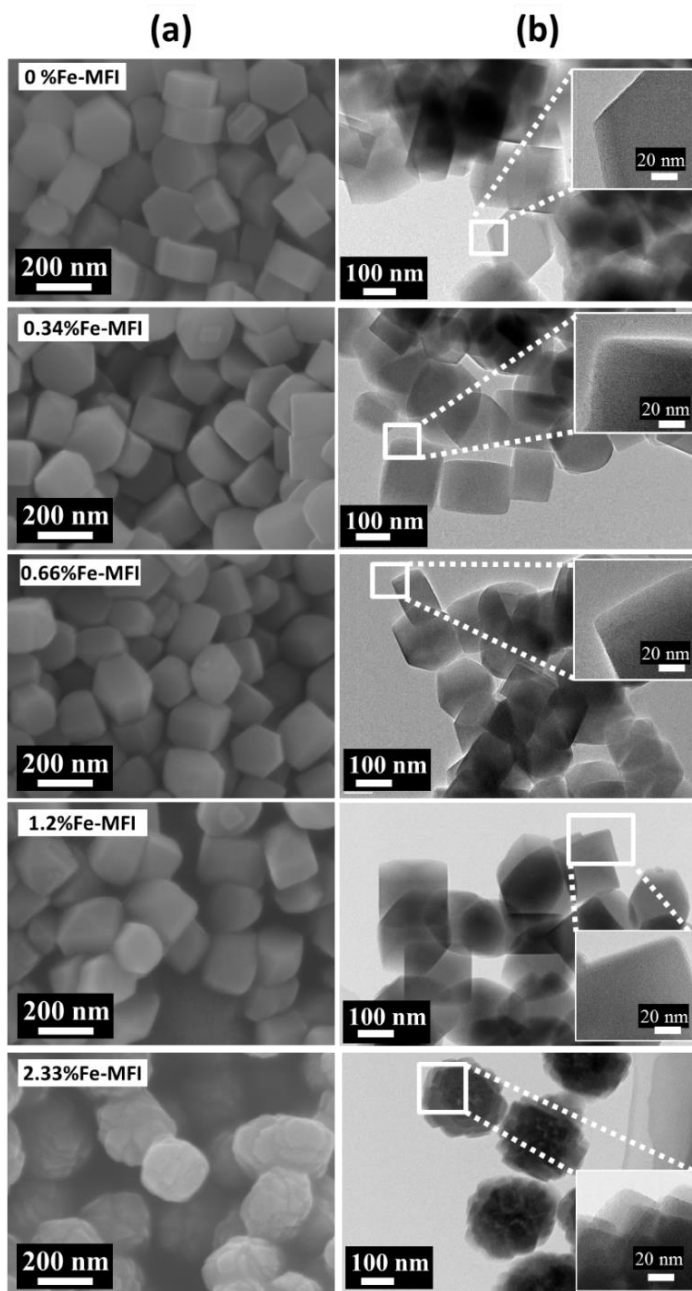
10 151 Table 1 lists the lattice parameters (a, b, and c) calculated from XRD patterns. As  
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12 152 expected for an isomorphous substitution of Si by Fe, the unit cell volume increased when  
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15 153 0.25% Fe was incorporated into the synthesis solution as compared with the blank 0%Fe-  
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17 154 MFI sample. However, the cell volume values did not correlate with the quantity of Fe  
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20 155 detected by EDS. Rather, the unit cell volume peaked as x increased from 0 to 0.34%,  
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22 156 before decreasing sequentially for higher Fe content. The  $\beta$  parameter, which is related  
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25 157 to the crystal lattice distortion, evolved by a different profile to the unit cell volume, peaking  
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27 158 at Fe concentration of 1.20%. Interestingly, no secondary iron oxide phase was detected  
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30 159 in the XRD patterns, thus confirming the presence of monoclinic crystal structure (#14,  
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32 160 P21/n1) (Treacy and Higgins, 2001). It is noteworthy that Fe-MFI zeolites were  
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35 161 synthesized with Fe concentration in excess of 1% (i.e. Si/Fe < 100).  
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39 163 Table 1. Fe concentration in both sols and derived solids, and lattice constants of the  
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42 164 corresponding MFI zeolites. x was measured by EDS. (atom %)  
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	x%Fe-MFI sample					
sol	0	0.25	0.50	1.00	2.00	
solid (x)	0	0.34	0.66	1.20	2.33	
a (Å)	20.056 (5)	20.030 (4)	20.250 (1)	20.110 (3)	19.970 (1)	
b (Å)	19.990 (5)	20.069 (5)	20.158 (8)	20.140 (3)	20.100 (1)	
c (Å)	13.401 (3)	13.396 (4)	11.197 (5)	11.140 (2)	11.045 (8)	
$\alpha, \beta$ (°)	90, 90	90, 90	90, 90	90, 90	90, 90	

