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**Photo-Fenton reaction in the presence of morphologically controlled hematite as iron source****This is the author's manuscript**

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(Article begins on next page)



# UNIVERSITÀ DEGLI STUDI DI TORINO

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1  
2 **Photo-Fenton reaction in the presence of morphologically controlled**  
3 **hematite as iron source**

4  
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12  
13 **Abstract**

14 Hematite particles with controlled size and shape (cubic, spherical and ovoidal, with size range  
15 from hundreds nm to  $\mu\text{m}$ ) were produced by modulating the conditions of synthesis and were  
16 characterized by different techniques (XRD spectroscopy, scanning electron microscopy, BET  
17 analysis, dynamic light scattering, UV-vis spectroscopy). The photoactivity of the synthesized  
18 hematite particles was tested towards the degradation of phenol under photo-Fenton conditions,  
19 obtaining optimal results in the pH range 3-4. Although the smaller particles have a larger contact  
20 interface between the solid and the solution, no obvious relationship was found between size and  
21 photoactivity. A possible explanation is that the smallest particles tested showed an important  
22 radiation scattering, which would interfere with radiation absorption and, therefore, with  
23 photoactivity. In contrast, the most photoactive samples were those showing the highest  
24 concentrations of leached iron. This issue would imply that photoactivity may be related to partial  
25 dissolution of hematite with formation of Fe(II) and of photo-active Fe(III) species, which activate  
26 the classic photo-Fenton process. Anyway, leached Fe was limited to the  $\mu\text{g L}^{-1}$  range that is safely  
27 far from the  $\text{mg L}^{-1}$  limits for wastewater.  
28  
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30  
31  
32 **Keywords:** Hematite colloids; Photo-Fenton reaction; Advanced oxidation processes; Shape and  
33 size control.  
34

35    **1. Introduction**

36

37    A major problem of emerging concern in the field of water quality is represented by the  
38    contamination of surface- and ground-waters with pollutants that are hardly removed by the  
39    traditional wastewater treatment plants (WWTPs) [1]. Therefore, WWTPs are increasingly regarded  
40    as potential emission sources for a wide range of substances such as pharmaceuticals and personal  
41    care products, flame retardants, artificial sweeteners and several industrial chemicals [2-4]. These  
42    compounds are often harmful to aquatic organisms because of toxicity, endocrine disruption  
43    properties and/or longer term effects, and they might also pose a threat to human health *via* their  
44    possible occurrence in drinking water [5-8]. To avoid such adverse effects, an important priority is  
45    represented by the technological update of WWTPs, so that they are enabled to remove recalcitrant  
46    pollutants [9,10]. Among possible solutions, Advanced Oxidation Processes (AOPs) are  
47    increasingly regarded as a viable option because of their ability to decontaminate water from  
48    compounds that are difficult to be treated by other techniques [11-13]. Such processes are based on  
49    the formation of reactive transient species (including most notably, but not exclusively, the  
50    hydroxyl radical,  $\cdot\text{OH}$ ), which show remarkable reactivity toward a wide range of refractory  
51    pollutants [14,15].

52    Heterogeneous photo-Fenton systems are gaining increasing importance as AOPs in the field of  
53    wastewater treatment [16,17]. They consist in the use of solid Fe species under irradiation, in the  
54    presence of  $\text{H}_2\text{O}_2$ . A general scheme of the process can be outlined as follows [18,19]:



56

57    Depending on pH, the  $\text{Fe}(\text{III})$  produced in reaction (2) may be dissolved, may form solid species or  
58    may precipitate on the surface of the existing oxide. In the latter cases,  $\text{Fe}^{\text{III}}\text{-OH}_{(\text{s})}$  represents a  
59    hydroxylated form of solid  $\text{Fe}(\text{III})$  that would occur at the interface with water [17,18]. The  
60    generation of  $\cdot\text{OH}$  in reaction (2) is unlikely to be quantitative and it is pH-dependent, because iron  
61    super-oxidized species (such as the ferryl ion,  $\text{FeO}^{2+}$ ) are also competitively formed as transients  
62    [20-22]. The heterogeneous photo-Fenton reaction combines several advantages that are extremely  
63    useful in the context of pollutant degradation [23-26]. The first advantage is the use of iron in the  
64    form of a solid catalyst, which is easily removed from the reaction system at the end of the  
65    treatment and can be recycled. In contrast, the removal of dissolved iron species to respect the Fe  
66    discharge limits in homogeneous processes usually requires a precipitation step that yields solid  
67     $\text{Fe(OH)}_3$ . The latter is hardly recycled, because it is very different from the photoactive compounds  
68    that were initially used. Another positive issue is the possibility to activate the process with sunlight  
69    [27].

70    Among the solid Fe species that can be used in photo-Fenton systems, hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) is a  
71    reasonable choice because of its significant photoactivity, promoted by the photoreduction of

74 surface Fe<sup>III</sup> species to Fe<sup>2+</sup>, sometimes in the presence of complexing and/or reducing agents [28-  
75 31]. Moreover,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is easily synthesized by low-cost techniques [32,33]. A very interesting  
76 feature is the possibility to finely tune the size and shape of hematite particles, thereby obtaining  $\alpha$ -  
77 Fe<sub>2</sub>O<sub>3</sub> specimens with peculiar morphological properties [34]. With the aim to optimize the  
78 hematite photoactivity toward the heterogeneous photo-Fenton reaction, in the present work we  
79 assessed the ability of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> samples, with different morphology and particle size, to degrade  
80 phenol as model compound under irradiation in the presence of H<sub>2</sub>O<sub>2</sub>. The structural and  
81 morphological properties of the synthesized hematites and the amount of photo-leached iron were  
82 compared with the photoactivity of the samples. The choice of phenol as substrate was motivated by  
83 various reasons. The first is that this compound has a well-known behavior under oxidative  
84 conditions [35], which makes its degradation very suitable to test the performance of newly  
85 synthesized photocatalysts. The second issue is that phenol is a widespread environmental pollutant.  
86 It is an important component of oil refinery wastes and it is also produced upon conversion of coal  
87 into gaseous or liquid fuels and during the manufacturing of metallurgical coke from coal. Its  
88 possible environmental sources include discharges of oil refineries, coal conversion plants,  
89 municipal waste treatment plants, or spills. Phenol is highly toxic to both humans and animals, and  
90 it is often incompletely removed by traditional treatment methods including physico-chemical and  
91 biological ones [36,37]. Therefore, it is important to investigate on techniques that are able to  
92 achieve its complete removal.

## 93 94 95 2. Experimental

### 96 97 2.1. Materials

98 Iron(III) chloride hexahydrate (> 99%), sodium hydroxide (> 99%), NaNO<sub>3</sub> (> 99%), perchloric  
99 acid (70%), hydrogen peroxide (35%), phenol (>99%), 1,4-benzoquinone (98%), sulfuric acid (95-  
100 97%) and methanol (>99.9%) were purchased from Sigma-Aldrich; Fe(III) perchlorate hydrate  
101 (99%) and Fe(III) nitrate nonahydrate (98%) were purchased from Alfa Aesar; iron(II) chloride  
102 tetrahydrate (> 99%), nitrilotriacetic acid trisodium salt (> 98%) and NH<sub>3</sub> were from Fluka;  
103 hydrochloric acid (37%), sodium chloride (> 99.5%), catechol (99%), resorcinol (99.5%) and  
104 ammonium thiocyanate (>99%) from Carlo Erba; hydroquinone (99%) and potassium persulfate  
105 (>98%) from Merck. Ultra-pure water was obtained with a Milli-Q<sup>TM</sup> system (Millipore).

