

Photo-Fenton degradation of methylene blue using hematite-enriched slag under visible light

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23 **Photo-Fenton degradation of methylene blue using hematite-**
24 **enriched slag under visible light**

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37 **Abstract:**

38 This study aims to find a suitable method to transform the amorphous iron oxides
39 obtained from the incineration of combustible waste slag (CWS) into hematite. The
40 resulting samples were utilized as heterogeneous photocatalysts for the photo-Fenton
41 degradation of methylene blue (MB) aqueous solution. A good correlation was found
42 between the MB degradation and the amount of hematite phase as confirmed by XRD
43 and Mössbauer measurements. The largest rate constant (k) was $(4.1 \pm 0.08) \times 10^{-2} \text{ min}^{-1}$
44 for MB decomposition under visible-light for the sample N5-50-800. The results are
45 promising for both low-cost photocatalysts and recycling of combustible waste slags.

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49 **Article highlights**

- 50 • A facile method for slag management into photocatalyst is presented
51 • The key component for degradation was the formation of hematite after heat-
52 treatment
53 • Hematite was confirmed using XRD and Mössbauer techniques
54

55 **Keywords** visible-light activated photocatalytic effect; photo-Fenton reaction; slag;

56 Hematite iron oxide; ⁵⁷Fe-Mössbauer spectroscopy

57

58 **1. Introduction**

59 Among many problems in our world today, two major problems grab the attention of
60 scientists and the public alike: combustible wastes, leading to scarcity of landfill and need
61 to find new recycling and circular economy approaches; and wastewater pollution. With
62 an increasing the world population, these two problems are becoming increasingly
63 serious unless more effective steps are taken [1].

64 For combustible wastes, many countries have established waste incineration or
65 waste-to-energy (WTE) plants to meet the lack of landfill whilst generating useful
66 energy, although the by-products from such processes (ashes and slags) can themselves
67 present both hazards and opportunities [2].

68 There are predominantly two types of slag; firstly, industrial slags which are
69 produced during ferrous and non-ferrous smelting processes. The smelting of copper,
70 lead and bauxite in non-ferrous smelting is designed to remove the iron and silica that
71 often occurs with those ores and separates them as iron-silicate-based slags [3]. On the
72 other hand, ferrous smelting in steel mills is designed to minimize iron loss so these slags
73 mainly consist of oxides of calcium, silicon, magnesium and aluminium. Secondly, there
74 are combustible waste slags (CWS) such as those produced by combustible waste
75 incineration and waste-to-energy (WTE) plants. Such wastes are incinerated at
76 temperatures of ca. 800°C, which reduces the volume to 1/20 of its original volume [4].

77 The compositions of CWS are similar to iron-containing silicate glasses, for which
78 the photocatalytic effect has previously been observed [5]. To date, CWS is used in civil
79 engineering works as a low-value base material or aggregate for the construction of roads
80 and concretes so new applications and new opportunities for valorization and recycling of
81 CWS is essential from both economic and environmental perspectives.

82 For wastewater, several techniques have been applied for the treatment of wastewater
83 effluents. Among these, photocatalysis is one of the most environmentally friendly
84 approaches. The most commonly-applied photocatalyst is TiO_2 , which shows
85 photocatalytic activity under UV light due to its wide bandgap of 3.2 eV [6]. This wide
86 bandgap limits the practical uses of TiO_2 as UV light is only available from solar
87 irradiation as a small percentage, ca. 5%, compared to visible light, ca. 40% [7]. Iron
88 oxides, mainly hematite (Fe_2O_3) are promising alternatives due to their lower bandgap
89 around 2.3 eV, low cost, chemical stability and comparatively environmentally friendly
90 nature. Moreover, applying the Fenton reaction and the light-accelerated Fenton reaction,
91 commonly known as the photo-Fenton reaction, provides an added value for using iron
92 oxides as photocatalysts [8].

93 Iida et al. [9] reported that iron alumino-silicate glass,
94 $15\text{Na}_2\text{O}\cdot 15\text{CaO}\cdot 40\text{Fe}_2\text{O}_3\cdot 11\text{Al}_2\text{O}_3\cdot 19\text{SiO}_2$ (weight %), which has a similar composition
95 to CWS, showed a photocatalytic effect after heat treatment at 1000 °C for 100 min, with
96 a k (pseudo-first-order rate constant) of $9.26 \times 10^{-3} \text{ min}^{-1}$ for MB degradation. Ishikawa
97 et al. [5] reported that heat treatment of waste slag recycled glass-ceramics (WSRG) with
98 additional Fe_2O_3 content of 10, 30 and 50 mass% decomposed MB aqueous solution
99 with first-order rate constants (k) of 2.6, 2.3 and $2.7 \times 10^{-3} \text{ min}^{-1}$, respectively, under
100 visible light irradiation. The degradation was related to the precipitated amount of α -
101 Fe_2O_3 nanoparticles. Khan et al. [10] also prepared iron-containing aluminosilicate glass
102 by a sol-gel method, which provided a k value of $8.61 \times 10^{-2} \text{ min}^{-1}$ in the photo-Fenton
103 degradation of MB, where the amount of precipitated hematite was increased by the
104 introduction of Al_2O_3 .