$\gamma$ (°)	89.922 (3)	90.124 (4)	90.266 (7)	90.900 (3)	90.420 (1)
Vol. (Å <sup>3</sup> )	5373	5385	4571	4511	4433

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167 Fig. 2 (a) SEM and (b) TEM with HR-TEM inset images of pure MFI (S-1) and Fe-MFI  
 168 (FeS-1) powders series.

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169 The FE-SEM images in Fig. 2a clearly show that the MFI zeolite morphology was  
170 influenced by the Fe concentration. For instance, by raising the Fe concentration from 0  
171 to 1.20%, the particles were getting rounder every time the Fe concentration was  
172 increased. Further increase of x from 1.20% Fe to 2.33% Fe yielded a packed and  
173 aggregated structure, resembling a cauliflower, comprised of smaller cubic crystals (<  
174 100 nm). TEM images in Fig. 2b confirmed the formation of single crystal particles in  
175 samples derived from sols with the lowest iron concentrations (0 to 1.20% Fe). They are  
176 common features of MFI type zeolite morphology. Further increase of the Fe content at  
177 2.33% resulted in a more complex polycrystalline structure made of aggregated cubic  
178 nanocrystals 40 nm in size.

179 To shed further light on Fe-MFI formation, Raman spectroscopy analysis was carried  
180 out to understand the incorporation of Fe ions. Fig. 3 shows two bands common to all  
181 samples (with and without Fe) at  $378\text{ cm}^{-1}$ . The band at  $378\text{ cm}^{-1}$  is associated to with  
182 the Si–O–Si vibrations. The bands at  $1165$ ,  $1019$  and  $516\text{ cm}^{-1}$  were common to the iron-  
183 containing samples only. The bands at  $1165$  and  $1019\text{ cm}^{-1}$  were assigned to vibrational  
184 bands of Si–O–Si near iron and Fe–O–Si, respectively, and the  $516\text{ cm}^{-1}$  band was  
185 assigned to  $\text{Fe}(\text{O})_4$  in the zeolite network (Fan et al., 2009). Any additional bands  
186 potentially allocated to iron oxide particles (li et al., 2012) could not be observed at given  
187 conditions. Coupled with the absence of nano-particle domains in the HR-TEM images in  
188 Fig. 2b, these results clearly indicate that Fe was mainly incorporated in MFI particles as  
189 intra-framework species rather than as iron oxide (i.e. extra-framework) particles.

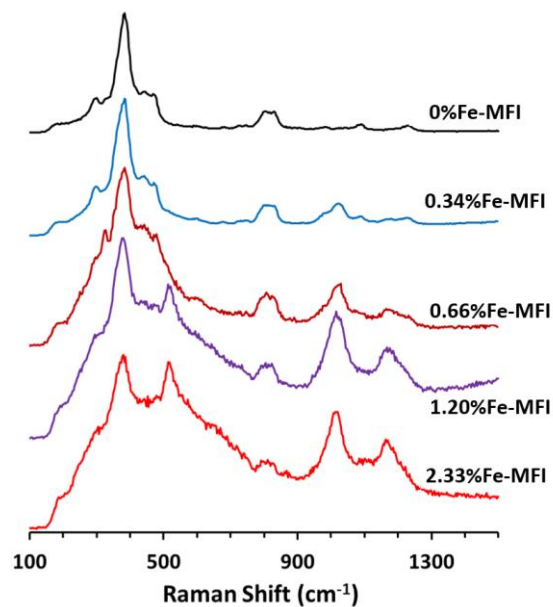


Fig. 3 Raman spectra of pure MFI and Fe-MFI samples.