### 106 107 2.2. Hematite synthesis

108 Six samples of monodisperse hematite particles with different size and shape were obtained by  
109 following three different procedures, all involving modifications at key steps of the synthesis  
110 methods from the literature.

111 The first procedure is a modification of the synthesis proposed by Sugimoto et al. [38] and it  
112 allows the production of large quantities of hematite particles through a two-step phase

transformation, from a highly condensed  $\text{Fe(OH)}_3$  gel to  $\alpha\text{-Fe}_2\text{O}_3$  via  $\beta\text{-FeOOH}$  (akaganeite) [39,40]. This is a gel-sol procedure, which differs from the usual sol-gel techniques because the conversion occurs from an initial dense gel of hydroxide to a final sol of hematite. First, 45 mL of NaOH (6 M) were added drop-wise to 50 mL of a well-stirred  $\text{FeCl}_3 \cdot 6 \text{ H}_2\text{O}$  solution (2 M) in a Pyrex bottle. The gel was maintained under stirring for additional 10 minutes, and then heated at 100°C for 6 hours. This time allows for the conversion of  $\text{Fe(OH)}_3$  into  $\beta\text{-FeOOH}$ . Later, the supernatant liquid was removed by centrifugation and the resulting  $\beta\text{-FeOOH}$  was washed twice with 0.5 M  $\text{NaNO}_3$ . The akaganeite precipitate was dispersed again in ultra-pure water by ultrasonication, to obtain 200 mL of stock suspension. To produce the hematite particles, well-stirred aliquots (20 mL) of the  $\beta\text{-FeOOH}$  stock suspension were added with 1.2 mL of HCl (1 M) and 8.8 mL of water. The final suspensions were stirred for 10 minutes and, afterwards, they were transferred in tightly closed bottles and heated at 100°C to allow conversion into hematite. This procedure allows for the synthesis of large hematite particles (diameter over 1  $\mu\text{m}$ ) with different morphologies, which can be obtained by using shape-control additives. Several anions have been reported to induce the anisotropic growth of hematite particles [39,40]. Anions can be selectively adsorbed at the surface of the nuclei and they can regulate the growth of specific crystal faces, thus determining the final particle morphology. The addition of anions such as chloride and nitrilotriacetate to the akaganeite suspensions was carried out before the final heat treatment. These modifications of the procedure allowed for the synthesis of pseudocubic (by adding chloride) and spherical hematite (with addition of nitrilotriacetate).

The second synthesis is a gel-sol procedure similar to the previous one, without the step of akaganeite washing [39,40]. First, 45 mL of NaOH (6 M) were slowly added to 50 mL of magnetically stirred  $\text{FeCl}_3$  solution (2 M). The system thus obtained was kept under stirring for additional 10 minutes. The obtained  $\text{Fe(OH)}_3$  gel was transferred into a tightly stoppered bottle and oven-heated at 100°C for at least 3 days to allow conversion into hematite. The shape control was obtained by adding chloride or nitrilotriacetate to the  $\text{Fe(OH)}_3$  gel, as described above. The size control was obtained by varying the temperature of the  $\text{FeCl}_3$  solution when NaOH was added. The nucleation rate is influenced by temperature, because a higher temperature causes the formation of a higher amount of nuclei and, subsequently, yields smaller particles. The temperature variation (25-90°C) allowed the synthesis of particles with diameters in the 300-1200 nm range (see Figure SM1a in the Supplementary Material, hereafter SM; *vide infra* for the determination of particle diameters).

The third method uses the catalytic phase-transformation mechanism proposed by Liu and co-workers [41], which enables lower conversion times by adding trace  $\text{Fe}^{\text{II}}$  to the initial  $\text{Fe(OH)}_3$  gel. The standard experimental conditions for this procedure were as follows: NaOH (6 M) was slowly added to 50 mL of a magnetically stirred  $\text{FeCl}_3$  solution (2 M unless otherwise reported) till pH 7 (measured with a Metrohm 691 pH meter, equipped with a Metrohm 6.0233.100 combined glass electrode). Then,  $\text{FeCl}_2$  was added to the gel to have a ratio  $[\text{Fe}^{\text{II}}]/[\text{Fe}^{\text{III}}] = 0.02$ , and pH was readjusted to 7 by adding dilute NaOH. The system was kept under stirring for additional 10 minutes and then refluxed for at least 30 min until conversion occurred. This procedure yielded

152 spherical particles with diameters in the 100-400 nm range. The size control was obtained by  
153 varying the FeCl<sub>3</sub> concentration, with particle diameters increasing as concentration increased (see  
154 Figure SM1b in the SM).

155 All the prepared hematite samples underwent a final washing with ultra-pure water (three  
156 times), 1 M NH<sub>3</sub> (one time) and again with ultra-pure water (three times). Finally, all samples were  
157 dried at 70°C.

158

### 159 **2.3. Physico-chemical characterization of hematite**

160 The size and shape of the synthesized hematite particles were determined by scanning electron  
161 microscopy, with a Phenom Pro instrument operating at 5, 10 and 15 kV, 50.0 µA beam current and  
162 50 pA probe intensity.

163 The particle hydrodynamic radii were determined by Dynamic Light Scattering (DLS). The  
164 used instrument was an ALV-NIBS High Performance Particle Sizer (ALV GmbH, Germany)  
165 equipped with a Ne-He laser and with an ALV-500 multiple tau digital correlator. Samples were  
166 suspended in ultra-pure water, and analyzed by recording the intensity of the scattered light at an  
167 angle of 173° for 30 seconds at 25°C. Suspensions with different hematite loadings were analyzed,  
168 and the results were extrapolated at infinite dilution.

169 The sample crystalline phases were determined by X-Ray Diffraction (XRD). XRD patterns  
170 were recorded with a PW3050/60 X'Pert PRO MPD diffractometer (PANalytical) working in  
171 Bragg-Brentano configuration. The X-ray source was a high-power ceramic tube (PW3373/10 LFF)  
172 with a Cu anode. The instrument was equipped with a Ni filter to attenuate Kb. Diffracted photons  
173 were collected by a real-time multiple strip X'celerator detector. Powder samples were hosted on an  
174 amorphous SiO<sub>2</sub> sample holder.

175 The specific surface area of the samples was determined by N<sub>2</sub> adsorption-desorption  
176 experiments. Analyses were carried out by means of an ASAP 2020 instrument (Micromeritics),  
177 which measures both the specific surface area (BET model, [42]) and the porosity (DFT model,  
178 [43,44]) of mesoporous samples. The Density Functional Theory (DFT) was applied to the  
179 simultaneous examination of the micro-, meso- and macroporosity of the samples (pores slit with  
180 low regularization). The analyses were performed on powders (*ca.* 0.7-1.0 g sample weight) that  
181 were outgassed for several hours at 30 °C *in vacuo* (the residual pressure was 10<sup>-2</sup> mbar), to ensure  
182 complete removal of atmospheric contaminants from both surface and pores.