105 In our previous work [11], we succeeded in preparing glass and glass-ceramics from
106 CWS by melt-quenching, obtaining k values of up to $2.2 \times 10^{-2} \text{ min}^{-1}$ by melting the slag
107 at 1400 °C, then subsequently heat treating it at 800 °C for 100 min. Here we aim to

108 enhance the results achieved by melt quenching by introducing a facile method for using
109 DSW as a photocatalytic material by treating as-collected DSW with HNO₃ and applying
110 the photo-Fenton reaction under visible light irradiation. The proposed method depends
111 on treating as-collected CWS with nitric acid at room temperature, which could further
112 reduce costs since no high preparation temperatures are required.

113 Reacting nitric acid with CWS compositions, which are mainly metal oxides, will
114 release the metals from the slag matrix in the form of nitrate salts. Iron oxide, Fe₂O₃, as
115 one of these oxides, will convert to iron nitrate which decomposes at high temperatures,
116 through a series of reactions, to form hematite, α -Fe₂O₃ [12], one of the iron oxides used
117 as a visible-light photocatalyst. If some levels of Fe (NO₃)₃ persist after heat treatment, it
118 will increase the degradation [13]. There is little literature concerning the acid treatment
119 of CWS. Most related studies have used acid treatment for metals recovery from smelting
120 slags or for neutralizing the acid by adding basic slags. For example, Akcil et al. [14]
121 used nitric acid for the recovery of rare earth metals and production of precipitated silicon
122 dioxide from phosphorus slag which contains inorganic oxides similar to CWS. They
123 used concentrated nitric acid (7.0 – 7.5 M) and slag to acid ratio S: L = 1.0:2.6 at a
124 temperature of 90 °C for 1 hour. Nitric acid was also used for extracting soluble
125 phosphorus from slag with high P₂O₅ content by selective leaching. When nitric acid was
126 used, 66.8% of the solid solution was dissolved [15]. Some researchers have studied
127 photoactivity using metallurgical slag combined with TiO₂, CdO/graphene or other
128 materials, however, some drawbacks exist as some use UV light [16-18], long irradiation
129 times (e.g. 300 min) [19], or low pH (e.g. 3) [20].

130 In this work, the relationship between the visible-light activated catalytic effect and
131 local structure of the slag treated by nitric acid was, for the first time, investigated by
132 ⁵⁷Fe-Mössbauer spectroscopy, X-ray diffraction (XRD), transmission electron
133 microscopy (TEM) and optical absorption spectroscopy (UV-Vis).

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139 **2. Experimental Procedures**

140 **2.1. Materials**

141 The slag used in this study was collected in July 2018 at the Tamagawa municipal
142 waste combustion plant (Ohta-ku, Tokyo, Japan) according to the agreement between
143 Tamagawa municipal waste combustion plant and faculty of science - Tokyo
144 metropolitan university. Chemical reagents of Nitric acid HNO₃ (13M CAS No. 141-
145 01361), hydrogen peroxide 30% (H₂O₂: CAS No. 081-04215) and methylene blue (MB:
146 C₁₆H₁₈N₃S Cl₃·H₂O, CAS No. 133-06962) were purchased from Wako, Japan.

147

148 **2.2. Sample preparation**

149 The as-collected slag was pulverized using an electric agate mortar and the XRF
150 compositional analysis is presented in Table 1. As one of the important parameters
151 affecting the dissolution rates, the ratio of slag/acid is very important [21], several ratios
152 were prepared to study the effect of HNO₃ amount on the structure and photocatalytic
153 ability. One gram of pulverized slag was added to different amounts (20, 10, 5 and 3 ml)
154 of concentrated HNO₃ in a glass beaker and stirred at room temperature. The time
155 required for full dissolution of the slag decreased with the amount of HNO₃. During the
156 dissolution process, black orange fumes were liberated so the whole experiment was
157 performed in an extraction hood. After the dissolution of the slag was complete, a green-
158 coloured solution was obtained. The solution was then directly moved to a dryer at 80 °C
159 in Petri dishes with thickness 2-3 mm, and held for 24 h. Over this period the colour
160 changed from greenish to dark orange, consistent with the change in the iron oxide
161 oxidation state from Fe²⁺ to Fe³⁺, which was confirmed by ⁵⁷Fe Mössbauer measurements
162 as shown in section 3.1.2. The dried samples were pulverized and heat-treated at 1000 °C
163 according to the thermal gravimetric analysis (TG) results (see Fig. 1) at a heating rate of
164 5 °C/min and the resulting samples are thus denoted N20-1000, N10-1000, N5-1000 and
165 N3-1000. For the samples prepared using dilute HNO₃, the same route was followed by
166 adding additional amounts of distilled water as shown in Table 2. The preparation route is
167 presented in scheme 1. The samples were denoted according to the percentage volume of

168 HNO₃ to the total volume of the solution and the heat treatment temperature. For
169 example, N5-75-800 means that for one gram of slag, the total volume of the solution is 5
170 ml while the HNO₃ volume is 75% and the heat treatment temperature is 800 °C. The
171 sample of 25% HNO₃ content did not fully dissolve so we obtained two samples, N5-75
172 and N5-50, which were heat-treated at 800 and 1000 °C.