A further insight into the microstructure of the synthesized zeolites is displayed by their pore size distribution (PSD) (Fig. 4a) determined by the density functional theory (DFT) from N<sub>2</sub> sorption isotherms (Fig. 4b). The incorporation of Fe into MFI conferred both mesoporosity and microporosity to the powders, contrary to the microporosity of pure MFI. This can be further verified by the shift in the average PSD from 10 Å of pores not related to zeolite framework for the pure 0%Fe-MFI to 22, 27 and 30 Å for the 2.33%, 1.20% and 0.66%Fe-MFI samples, respectively. Although microporous features were maintained with the incorporation of Fe, the isotherms of the Fe-MFI powders clearly indicates the formation of large micropores and finally mesopores for the higher Fe concentrations. The BET surface areas increased by Fe incorporation from 336 (0%Fe-MFI) to 414 (0.34%Fe-MFI), 415 (0.66%Fe-MFI), 386 (1.2%Fe-MFI) and 396 m<sup>2</sup> g<sup>-1</sup> (2.33%Fe-MFI), which were in the range of literature data for MFI zeolites (Jung et al., 2009 and Li et al., 2013).

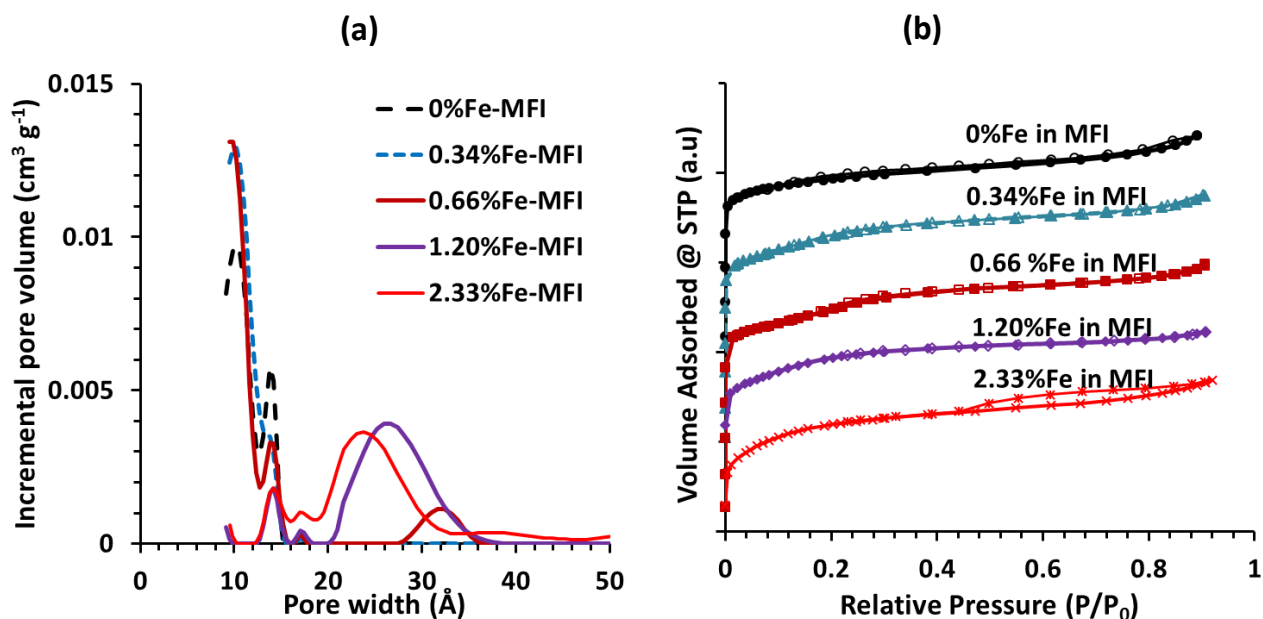


Fig. 4 (a) Pore size distribution and (b) nitrogen sorption isotherms of Fe-MFI and MFI samples.