183

### 184 **2.4. Photo-Fenton experiments**

185 Photo-Fenton experiments were carried out in magnetically stirred Pyrex beakers, initially  
186 containing a stock hematite suspension. Milli-Q water, phenol, H<sub>2</sub>O<sub>2</sub> and HClO<sub>4</sub> were added to  
187 achieve a volume of 50 mL and concentrations/loadings of 0.1 mM (phenol), 1.0 mM (H<sub>2</sub>O<sub>2</sub>) and  
188 200 mg L<sup>-1</sup> (α-Fe<sub>2</sub>O<sub>3</sub>), as well as to fix initial pH to the target value (HClO<sub>4</sub>). Irradiation was  
189 carried out under a Philips TL09N lamp, with maximum emission at 355 nm and an irradiance of 18  
190 W m<sup>-2</sup> in the 295-400 nm range, measured with a CO.FO.ME.GRA. (Milan, Italy) power meter.

191 Dark runs were carried out by placing, under the same lamp, beakers wrapped with aluminum foil,  
192 to achieve comparable temperature and stirring conditions as for the irradiation experiments.

193 Each sample was irradiated for up to 4 hours and, every 30 minutes, 1.5 mL suspension aliquots  
194 were withdrawn and immediately filtered on hydrophilic PTFE Millex-LCR filters (0.45 µm pore  
195 diameter). A 0.7 mL volume of the filtered solution was put into a vial, containing 0.7 mL methanol  
196 to quench the Fenton reaction [27].

197 The concentrations of phenol and its intermediates were measured by High-Performance Liquid  
198 Chromatography coupled to Diode Array Detection (HPLC-DAD). The instrument used was a  
199 VWR Hitachi Elite chromatograph, equipped with L-2200 Autosampler (injection volume 60 µL),  
200 L-2130 quaternary pump for low-pressure gradients, L-2300 column oven (set at 40°C), and L-2455  
201 DAD detector. The column used was a RP-C18 LichroCART (VWR Int., length 125 mm, diameter  
202 4 mm), packed with LiChrospher 100 RP-18 (5 µm diameter). Elution was carried out with a 10:90  
203 mixture of methanol: aqueous H<sub>3</sub>PO<sub>4</sub> (pH 2.8) at 1.0 mL min<sup>-1</sup> flow rate, with detection at 220 nm.  
204 The retention times were 16.1 min for phenol, and 3.4, 5.8, 6.4 and 7.3 min for hydroquinone,  
205 resorcinol, 1,4-benzoquinone and catechol, respectively. The column dead time was 0.9 min.

206 The determination of Fe released in solution was evaluated by a spectrophotometric procedure.  
207 A 1.5 mL aliquot of hematite suspension was withdrawn every 60 minutes of irradiation and filtered  
208 on hydrophilic PTFE Millex-LCR filters (0.45 µm pore diameter). Total iron was determined by  
209 oxidizing any Fe(II) to Fe(III) with persulfate (4 mg/L) and by complexing Fe(III) with thiocyanate  
210 (50 mg/L) in acidic conditions (1.25 M sulfuric acid). The absorption of the iron-thiocyanate  
211 complex was determined at 474 nm. Fe<sup>III</sup> was determined in the same way, without the oxidative  
212 step, and Fe<sup>II</sup> was obtained as the difference between total iron and Fe<sup>III</sup> [45]. Spectrophotometric  
213 analyses were performed using a Varian CARY 100 Scan double-beam UV-Vis spectrophotometer,  
214 using quartz cuvettes with 10 cm path length. The detection limit of the technique was ~3 µg Fe  
215 L<sup>-1</sup>, the quantification limit was ~10 µg Fe L<sup>-1</sup>. The same spectrophotometric technique, with  
216 quartz cuvettes having an optical path length of 10 mm, was used to determine the exact Fe<sup>III</sup>  
217 content in Fe(ClO<sub>4</sub>)<sub>3</sub> hydrate, using Fe(NO<sub>3</sub>)<sub>3</sub> · 9 H<sub>2</sub>O as reference compound.

218 The same UV-vis spectrophotometer, with 10 mm cuvettes, was used to measure the extinction  
219 spectra (absorption + scattering) of the studied hematite samples at a loading of 100 mg L<sup>-1</sup> α-  
220 Fe<sub>2</sub>O<sub>3</sub>.

### 221 **3. Results and discussion**

#### 222 **3.1. Hematite characterization**

223 Six hematite samples with different size and shape were prepared and tested. Three of the samples  
224 (C1, C2, C3) had cubic morphology, while the other three were either spherical (S1, S2) or ovoidal  
225 (O1). Table 1 reports the hydrodynamic radii determined by DLS measurements, as well as the  
226 particle size measured by SEM. Figure 1 shows the SEM micrographs of the samples. The data in  
227 Table 1 suggest that aggregation of particles in aqueous suspension was quite limited.  
228

230 Cubic hematites were synthesized by gel-sol procedures with chloride as shape controller. The  
231 low- and medium-size particles (C1 and C2, with diameters of 250 and 990 nm, respectively) were  
232 obtained without the akaganeite washing step (second method), adopting a single heat treatment and  
233 temperatures of 120°C and 50°C for C1 and C2, respectively. The larger particles (C3, 1480 nm)  
234 were synthesized following the gel-sol procedure through the akaganeite washing step (first  
235 method). The concentration of chloride ions, used as shape controllers in the final heat treatment,  
236 was 1 M for C1 and C2, and 0.3 M for C3.

237 Spherical particles with low diameter (150 nm, sample S1) were obtained through the catalytic  
238 phase-transformation procedure (third method) with 0.5 M FeCl<sub>3</sub> (chloride was used as shape  
239 controller). Sample S2 (560 nm) was obtained via gel-sol at 90°C (second method), using  
240 nitrilotriacetate as shape controller. Finally, large ovoidal hematite particles (sample O1, 1690 nm)  
241 were obtained *via* gel-sol with the akaganeite washing step (first method), using 0.3 M  
242 nitrilotriacetate.

243 Figure 2 shows the XRD patterns of the obtained hematite particles. Each sample gave signals  
244 related to the  $\alpha\text{-Fe}_2\text{O}_3$  phase, thereby confirming that hematite was actually present. In the case of  
245 S1, the use of trace Fe<sup>II</sup> in the synthetic route may be responsible for the detection of some  
246 additional peaks as impurities. The relevant XRD spectrum showed in fact signals related to  
247 magnetite ( $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$ ) and maghemite ( $\gamma\text{-Fe}^{\text{III}}_2\text{O}_3$ ). In contrast, the other samples only had signals  
248 related to hematite ( $\alpha\text{-Fe}^{\text{III}}_2\text{O}_3$ ).