173

174 **2.3. Characterization techniques**

175 Sample structure before and after heat treatment were characterized by ⁵⁷Fe
176 Mössbauer spectroscopy, X-ray diffractometry (XRD), Scanning electron microscopy
177 (SEM), Transmission electron microscopy (TEM) and the Brunauer-Emmett-Teller
178 (BET) specific surface area analysis. ⁵⁷Fe Mössbauer spectra were measured using a
179 constant acceleration spectrometer. A source of 925 MBq ⁵⁷Co (Rh) was attached to an
180 MVT-1000 transducer connected to an MDU-1200 drive unit. The drive unit was
181 connected to a DFG-1200 digital function generator with 1200 channels. Transmitted γ -
182 rays were detected by a proportional counter. The signals were amplified by an ORTEC
183 142 preamplifier. The applied voltage (2 kV) was obtained by using an ORTEC 556 High
184 voltage–power supply, and an ORTEC 570 amplifier. The amplified signals were
185 monitored with a PC via an ORTEC EASYMSC. Samples with weight = 40 mg were
186 homogeneously dispersed in a circular sample holder with 10 mm diameter; inserted into
187 the spectrometer, and measured until the total counts collected were greater than 10⁶.
188 Isomer shifts are given relative to α -Fe, which was measured as a reference. The
189 Mösswinn 3.0i XP software was used to analyze the obtained spectra. XRD patterns were
190 recorded using a RINT TTR3, Rigaku diffractometer between 2 θ of 10° to 80°, with
191 precision and scan rates of 0.02 and 5°/ min, respectively. Cu-K α X-rays (λ = 0.1541 nm)
192 were generated at 50 kV and 300 mA, and monochromated. SEM images were taken by
193 Keyence VE 9800 with the applied voltage of 2 kV, and magnification of 2000x. TEM
194 images were obtained using a JEM-3200FS Field Emission Energy Filter Electron
195 Microscope. The Brunauer-Emmett-Teller (BET) specific surface area was estimated
196 from N₂ isotherms obtained using a BELSORP mini II (BEL Japan, Osaka, Japan) at 77
197 K. The analyzed samples were evacuated at 573 K for 3 h before each measurement.

198

199 **2.4. Photo-Fenton Reaction**

200 For the evaluation of photocatalytic properties, we used 40 mg of pulverized sample
201 and 10 mL of methylene blue aqueous solution (MB_{aq}) with an initial concentration of
202 20 $\mu\text{mol L}^{-1}$. Additional amounts of hydrogen peroxide (9.79 M) (Wako: 081-04215 30%
203 mass/mass) was added to the MB solution. UV–Vis optical absorption spectra of the MB
204 solution before and after the photocatalytic reaction test were measured from the
205 absorbance of the peak at 665 nm, using a GENESYS™ 10S UV-Vis spectrophotometer.
206 The light was emitted by a metal-halide lamp with output wavelengths from 420 to
207 750 nm, an output power of 100 W and an intensity of 6 mW cm^{-2} , with the distance
208 between the sample and the light source maintained at 20 cm, and a UV filter was used.
209 All samples were also measured in the dark to investigate the effect of adsorption as a
210 control. All measurements were performed at room temperature.

211

212 **3. Results and discussion**

213 **3.1. Structural characterization**

214 **3.1.1 XRD**

215 Figure 2(a) shows the XRD patterns for the samples dissolved in concentrated HNO₃
216 heat-treated at 1000 °C for 100 min. The samples N20, N10 and N5 show crystalline
217 peaks ascribed to hematite (Fe₂O₃, PDF No. 01-089-0598), gehlenite (Ca₂Al (Al Si) O₇,
218 PDF No. 01-089-5917) and esseneite (CaFe_{0.6}Al_{1.34}Si_{1.08}O₆, PDF No. 01-084-1206). The
219 sample N3 does not evidence peaks related to hematite but shows peaks consistent with
220 gehlenite and esseneite, with the same PDF numbers previously mentioned. This sample
221 also produces diffraction peaks attributed to Andradite (Ca₃Fe₂O₁₂Si₃, PDF No. 01-084-
222 1206). The intensity of hematite peaks decreases, with decreasing HNO₃ addition from 20
223 to 5 ml for the samples N20 to N5, respectively. These results indicate that the amount of
224 HNO₃ has a large impact on the development of the hematite phase obtained from heat-
225 treatment. Since hematite is known as a visible light photocatalyst, it was expected that
226 the sample N20 would produce the highest MB_{aq} degradation values due to the existence