The as-synthesized Fe-MFI samples were used as catalysts in a Fenton-like heterogeneous reaction as described in the experimental section. Fig. 5a clearly shows that the blank sample (%Fe-MFI) was unable to breakdown caffeine within 7 hours reaction, and only minor degradation was observed by 22 hours. Similar trends were also observed for the 0.34% and 0.66%Fe-MFI samples, which gave very low caffeine degradation rates. However, the results in Fig. 5a strongly suggest that the Fe has to be above a certain concentration to be effective in catalysis, in this case at least 1.20% Fe within the MFI powder. For comparison purpose, a commercially available Fenton like catalyst Fe<sub>3</sub>O<sub>4</sub> was also tested for the degradation of caffeine reaching. The results in Fig 5a confirm that the Fe-MFI zeolite catalysts were more efficient than the Fe<sub>3</sub>O<sub>4</sub> catalyst. For instance, caffeine degradation of up to 98% and 90% were achieved by the 2.33%

and 1.23% Fe-MFI at 20 h, respectively, whilst the  $\text{Fe}_3\text{O}_4$  catalyst reached a maximum degradation of 82%.

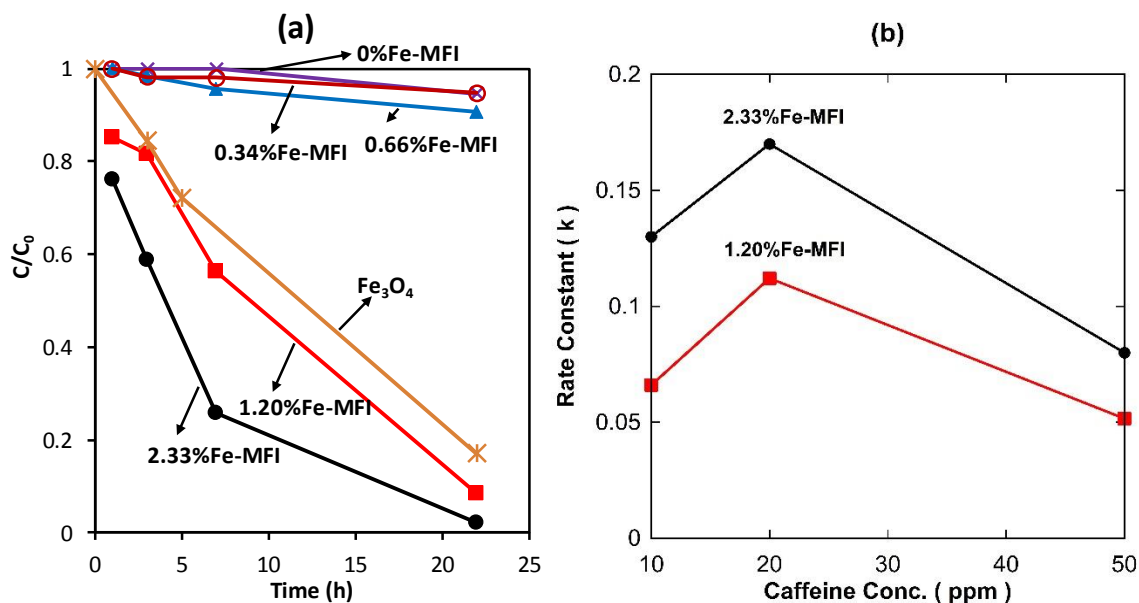


Fig. 5 (a) Caffeine degradation at concentration of 10 ppm in aqueous solution, and (b) rate constant at 10, 20 and 50 ppm @ 7 hours. All experimental conditions:  $\text{H}_2\text{O}_2=22$  mM, pH=3 and 25 °C.