249 The porosities of the synthesized hematite materials were investigated by means of BET surface  
250 area and DFT model, applied to N<sub>2</sub> adsorption/desorption isotherms carried out at 77 K. The results  
251 are summarized in Table 2, while the experimental BET curves are reported in Figure SM2 in the  
252 SM. All the obtained isotherms are of the IV type (IUPAC classification), which applies to  
253 mesoporous and macroporous systems.

254 Pseudo-cubic systems had low BET surface areas, with absence of microporosity and a DFT  
255 total volume calculated in the range of 0.01-0.04 cm<sup>3</sup> g<sup>-1</sup> (slit pore shape). The measured porosity  
256 was probably due to inter-particle voids. S1 and O1 showed the highest BET surface areas among  
257 the studied samples (73 and 53 m<sup>2</sup> g<sup>-1</sup>, respectively), together with the highest DFT pore volumes  
258 (0.15 and 0.05 cm<sup>3</sup> g<sup>-1</sup>, respectively). Similar results were obtained by using the BJH method. In  
259 this case, it was not possible to exclude an intrinsic inter-particle porosity. Pseudo-cubic samples  
260 were less porous than the spherical ones. This phenomenon could be attributed to the different  
261 aggregation packing induced by the different geometry of the systems.

262 An interesting issue is that the surface areas were not inversely correlated with particle  
263 diameters: within cubic hematites the middle-sized sample (C2) had the largest surface area, while  
264 in the case of spherical/ovoidal ones the corresponding sample (S2) had the lowest area. SEM  
265 micrographs (Figure 1) suggest that particles had smooth surfaces, thus the unexpected BET trend  
266 might be due to particle aggregation. This issue could be consistent with porosity measures, which  
267 suggest the occurrence of inter-particle voids.

268       Figure 3 reports the extinction spectra of the cubic (3A) and spherical/ovoidal (3B) hematite  
269       samples, which are the result of the contributions of both absorption and scattering. Because  
270       hematite does not absorb radiation above 520 nm [46,47], the signals above that wavelength would  
271       be accounted for by scattering only. The spectra suggest that scattering of radiation is most  
272       important for the smallest particles (C1, S1). Although the assessment of the scattering is easy  
273       above 520 nm but much less straightforward below that wavelength, it is highly likely that the  
274       smallest particles also show important radiation scattering in the UV region.

275

### 276       **3.2. Hematite photoactivity in photo-Fenton reactions**

277       Preliminary experiments were carried out to assess the importance of H<sub>2</sub>O<sub>2</sub>, hematite and irradiation  
278       for phenol degradation. Insignificant degradation was observed upon irradiation of phenol and  
279       hematite alone, without H<sub>2</sub>O<sub>2</sub>, as well as in the presence of phenol, hematite and H<sub>2</sub>O<sub>2</sub> in the dark.  
280       The dark experiments also ruled out a significant adsorption of phenol onto hematite. The direct  
281       photolysis of phenol and the degradation of phenol by irradiated H<sub>2</sub>O<sub>2</sub> (irradiation without hematite  
282       in both cases) were negligible as well. Therefore, to achieve significant phenol degradation under  
283       the studied conditions, the contemporary presence of hematite, H<sub>2</sub>O<sub>2</sub> and irradiation was required.  
284       The results of the preliminary experiments can be rationalized as follows:

285       (i) Phenol adsorption on hematite is at most very limited, which is reasonable considering the high  
286       phenol affinity for water. This issue does not rule out the possibility that degradation involves  
287       reactive species formed at the oxide surface [48], but one should also consider the alternative  
288       possibility that the reaction takes place in the solution bulk.

289       (ii) The lack of phenol degradation by hematite + H<sub>2</sub>O<sub>2</sub> in the dark suggests that Fe<sup>III</sup> on the oxide  
290       surface is much less reactive towards H<sub>2</sub>O<sub>2</sub> compared to dissolved Fe<sup>III</sup> species. This finding is  
291       consistent with the low (dark) Fenton reactivity reported for mineral surfaces containing Fe<sup>III</sup> [49].

292       (iii) Irradiated hematite alone is unable to cause significant degradation of phenol. There is evidence  
293       that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> under irradiation can induce charge-transfer reactions that are, however, considerably  
294       more effective towards inorganic ions compared to phenolic compounds [50]. The ability of  
295       inorganic ions (such as nitrite) to act as electron shuttles and favor the photodegradation of phenols  
296       by hematite (through the generation of reactive radical species, e.g. •NO<sub>2</sub>) [31,50] suggests that the  
297       direct (shuttle-free) process is prevented by kinetic rather than by thermodynamic issues.

298       (iv) The negligible degradation of phenol by H<sub>2</sub>O<sub>2</sub> alone under irradiation (without hematite) is  
299       most likely accounted for by the limited absorption by H<sub>2</sub>O<sub>2</sub> of the radiation emitted by the lamp  
300       [51].

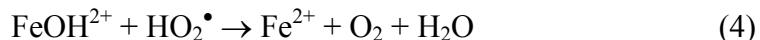
301

302       All of the above issues suggest that the degradation of phenol by hematite requires photo-Fenton  
303       conditions. First of all, the optimal pH for the heterogeneous photo-Fenton system was investigated.  
304       Using sample C2, 0.1 mM phenol + 1 mM H<sub>2</sub>O<sub>2</sub> + 200 mg L<sup>-1</sup> hematite were irradiated in the pH  
305       interval 2-5, adjusted with HClO<sub>4</sub>. The variation of pH during irradiation was very limited and  
306       could be neglected. Figure 4 shows that low degradation of phenol was observed at pH 2 and 5 at

307 the adopted irradiation time scale (up to 4 h). In contrast, at pH 3 and 4 the degradation was slow in  
308 the first 2 h and then accelerated to produce complete phenol disappearance in less than 4 h. Such a  
309 trend (initially slow reaction followed by a considerable acceleration) can be due to two phenomena  
310 (in alternative, or even operational at the same time): (*i*) the reaction involves dissolved Fe species,  
311 and time is required for Fe to get dissolved and to reach a sufficiently high concentration in solution  
312 to trigger the degradation; (*ii*) the transformation intermediates of phenol (*e.g.* catechol and  
313 hydroquinone, which need time to accumulate) favor the reduction of Fe<sup>III</sup> (either dissolved or on  
314 the oxide surface) to Fe<sup>II</sup>. The latter undergoes much faster reaction with H<sub>2</sub>O<sub>2</sub> compared to Fe<sup>III</sup>,  
315 which enhances the Fenton degradation of phenol [52,53]. Coherently, transformation intermediates  
316 were detected upon phenol degradation at pH 3 and especially 4. Their levels were 1,4-  
317 benzoquinone > catechol > hydroquinone, with a cumulated concentration that was maximal at 2-3  
318 h irradiation and did not exceed 0.025 mM.