227 of hematite as the most prominent phase. It was also expected that the MB_{aq} degradation
228 of the samples N10, N5 and N3 would decrease gradually due to the gradual decrease in
229 hematite content. It should be noted that in our previous work [11], we could not detect
230 any XRD peaks related to hematite in the slag after melting at 1400 °C and heat-
231 treatment at 800 °C for 100 min unless Fe₂O₃ additions were made to increase the Fe₂O₃
232 content of the resulting material to 50%. Figure 2(c) shows the XRD pattern of the slag
233 (same slag used in this study), melted at 1400 °C and heat-treated at 800 °C for 100 min.
234 The identified phases are iron silicon oxide (Fe_{2.95}Si_{0.05}O₄, PDF No. 00-052-1140) and
235 calcium silicate (Ca₂SiO₄, PDF No. 00-024-0234). This means that dissolving the slag in
236 HNO₃ can produce hematite without the requirement for additional Fe₂O₃, leading to
237 better degradation results and simpler production.

238 Figure 2(b) shows the XRD patterns for the samples dissolved in dilute HNO₃ (75
239 and 50%) after heat treatment at 800 and 1000 °C for 100 min, respectively. Clear
240 diffraction peaks can be detected for gehlenite (Ca₂Al (Al, Si) O₇, PDF No. 01-089-
241 5917), hematite (Fe₂O₃, PDF No. 01-089-0596) and andradite (Ca₃Fe₂ (SiO₄)₃, PDF No.
242 01-084-1935) for all samples. Heat treatment at 1000 °C for both N5-75 and N5-50
243 samples increased their crystallinity as demonstrated by the narrower diffraction peaks
244 compared to those obtained in the corresponding samples heat-treated at 800 °C,
245 suggesting that the crystallite size increased as the temperature increased, which is also
246 reflected in the measured surface area. Also, the intensity of hematite peaks decreased
247 while the intensity of gehlenite peaks increased for heat treatment at 1000 °C compared
248 to 800 °C. It is thus concluded that HNO₃ concentration plays a major role in controlling
249 the obtained phases while heat treatment temperature affects the phase distribution and
250 the crystallite size. These results are consistent with that obtained from Mössbauer
251 spectra.

252

253 **3.1.2 Mössbauer Spectroscopy**

254 **3.1.2.1 Mössbauer spectroscopy of slag dissolved in concentrated HNO₃**

255 The as-collected slag spectra and fitted data, in Fig. 4(c) and Table 3, show two
256 paramagnetic doublets with $\delta = 1.01 \pm 0.01 \text{ mm s}^{-1}$ and $0.48 \pm 0.06 \text{ mm s}^{-1}$ related to

257 $\text{Fe}^{\text{II}} O_{\text{h}}$ and $\text{Fe}^{\text{III}} O_{\text{h}}$, respectively. The spectra and parameters for all samples prepared
258 using concentrated HNO_3 after heat treatment at 1000 °C for 100 min are shown in Fig. 3
259 and Table 3, respectively. The spectra of the samples N20, N10 and N5 exhibit two
260 doublets related to Fe^{III} and one sextet related to hematite. The sample N3 shows only
261 two doublets with $\delta = 0.29 \pm 0.01$ and $0.38 \pm 0.01 \text{ mm s}^{-1}$ related to $\text{Fe}^{\text{III}} T_{\text{d}}$ and $\text{Fe}^{\text{III}} O_{\text{h}}$,
262 respectively. These results show that Fe^{II} in the slag was oxidized to Fe^{III} upon dissolution
263 in HNO_3 and drying, while hematite can be formed by heat treatment. On the other hand,
264 the spectra and fitted parameters for the sample prepared by melt-quenching after heat
265 treatment at 800 °C for 100 min, shown in Fig. 4(c) and Table 3, show two doublets with
266 $\delta = 0.36 \pm 0.01$ and $0.34 \pm 0.01 \text{ mm s}^{-1}$, related to $\text{Fe}^{\text{III}} O_{\text{h}}$, which is similar to
267 $\delta = 0.38 \pm 0.04 \text{ mm s}^{-1}$ obtained for the sample prepared by melt-quenching reported in
268 our previous paper [11]. The detection of hematite in the dissolved slag following heat
269 treatment is interesting behaviour compared to melt-quenching, although both samples
270 have the same total iron content. In our previous paper [11], where the samples were
271 prepared using melt-quenching, hematite was detected by RT-Mössbauer only for the
272 sample containing 50% Fe_2O_3 . The existence of hematite in the dissolved slag was found
273 to be effective for MB degradation, as will be discussed in degradation measurements
274 section. This demonstrates the advantage of dissolving slag in HNO_3 over melt-
275 quenching, to prepare an effective, low-cost photocatalyst. It is noticed that the hematite
276 absorption peak decreases as the amount of HNO_3 decreased, where it was 33, 29 and
277 20% for N20, N10 and N5, respectively. This may be due to the lower amount of HNO_3
278 resulting in the incomplete dissolution of iron oxide in slag. As a result, a lower amount
279 of iron nitrate may be formed, and consequently, the hematite, which results from thermal
280 decomposition of iron nitrate, was decreased. This can be seen in the case of sample N3,
281 for which no hematite was detected for the above-mentioned reason. The Mössbauer
282 results are consistent with the XRD results.