Fig. 5b displays the rate constant ( $k$ ) for the same experimental work by varying the initial concentration of caffeine from 10 to 50 ppm for the most active samples (2.33% and 1.20% Fe-MFI). Again these results demonstrate that the  $k$  values were greater for higher Fe content in the zeolite structure (2.33% Fe-MFI). The  $k$  value consistently increased from 10 to 20 ppm, and then reduced when caffeine concentration increased further to 50 ppm. The reduction of the  $k$  value is associated with mass transfer limitations as adsorption was found to be negligible (~1%). Further, as the surface area of the Fe containing MFI samples were very similar, the higher  $k$  values of 2.33% Fe-MFI were therefore related to the amount of incorporated Fe.

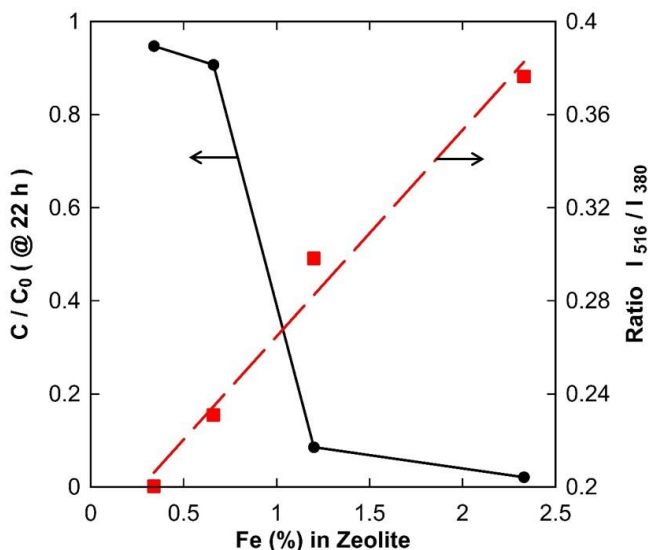


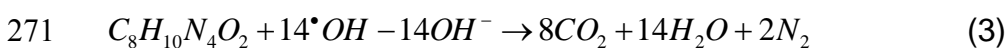
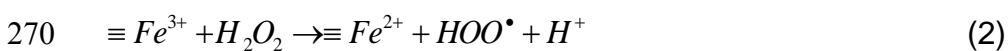
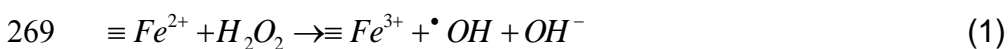
Fig. 6 Caffeine degradation and ratio of Raman peak areas at 516 and 378  $\text{cm}^{-1}$  as the function of iron fraction in Fe-MFI zeolite powders.

In order to explain the improved performance of Fe-MFI samples, the Raman spectra in Fig. 3 were deconvoluted to calculate the ratio of peak areas assigned to vibrational bands of the intra-framework species containing iron oxygen bonds ( $\text{Fe}(\text{O})_4$ ) at 516  $\text{cm}^{-1}$  over the MFI building units band at 378  $\text{cm}^{-1}$ . Fig. 6 shows that the  $I_{516}/I_{378}$  ratio increased almost linearly with an increase of iron content, showing good  $R^2$  fitting correlations (0.982). This fitting confirmed the linearity within the Fe-MFI range in this work and the validity of the Raman deconvolution proposed by Fan and co-workers (Fan et al., 2010). In conjunction with the catalyst activity in Fig. 4a, the results in Fig. 6 strongly suggest that there is significant correlation between the presence of  $\text{Fe}(\text{O})_4$  sites and enhanced degradation of caffeine for Fe concentrations higher than 1.20% in the zeolite. The  $\text{Fe}(\text{O})_4$  sites are thus active in a Fenton-like process. This was accompanied by the presence of mesopores ( $20 < d < 35 \text{ \AA}$ ) in the 1.20% and 2.33%Fe-MFI samples which favored the