319 Some of the detected intermediates, and in particular catechol and hydroquinone, could be able  
320 to enhance the formation of •OH and other oxidizing species by favoring the reductive dissolution  
321 of hematite to produce Fe<sup>II</sup>, which reacts in the Fenton process (reaction 2) [27,33,54]. However,  
322 the same intermediates could also act as scavengers of the photogenerated reactive species, which  
323 could inhibit the degradation of phenol. In the present case the addition of 0.01-0.02 mM levels of  
324 catechol or hydroquinone before irradiation did not modify significantly the degradation of phenol,  
325 suggesting either a compensation of the two phenomena, or a too low concentration of the  
326 photoproduced intermediates for a measurable effect to be detected.

327 The optimal pH value for the homogeneous Fenton process is usually around 3 [55-57]. The  
328 most likely reasons are the decrease of •OH *vs.* ferryl production at higher pH (FeO<sup>2+</sup> is less  
329 reactive than the hydroxyl radical) and, at pH ≠ 3 (either higher or lower), the slow reduction of the  
330 Fe<sup>III</sup> species formed in reaction (2). The latter issue is accounted for by the fact that FeOH<sup>2+</sup>, which  
331 prevails at pH ~ 3, is the Fe<sup>III</sup> species undergoing the easiest reduction to Fe<sup>II</sup> [58]:



335 Under heterogeneous conditions, in the presence of α-Fe<sub>2</sub>O<sub>3</sub> under irradiation, reactions (3,4) are  
336 probably of lesser importance because the key Fe<sup>2+</sup> source is reaction (1). Moreover, the speciation  
337 of Fe<sup>III</sup> might be less pivotal because most of it would be present as α-Fe<sub>2</sub>O<sub>3</sub>. A less important role  
338 played by Fe<sup>III</sup> recycling to Fe<sup>2+</sup> (reactions 3,4) might explain why, in the presence of hematite, the  
339 reaction did not lose efficiency when increasing the pH from 3 to 4.

341 The results reported in Figure 4 suggest that phenol transformation was practically the same at  
342 pH 3 and 4. Subsequent experiments were carried out at pH 4, which is preferable in practical  
343 applications because it saves reactants for pH adjustment.

344 Figure 5 reports the degradation of phenol in the presence of cubic (Figure 5a) and of  
345 spherical/ovoidal hematite samples (Figure 5b). In the latter case the middle-sized particles (S2, 580

346 nm) proved to be the most photoactive ones. This finding might look surprising when considering  
347 that S2 was the spherical/ovoidal sample with the lowest surface area (Table 2). However, a limited  
348 to negligible effect of particle size and surface area in heterogeneous photo-Fenton processes has  
349 already been observed in the case of magnetite [27], presumably because the process also depends  
350 on other issues such as iron dissolution. Moreover, as far as the measured BET surface area is  
351 concerned, the observed differences among the studied samples were possibly due to aggregation in  
352 the solid phase (inter-particle voids). Such an aggregation is likely lost in the aqueous suspensions,  
353 as suggested by the laser light scattering data reported in Table 1.

354 In the case of the cubic samples, the small-sized particles (C1, 250 nm) had the lowest activity.  
355 This issue might apparently be consistent with their very low surface area ( $9 \text{ m}^2 \text{ g}^{-1}$ , the lowest  
356 among the studied samples). However, caveats concerning the application of solid-phase BET  
357 measurements (where particle aggregation was probably important) to the suspension properties  
358 (where no evidence of aggregation was found) have already been reported. On the other hand, the  
359 largest cubic particles (C3, 1480 nm) were more active than the middle-sized ones (C2, 990 nm).

360 The quite (and somewhat unexpected) low photoactivity of the small hematite particles (C1, S1)  
361 could be accounted for by their elevated scattering of radiation, as suggested by the extinction  
362 spectra reported in Figure 3. Indeed, radiation scattering by semiconductor suspensions is able to  
363 interfere with absorption and to limit the rate of photocatalytic reactions [48]. In contrast, there  
364 could be some relationship between the photoactivity toward phenol degradation and the amount of  
365 dissolved Fe in solution. Figure 6 reports the trend of total dissolved Fe upon irradiation of the  
366 photoactive samples C3, C2 and S2, showing that the Fe levels were in the tens  $\mu\text{g L}^{-1}$  range. For  
367 the other hematite samples under irradiation, total dissolved Fe was detectable but it was below the  
368 quantification limit of the analytical method (*i.e.*  $< 10 \mu\text{g Fe L}^{-1}$ ). Note that dissolved Fe mainly  
369 occurred as  $\text{Fe}^{\text{III}}_{(\text{aq})}$  in all the samples, due to the presence of  $\text{H}_2\text{O}_2$  at acidic pH (the  $\text{Fe}^{\text{II}}_{(\text{aq})}$  levels  
370 would be kept low by reaction (2)).

371 The importance of dissolved Fe in the studied photo-Fenton process was further highlighted by  
372 additional control experiments. By irradiating  $\text{Fe}(\text{ClO}_4)_3$  at tens  $\mu\text{g Fe L}^{-1}$  levels in the presence of  
373 1 mM  $\text{H}_2\text{O}_2$  at pH 4, the degradation kinetics of phenol was comparable to that observed in the  
374 presence of hematite (see Figure 5b). This issue suggests that an important fraction of phenol  
375 degradation would take place in the dissolved phase.

## 376 377 4. Conclusions

378 Hematite samples with controlled size and morphology were obtained by introducing variants in  
379 key points of the reported synthesis techniques. Cubic, spherical and ovoidal particles differed for  
380 both size and surface area but, in the present case, surface area measurements might not be a  
381 suitable indicator of the actual behavior of the suspended particles. Indeed, BET measurements  
382 suggested that particle aggregation in the solid phase might be important, while no evidence of

384 aggregation in aqueous suspension could be obtained by comparison between SEM measurements  
385 (solid phase) and DLS data (suspended particles in water).

386 One might expect smaller particles to be more photoactive, due to a larger contact interface  
387 between the solid and the solution. However, no obvious relationship could be obtained between the  
388 size of particles and their ability to induce phenol degradation under photo-Fenton conditions. The  
389 most likely reason is that the smallest particles (C1, S1) showed an important scattering of  
390 radiation, which would interfere with absorption and decrease their photoactivity. In contrast,  
391 middle-size or even large particles (S2, C2, C3) showed much smaller scattering and considerable  
392 photoactivity, which would be probably linked to a relatively large amount of dissolved Fe. In the  
393 studied systems, solid hematite would probably act as a Fe reservoir that would be released and/or  
394 activated under irradiation ( $\text{Fe}^{\text{III}}$  photoreduction to  $\text{Fe}^{2+}$ ) for the Fenton process to take place in  
395 solution ( $\text{Fe}^{2+} + \text{H}_2\text{O}_2$ ).

396 As far as the level of dissolved Fe is concerned, there would still be wide margins to increase it  
397 because the concentration of leached Fe for all the studied samples was in the  $\mu\text{g L}^{-1}$  range. This is  
398 safely below the  $\text{mg L}^{-1}$  limits for wastewater. Similar degradation results as for hematite could be  
399 obtained by using  $\text{Fe}(\text{III})$  salts in the same concentration range (tens  $\mu\text{g Fe L}^{-1}$ ): in practical  
400 applications, the choice between the two approaches (dissolved  $\text{Fe}(\text{III})$  or hematite) could depend  
401 on the cost comparison between the use of a salt (to be discharged with wastewater) and the  
402 recovery of hematite from the aqueous suspension.