283

284 **3.1.2.2 Mössbauer spectroscopy of slag dissolved in diluted HNO_3**

285 The spectra and fitted parameters for the samples dissolved in dilute HNO_3 (75 and
286 50%) before and after heat treatment at 800 and 1000 °C for 100 min are shown in Fig.

287 4(a), (b) and Table 4, respectively. Using diluted HNO₃ (with HNO₃ of 75%) resulted in
288 hematite content with absorption peaks of 38 and 40% for the samples N5-75-1000 and
289 N5-75-800 °C, respectively. Further decrease in HNO₃ concentration to 50% resulted in
290 more hematite with absorption peaks of 33 and 50% for the samples N5-50-1000 and N5-
291 50-800 °C, respectively. Compared to the hematite content (20%) in the case of the
292 sample produced using concentrated HNO₃ (N5-1000), it can be observed that more
293 dilute HNO₃ is more effective for obtaining high hematite contents in the final materials,
294 which can enhance the photocatalyst performance. This can be explained by the
295 hydrolysis being affected by the ratio of water in the solution. Before heat treatment, both
296 samples show two doublets related to Fe^{III} O_h with $\delta = 0.37 \pm 0.02$ and 0.57 ± 0.04
297 mm s⁻¹ for N5-75, $\delta = 0.36 \pm 0.01$ and 0.39 ± 0.05 mm s⁻¹ for N5-50, respectively,
298 indicating the oxidation of Fe^{II} in the slag to Fe^{III} after drying, however, heat treatment is
299 required for the formation of hematite. To obtain more investigation about the effect of
300 heat treatment temperature on the obtained hematite, the sample N5-50 was heat-treated
301 at 600 °C for 100 min. From Mössbauer measurements shown in Fig 4(c) and Table 4,
302 only two doublets were obtained with $\delta = 0.32 \pm 0.01$ and 0.35 ± 0.02 mm s⁻¹ and
303 assigned as Fe^{III} T_d and Fe^{III} O_h, respectively, with no hematite detected. These results
304 show that, of those temperatures studied here, the most effective heat treatment
305 temperature to obtain hematite is 800 °C.

306

307 **3.1.3. Morphology**

308 Fig. 5 (A, B) show the SEM and TEM images of the samples N5-75 and N5-50 heat-
309 treated at 800 and 1000 °C, respectively. From SEM images, all samples show uneven
310 surfaces with different sizes and morphologies. The size and morphology are smaller,
311 more porous and uniform in the case of lower heat-treated samples N5-75-800 and N5-
312 50-800 compared to higher heat-treated samples N5-75-1000 and N5-50-1000. The
313 average aggregate' sizes are 4.2, 5.4, 3.9, and 4.4 μm for N5-75-800, N5-75-1000, N5-50-
314 800 and N5-50-1000, respectively. Average aggregate' sizes are lower in the case of
315 lower heat-treatment which is an advantage for using these samples in practical
316 applications. The TEM images give a more clear analysis of these samples, for which the

317 particle size for N5-75-800 varies from 5 to 9 nm, having the smallest particle size among
318 all samples studied. For sample N5-75-1000, the particle size has grown slightly to
319 approximately 12 nm. The sample N5-50-800 has particles with a size approximately 21
320 nm while sample N5-50-1000 exhibits particles with sizes varies from 15 to 24 nm.
321 These larger particle sizes for samples heat-treated at 1000 °C are consistent with their
322 higher heat treatment temperatures.

323

324 **3.2. Photocatalytic properties**

325 **3.2.1. Photo-Fenton reaction for the concentrated HNO₃ treated** 326 **samples**