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249 diffusion of the small caffeine molecules (length: 10 Å) (Banerjee et al., 2012) into the  
zeolite structure. The very low catalytic activity of the other Fe-MFI samples was attributed  
250 to both insufficient Fe concentration, below 1.20% Fe, and microporosity leading to mass  
251 transfer limitations.  
252

253 Due to the large surface areas of the Fe-MFI powders (~380–390 m<sup>2</sup> g<sup>-1</sup>), solid-liquid  
254 interface reactions occurred preferentially at the Fe(O)<sub>4</sub> sites. This reaction is  
255 schematically shown in Fig. 8 as isomorphic Fe(O)<sub>4</sub> sites embedded into the zeolite  
256 structure degrade caffeine. In this reaction, H<sub>2</sub>O<sub>2</sub> was catalytically decomposed at the  
257 Fe<sup>2+</sup> active sites into •OH radicals and OH<sup>-</sup> hydroxyl ions (Eq. 1). As proposed by  
258 Gonzalez-Olmos and co-workers (Gonzalez-Olmos, 2011), Fe<sup>2+</sup> active sites are  
259 generated by the reaction of H<sub>2</sub>O<sub>2</sub> with isolated Fe<sup>3+</sup> sites at the Fe-MFI surface or by  
260 •OOH radicals formed previously in the reaction of H<sub>2</sub>O<sub>2</sub> with Fe<sup>3+</sup> (Eq. 2). As confirmed  
261 by TOC analysis (Fig. 7), the powerful •OH radicals mineralized the caffeine (C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>)  
262 into CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> species (Eq. 3). TOC analysis also confirms the degradation ratio  
263 ascertained by UV-vis measurement (Fig. 6), showing very high level of mineralization of  
264 caffeine at 94.5 and 96.0% for the 1.20% and 2.33% Fe-MFI samples, respectively.  
265 Therefore, this reaction is characterized by the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> and oxidation of  
266 Fe<sup>2+</sup> to Fe<sup>3+</sup>, concomitantly with the mineralization of caffeine. Provided H<sub>2</sub>O<sub>2</sub> is supplied,  
267 these results demonstrate the potential of Fe-MFI zeolites to treat waters contaminated  
268 with caffeine micro-pollutants.





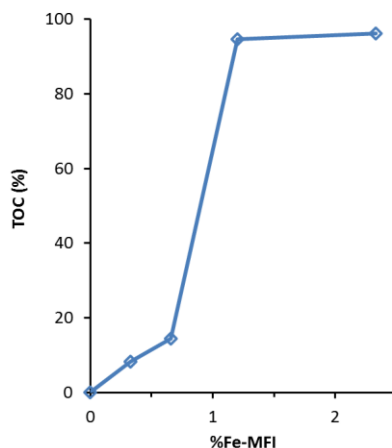


Fig. 7 TOC values of 10 ppm caffeine solution after 22h using Fe-MFI zeolites with varying Fe content.