#### 403

#### 404

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#### 408

#### 409

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570   **Table 1.** Particle size (edge length or diameter) and hydrodynamic radii (HR) of the synthesized  
571       hematite particles.  
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Sample	Size, nm	HR, nm	Preparation method
C1	250	190	120°C, no akaganeite washing, 1 M Cl <sup>-</sup> as shape controller
C2	990	460	50°C, no akaganeite washing, 1 M Cl <sup>-</sup> as shape controller
C3	1480	480	Akaganeite washing, 0.3 M Cl <sup>-</sup> as shape controller
S1	150	100	Catalytic phase transformation, 0.5 M FeCl <sub>3</sub> , chloride as shape controller
S2	560	280	90°C, no akaganeite washing, nitrilotriacetate as shape controller
O1	1690	510	Akaganeite washing, nitrilotriacetate as shape controller

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579   **Table 2.** BET specific surface areas and porosity details of hematite samples.  
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Sample	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	DFT pore volume (cm <sup>3</sup> g <sup>-1</sup> )
C1	9	0.04
C2	26	0.03
C3	12	0.01
S1	73	0.15
S2	21	0.02
O1	53	0.05

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584 **Captions to the Figures**

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**Figure 1.** SEM micrographs of the synthesized hematite particles. Particle sizes are reported in Table 1.

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**Figure 2.** X-Ray Diffraction patterns of the synthesized hematite samples.

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**Figure 3.** Extinction spectra of the cubic (A) and spherical/ovoidal (B) hematite samples (loading of 100 mg L<sup>-1</sup>  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). Data are referred to an optical path length of 10 mm.

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**Figure 4.** Phenol degradation as a function of pH. Initial conditions: 0.1 mM phenol, 1 mM H<sub>2</sub>O<sub>2</sub>, 200 mg L<sup>-1</sup> hematite (C2) loading, UV irradiation.

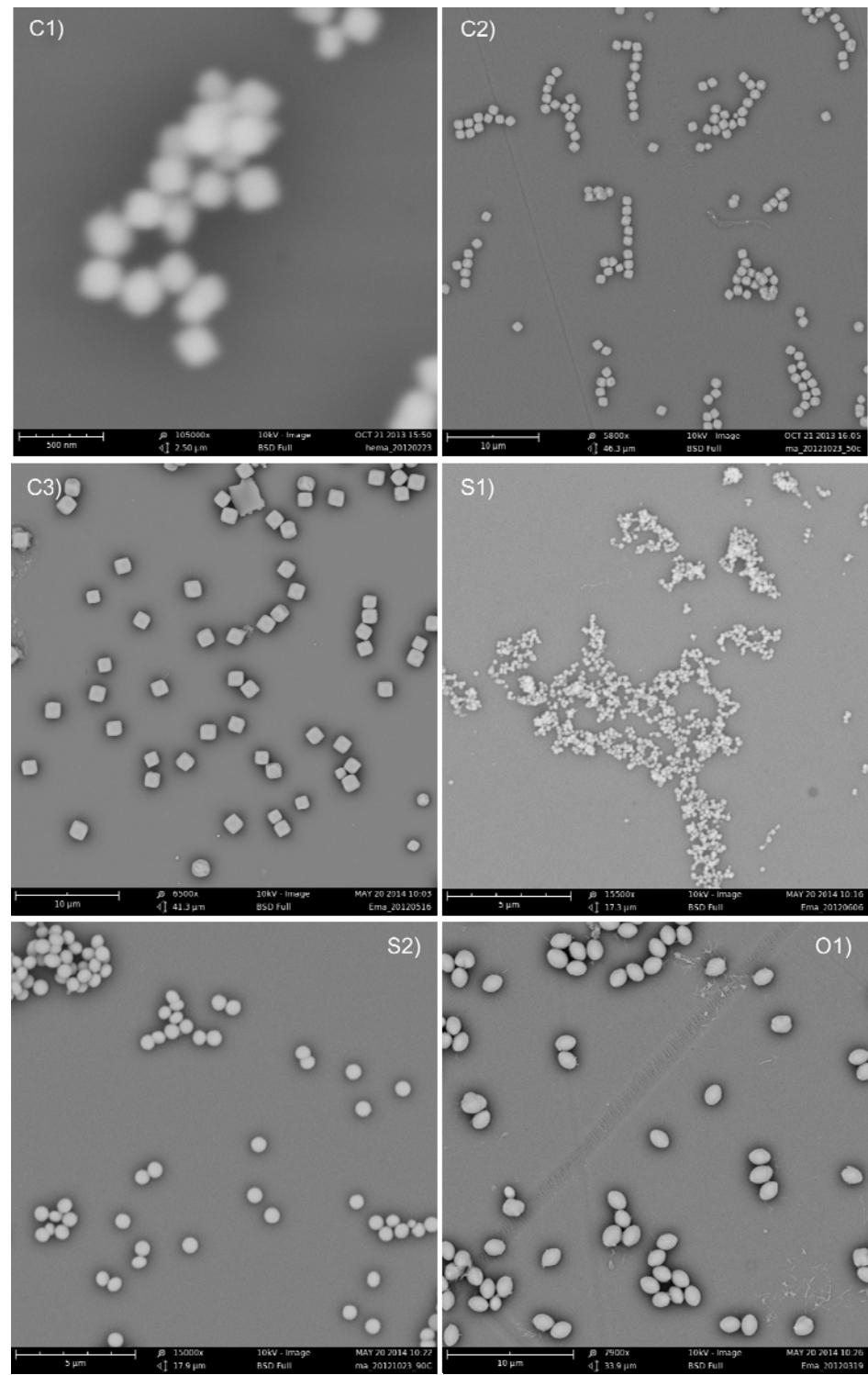
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**Figure 5.** Plot of phenol degradation in presence of cubic (a) and spherical/ovoidal (b) hematite samples at pH 4. Initial conditions: 0.1 mM phenol, 1 mM H<sub>2</sub>O<sub>2</sub>, 200 mg L<sup>-1</sup> hematite loading, UV irradiation. The error bars represent the standard errors of duplicate experiments. Figure 5(b) also reports the results of experiments carried out upon irradiation of Fe(ClO<sub>4</sub>)<sub>3</sub> at 10 and 50 µg Fe L<sup>-1</sup>, under otherwise identical conditions as for the hematite runs but by replacing hematite with Fe(ClO<sub>4</sub>)<sub>3</sub> as Fe compound.