327 The results of MB degradation under the photo-Fenton reaction of the heat-treated
328 samples N20, N10, N5 and N3 (see Fig. 6) show that the degradation and k values
329 increase with the amount of HNO₃ used for dissolving the slag. This trend can be
330 explained by considering the structural characterization from both XRD and Mössbauer
331 spectroscopy; it is correlated with the amount of hematite in the sample. The apparent k
332 values for the samples N20, N10, N5 and N3 were $(8.1 \pm 0.2, 5.0 \pm 0.2, 3.0 \pm 0.1$ and
333 $1.4 \pm 0.1) \times 10^{-2} \text{ min}^{-1}$ after 60 min of irradiation where the hematite contents were 33%,
334 29%, 20% and zero, respectively. To clarify the greater effectiveness of this method over
335 melt-quenching, another sample was prepared by melt-quenching using the same
336 collected slag, and then heat-treated at 800 °C for 100 min. The MB test for this sample
337 resulted in a k value of $2.2 \pm 0.1 \times 10^{-2} \text{ min}^{-1}$ after 3h of irradiation. These results show
338 that the acid dissolution and heat treatment method resulted in cost-effective visible light
339 photocatalysts also reducing the time required for the MB degradation from 3h to 1h. The
340 degradation of the blank sample (without catalyst) and dark samples (measured in the
341 dark) have small k values of $(0.25 \pm 0.01, 0.28 \pm 0.01, 0.25 \pm 0.01, 0.21 \pm 0.01,$ and
342 $0.10 \pm 0.01) \times 10^{-2} \text{ min}^{-1}$, respectively, which means that the degradation is due mainly to
343 photoactivity rather than photolysis or adsorption. The advantage of the photo-Fenton
344 reaction over photoactivity can be clarified by measuring all samples under the same
345 conditions without applying the photo-Fenton reaction. The k values for samples N20,
346 N10, N5 and N3 were $(1.32 \pm 0.03, 1.01 \pm 0.02, 0.48 \pm 0.01$ and $0.3 \pm 0.01) \times 10^{-2} \text{ min}^{-1}$,

347 respectively, which are far smaller compared to k values from the photo-Fenton reaction,
348 however, it has the same trend in variation of k as a function of hematite content.

349

350

351 **3.2.2. Photo-Fenton reaction for the diluted HNO₃ treated samples**

352 We aimed to prepare a cost-effective catalyst so the k / acid ratio was calculated to
353 choose the most practical sample. From these results, shown in Fig. 6 inset, sample N5
354 was chosen since it provided the highest k / acid ratio. The amount of HNO₃ was diluted
355 with distilled water to 75, 50 and 25%. The slag could not be fully dissolved at the low
356 HNO₃ concentration of 25% so two samples denoted as N5-75 and N5-50 were obtained
357 for the corresponding HNO₃ concentrations of 75 and 50%, respectively. Both samples
358 were heat-treated at 1000 and 800 °C according to the TG results (see Fig. 1) and denoted
359 as samples N5-75-1000, N5-75-800, N5-50-1000 and N5-50-800, respectively. The
360 photo-Fenton measurements for these samples are shown in Fig. 7, and the results can be
361 summarized as follows:

362 Firstly, the k values in the case of samples N5-75-1000 and N5-75-800 were
363 $(3.9 \pm 0.1$ and $4.5 \pm 0.1) \times 10^{-2} \text{ min}^{-1}$, respectively, while for samples N5-50-1000 and
364 N5-50-800 it was $(3.4 \pm 0.1$ and $4.1 \pm 0.1) \times 10^{-2} \text{ min}^{-1}$, respectively. The higher k values
365 in the case of higher acid content indicate that the slag / acid ratio plays a major role in
366 the effectiveness of the prepared catalyst.

367 Secondly, the results of photo-Fenton reactions are correlated with the hematite
368 content of the sample. The Mössbauer absorption area (Table 4) for sample N5-50-800
369 was detected to be 50%, having a k value of $(4.1 \pm 0.1) \times 10^{-2} \text{ min}^{-1}$ while absorption area
370 was 33% for sample N5-50-1000 with a lower k value of $(3.9 \pm 0.1) \times 10^{-2} \text{ min}^{-1}$. The
371 same trend can be observed for the sample N5-75 although the difference in the
372 absorption area is not large (40% for 800 °C and 38% for 1000 °C) but it is also
373 important to consider the additional doublet for the sample prepared at 800 °C with the
374 octahedral site and absorption area of 10%.

375 Thirdly, for each sample, it can be seen that the lower heat treatment temperature
376 resulted in higher MB degradation. This can be an indication of particle size (and

377 therefore higher surface area) contribution where the particle size is larger in the higher
378 temperature samples. From XRD shown in Fig. 2(a) and (b), it can be observed that both
379 samples N5-75-1000 and N5-50-1000 produce sharp diffraction peaks with narrow full-
380 width, half-maximum (FWHM) line widths compared to XRD patterns for samples N5-
381 75-800 and N5-50-800. Sharp diffraction peaks correspond to larger crystallite size,
382 which is reflected in the surface area, an important parameter for effective photocatalysts.
383 To clarify the contribution of surface area and its relation to MB degradation, the surface
384 areas of these samples were measured. The BET results (Table 5) clearly show that the
385 surface area has a positive correlation with MB degradation, where it is larger in the case
386 of higher HNO₃ content and low heat treatment temperature, (3.64 and 5.38 m² / g) for
387 samples N5-75-1000 and N5-75-800 compared to the lower HNO₃ content (2.16 and 2.63
388 m² / g) for samples N5-50-1000 and N5-50-800, respectively.