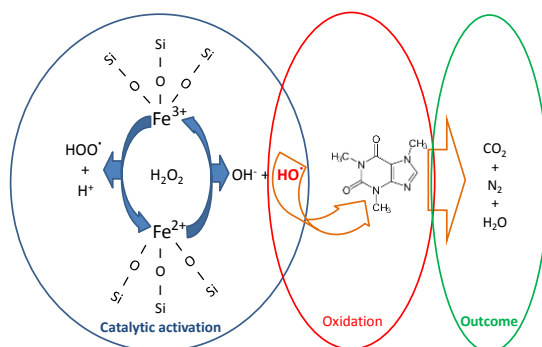
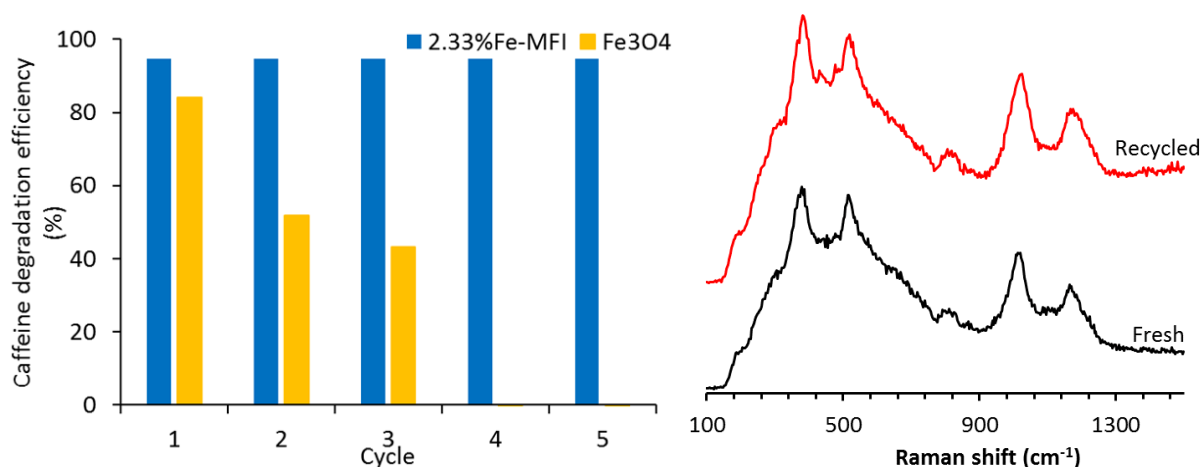


Fig. 8 Schematic representation of the reaction mechanism using Fe-MFI zeolite in the heterogeneous Fenton-like reaction for caffeine degradation in this work.

The best performing 2.33%Fe-MFI catalyst was also tested for multiple reaction cycles and compared against the commercial Fe<sub>3</sub>O<sub>4</sub>. Fig. 9a shows that the 2.33%Fe-MFI catalyst maintained a constant caffeine degradation efficiency of 98% up to the tested 5 cycles. Contrary to this, the commercial Fe<sub>3</sub>O<sub>4</sub> catalyst degradation declined very quickly after the first cycle, and at the fourth cycle this catalyst was unable to degrade caffeine. This fast decrease in degradation efficiency is associated with the oxidation of the active

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4 285 phase  $\text{Fe}^{2+}$  into a non-active phase  $\text{Fe}^{3+}$  in  $\text{Fe}_3\text{O}_4$  based catalysts (Zubir et al., 2015). In  
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7 286 the case of the Fe-MFI catalyst, the multiple cycling stability strongly suggests that the  
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9 287 active phase was maintained. This is confirmed by the Raman analysis (Fig.9b) which  
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11 288 shows that the spectrum of the fresh sample remained unaltered after 5 cycles of caffeine  
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14 289 degradation, thus confirming the catalytic stability of Fe-MFI upon cycling.



290  
291 Fig. 9 (a) Cycling experiment conducted on 2.33%Fe-MFI zeolites and commercial  
292 Fe<sub>3</sub>O<sub>4</sub> in a caffeine degradation ( $C_{\text{caffeine}} = 10$  ppm) at 20 h per cycle; (b) Raman spectra  
293 of fresh and a sample 2.33%Fe-MFI zeolite exposed to 5 cycles of caffeine degradation.

#### 294 4. Conclusions

295 The incorporation of Fe with concentrations above 1.0% conferred mesoporosity to the  
296 Fe-MFI, thus facilitating the access of caffeine to the zeolite porous structure. The  $\text{Fe}(\text{O})_4$   
297 bonds in the Fe-MFI zeolite structure were very active leading to the decomposition of  
298  $\text{H}_2\text{O}_2$  into radicals, thus promoting the degradation of caffeine in the heterogeneous  
299 Fenton-like reaction. The significant increase in catalytic activity was attributed to

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300 mesoporosity coupled with Fe concentrations at and above 1.20% in the MFI structure.  
301 TOC removal of 96% with 2.33%Fe-MFI sample was achieved.

302  
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