605

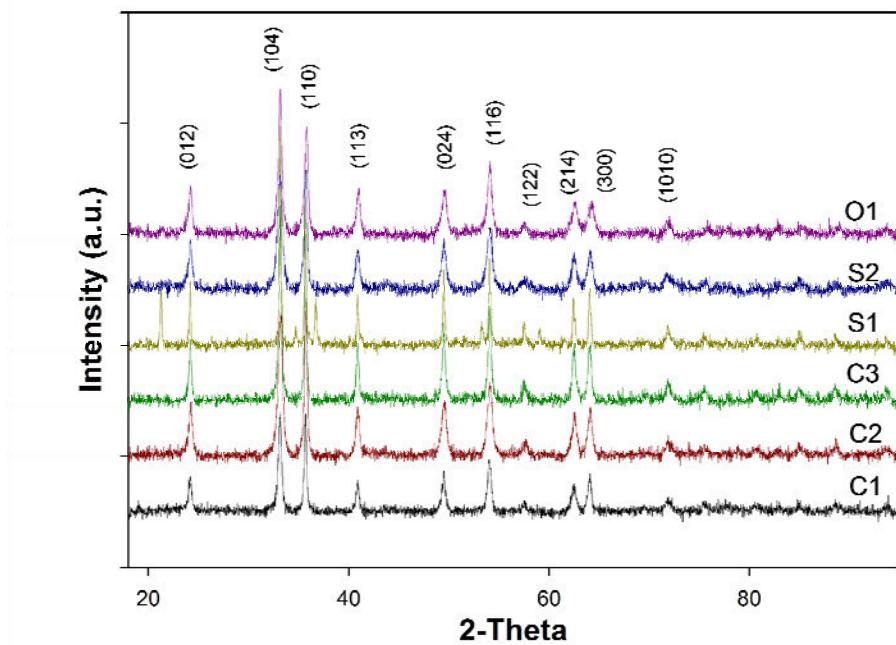
**Figure 6.** Time trend of total dissolved Fe upon UV irradiation of 0.1 mM phenol, 1 mM H<sub>2</sub>O<sub>2</sub> and 200 mg L<sup>-1</sup> hematite (C2, C3 and S2) at pH 4. Total dissolved Fe was mainly in the form of Fe(III).

610 **Figure 1**



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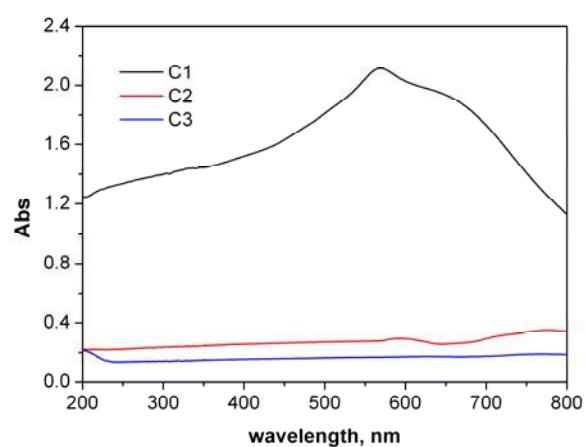
613      **Figure 2**



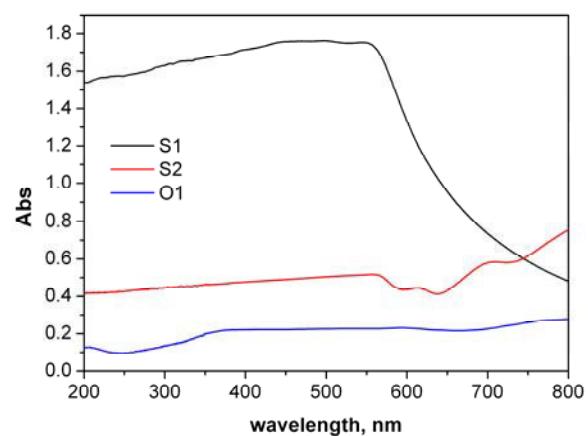
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615

616 **Figure 3**

A



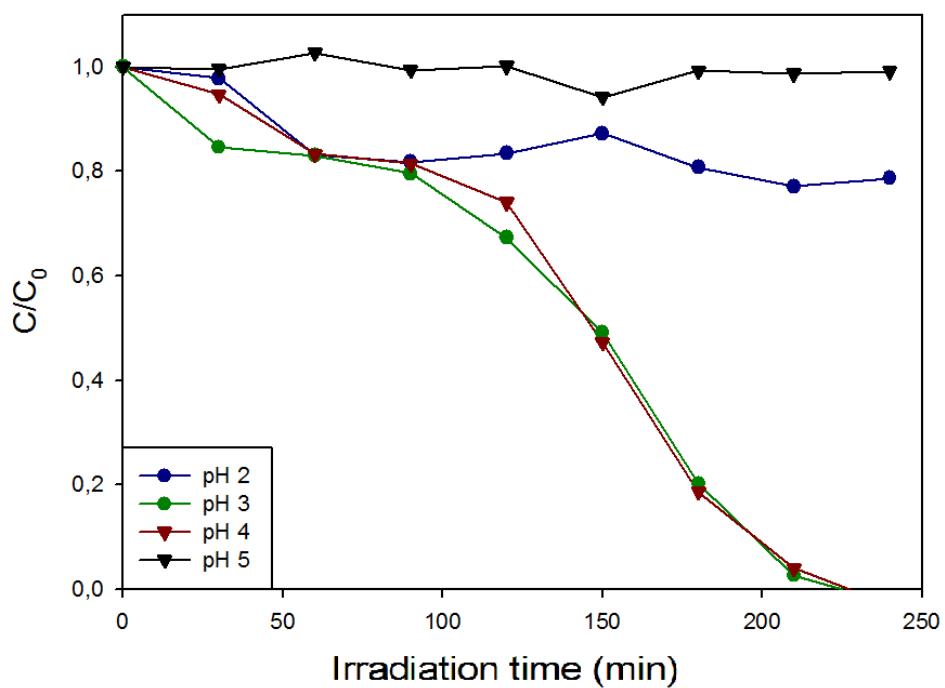
B



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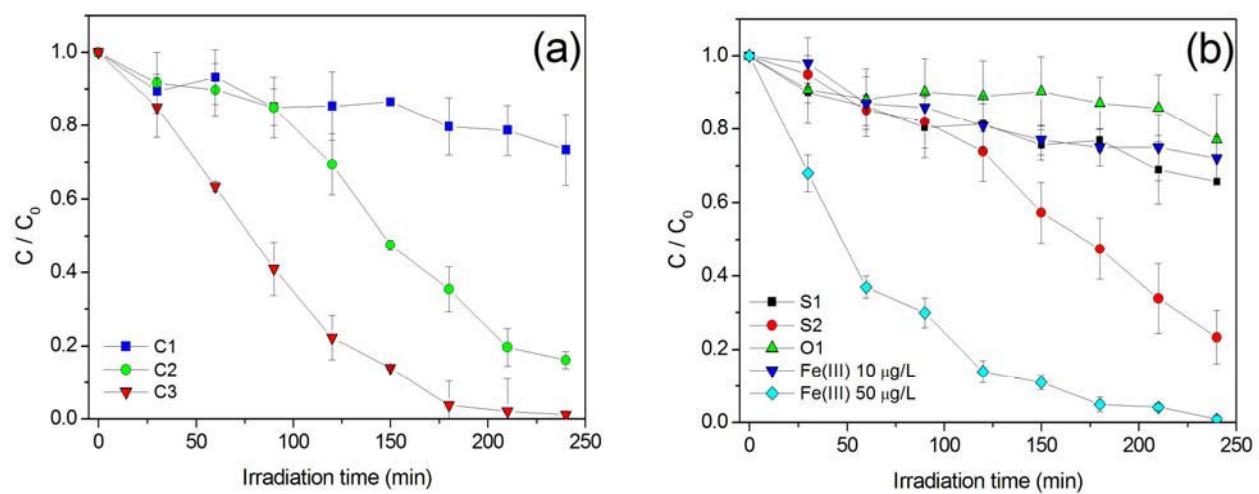
619 **Figure 4**