389 Fourthly, the sample prepared by melt-quenching has a k value of $(2.2 \pm 0.1) \times 10^{-2}$
390 min⁻¹ which is almost half of that for the HNO₃ produced samples. By considering the
391 structural analysis of this sample, it can be seen that it produces only Mössbauer doublets
392 and no hematite sextets, and thus no hematite can be observed by either XRD Fig. 2(c) or
393 Mössbauer spectroscopy Fig. 4(c). This may be the reason for the low k value obtained
394 for this sample in addition to the fact that the melt-quenching method results in lower
395 surface area.

396 Fifthly, before heat treatment, the photoactivity of both samples N5-75 and N5-50
397 were measured. It was found that they produce much higher MB degradation than the
398 heat-treated samples, with 88% of MB removal for both samples after only 20 min. Both
399 samples were measured in dark conditions and also provide high MB degradation of 68%
400 and 61% after 20 min for samples N5-75 and N5-50, respectively. These values were
401 mainly due to the effect of adsorption and homogeneous Fenton reaction rather than the
402 photo-Fenton reaction. Iron nitrate salts (present in the samples before heat treatment)
403 accompanied by low pH (due to the presence of HNO₃ which is not completely removed
404 after drying at 80 °C) are a good environment for the homogeneous Fenton reaction. The
405 sample N5-50 was heat-treated at 600 °C for 100 min and shows a lower k value of
406 $(1.5 \pm 0.1) \times 10^{-2}$ min⁻¹ compared to sample N-5-50-800. By considering the fitted
407 Mössbauer parameters for this sample (Table 4), the spectra are composed of two

408 doublets with $\delta = (0.35 \pm 0.02$ and $0.32 \pm 0.01)$ mm s⁻¹ assigned as Fe^{III} O_h and Fe^{III} T_d,
409 respectively, where hematite is not detected (lack of sextet), which confirms that hematite
410 plays the major role in the MB degradation and it can be obtained only by heat treatment
411 at 800 °C.

412

413 **3.2.3. Parameters affecting MB degradation**

414 The sample N5-50-800 has lower acid content and lower heat treatment temperature,
415 hence, it was chosen for further study.

416

417 **a- Effect of H₂O₂**

418 The oxidation of organic pollutants using Fenton reactions is strongly dependent on
419 the addition of H₂O₂ because it controls the generation of active radicals. The MB
420 degradation has been studied under a range of H₂O₂ concentrations (0.1 to 1.6 M); the
421 results are shown in Fig. 8(a). By increasing the H₂O₂ concentration from 0.1 to 0.35 M
422 the degradation increases from 70.3% to 90.6% removal of MB where more H₂O₂
423 produces more active radicals [22]. However, excess H₂O₂ decreases the degradation
424 from 90.6% to 80.8%, mostly because it acts as a scavenger of hydroxyl radicals [22, 23].
425 Also, more H₂O₂ can generate more ·OH, which can be dimerized to form H₂O₂ so
426 cumulative effects can inhibit the MB degradation. The excess of H₂O₂ may also
427 encourage the formation of less active hydroperoxyl radicals which can react with
428 hydroxyl radicals to form water [24]. The best-performing H₂O₂ concentration was found
429 to be 0.35 M, which produced a k value of 4.1×10^{-2} min⁻¹.

430

431 **b- Effect of MB concentration**

432 Dye concentration affects the intensity of light passing through the reaction medium
433 to reach the surface of the photocatalyst. The photodegradation of MB was conducted
434 under initial concentrations of 20, 40 and 60 µM. MB degradation is shown in Fig. 8(b)
435 and displays an inverse relation with the initial concentration, where it was 90.6%, 69.2%
436 and 65.5% for MB of 20, 40 and 60 µM after 60 min of irradiation, respectively. This can

437 be attributed to the decrease in $\cdot\text{OH}$, radical generation due to the coverage of catalyst
438 active sites by the adsorbed dye [24, 25]. Moreover, the intermediate compounds formed
439 during the degradation process increase with the increase in the initial dye concentration
440 and might consume some active radicals that are supposed to react with the dye
441 molecules [26].

442

443 **c- Effect of catalyst loading**

444 Determining the optimum catalyst loading is essential in photodegradation reactions,
445 since it helps in consequently scaling up the photocatalytic process, thereby affecting the
446 economics of the whole process. This includes the production cost which should be
447 minimized. Not only this but also catalyst recovery after the end of the reaction must be
448 considered. In our case, the prepared catalyst (iron silicate powder) loading was varied
449 from 2 to 24 g L⁻¹. The results of MB degradation measured after 60 min as a function of
450 the catalyst loading are presented in Fig. 8(c). Increase in the MB degradation was
451 observed, from 84.4% for 2 g L⁻¹ to 90.6% for 4 g L⁻¹. This increase in degradation is due
452 to the increase in the active surfaces for the same unit volume of MB [24], which will
453 lead to an increase in the absorbed photons and consequently in the generation of $\cdot\text{OH}$
454 radicals which initiate the reaction [25]. Further increase leads to a decrease in MB
455 degradation from 90.6% for 4 g L⁻¹ to 81.8% for 24 g L⁻¹, mostly caused by a reduction in
456 light intensity as the solution opacity increases [27, 28]. It is also possible that at higher
457 catalyst loading, the iron act as a scavenger and reacts with $\cdot\text{OH}$ radicals [24]. The
458 optimum catalyst loading was found to be 4 g L⁻¹.