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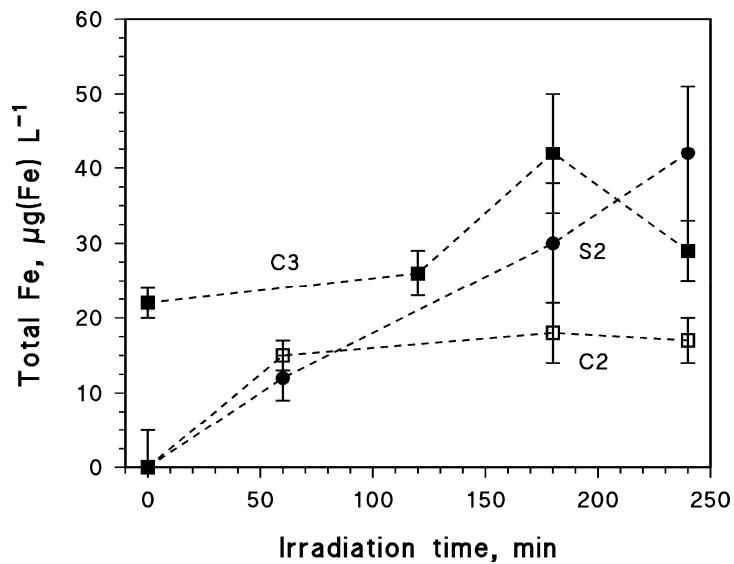
622 **Figure 5**



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625 **Figure 6**



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# **SUPPLEMENTARY MATERIAL**

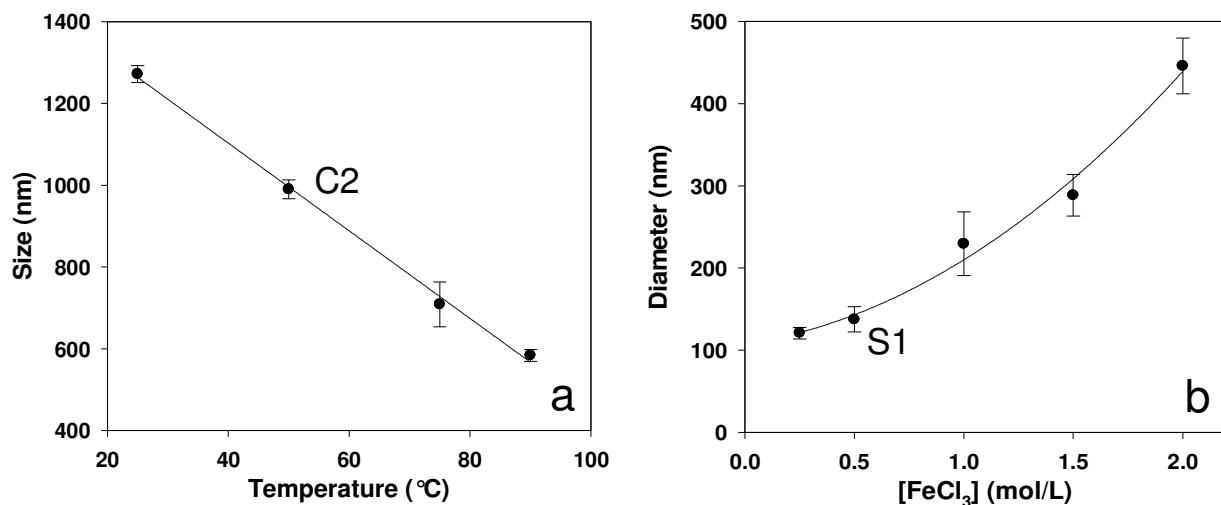
## **Heterogeneous photo-Fenton reaction in the presence of morphologically controlled hematite**

**Luca Demarchis, Marco Minella, Roberto Nisticò, Valter Maurino, Claudio Minero, Davide Vione\***

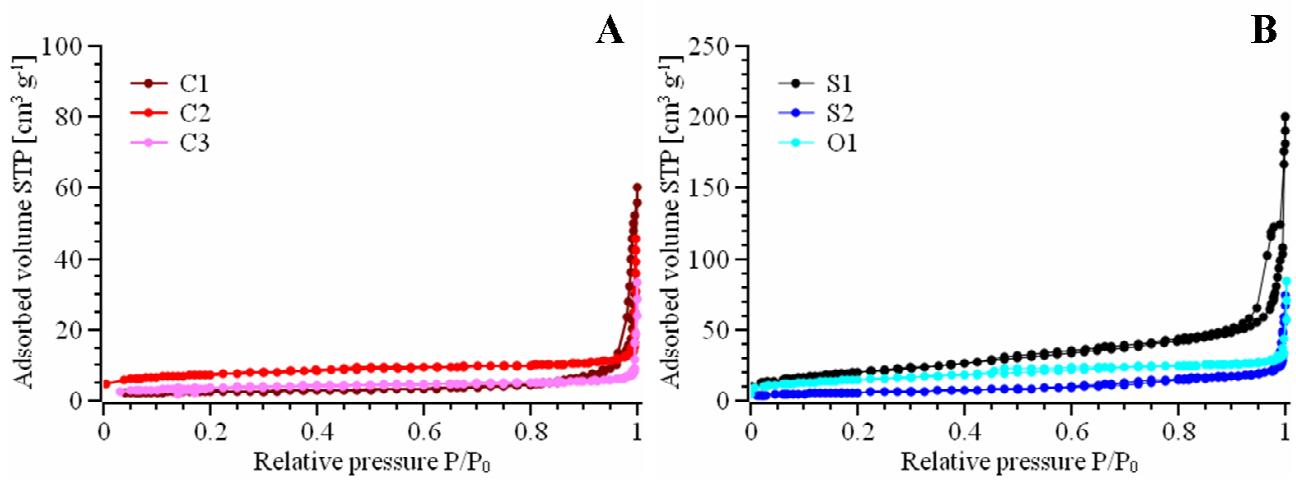
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**Figure SM1.** **(a)** Size of hematite cubic particles (edge length) obtained via the gel-sol method, as a function of the initial temperature. Chloride was used as shape controller. Other conditions are described in the text. **(b)** Diameter of spherical hematite particles obtained with the catalytic phase-transformation method, as a function of  $\text{FeCl}_3$  concentration. Other conditions are described in the text. Samples C2 and S1 are highlighted on the plots.



**Figure SM2.** N<sub>2</sub> adsorption/desorption isotherms at 77 K for (A) pseudo-cubic and (B) spherical/ovoidal hematite samples.