459

460 **d- Effect of temperature**

461 The reaction temperature is a critical operating parameter. Fig 8(d) shows the
462 influence of the reaction temperature on MB removal. The experiments were performed
463 at four different temperatures, namely, 303K, 313K, 323K, and 333K. It can be seen that
464 with increasing temperature, the rate of the reaction increases from $4.1 \times 10^{-2} \text{ min}^{-1}$ at
465 303K to $13.0 \times 10^{-2} \text{ min}^{-1}$ at 333K. The increase in temperature increases interaction of

466 the hydroxyl radicals and the dye molecules and the reaction competes more efficiently
467 with electron-hole recombination [11, 28].

468 The activation energy (E_a), estimated using the rate constants (k_t) from the Arrhenius
469 equation [22], were calculated according to Eq. (1)

470

$$471 \ln k_t = - E_a/RT + \ln A \quad (1)$$

472

473 Where k_t is the reaction rate constant as a function of temperature; E_a ($\text{J}\cdot\text{mol}^{-1}$) is the
474 apparent activation energy; R is the universal gas constant of $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{L}^{-1}$; T (K) is
475 the absolute temperature; A is the Arrhenius pre-exponential factor

476 The apparent activation energy of MB obtained in this study Fig. 8(d) (inset) was
477 $31.5 \text{ KJ}\cdot\text{mol}^{-1}$ which is higher than values obtained from other studies reported by
478 Okamoto [29] for the photodegradation of phenol (10.0 kJ / mole) and by Al-Sayyed [30]
479 for the degradation of 4-chlorophenol (5.4 kJ / mole). The high value obtained in this
480 study suggests that thermal activation is important to accelerate the photo-degradation
481 [31].

482

483 e- **Effect of pH**

484

485 The pH is considered the main parameter affecting the adsorption/desorption
486 processes due to its impact on the surface charge of the catalyst. This affects the
487 adsorption of reactants and dye molecules on the surface of the catalyst, and desorption
488 of the reaction products back into solution [26]. The effect of the solution pH within the
489 range of 3 to 11 on the degradation efficiency was investigated; the results are presented
490 in Fig. 9. An increase in the degradation efficiency was observed with increasing pH
491 from 3 to 11. At pH 11 the MB degradation is highest at 93.8% in 20 min, while the
492 maximum degradation at lower pH was 32.2% and 80.5 % for pH of 9 after 20 and 60
493 min, respectively. The pH of the solution can enhance the degradation and ensure strong
494 adhesion of dye molecules on the surface of the catalyst. This depends on the nature of

495 the dye (cationic, anionic or neutral). In our case, MB, which is a cationic dye, will be
496 adsorbed more quickly at higher pH and consequently, an increase in the MB degradation
497 rate is expected [25, 26]. The alkaline medium can also facilitate the formation of $\cdot\text{OH}$
498 ions which are responsible for the generation of $\cdot\text{OH}$ radicals; this will lead to an increase
499 in photodegradation rate [32]. It was reported that in acidic solutions, the surfaces of
500 photocatalysts are positively charged while they are negatively charged in alkaline
501 solutions [33]. As a result, the efficiency of MB photodegradation is expected to increase
502 with pH, owing to electrostatic interactions between the negative surface and the MB
503 cations.

504 To understand the influence of the solution pH on the Fenton process, the point of
505 zero charge (PZC) of the N-5-50-800 sample was estimated (Inset Fig. 9). The obtained
506 PZC value of 10.6 suggests that the surfaces of the catalyst were negatively charged at
507 pH higher than 10.6, which is ideal for the degradation of the cationic MB due to
508 electrostatic interactions [22]. The high value of PZC explains the rapid increase in the
509 degradation from 32.2% to 93.8% for pH of 11 and 9 after 20 min, respectively.

510

511 **3.2.4. Stability and Recyclability**

512 Catalyst recyclability is an increasingly important feature of catalysts for industrial
513 applications. In this study, the reusability of the best-performing sample, N5-50-800, was
514 tested at an initial pH of 11. Fig. 10 illustrates the relationship between MB degradation
515 efficiency and the number of cycles, tested at 20 min of irradiation after 7 successive
516 cycles where the degradation was decreased by only 6.3%. The repeated measurements
517 were carried out by centrifuging the solution followed by removing and replacing it with
518 a new MB solution. No further filtration or drying of the powder was carried out between
519 subsequent experiments, which can further lower the operational cost if the catalyst were
520 applied in a large-scale process.

521

522 **Conclusions**

523 A visible light photocatalyst was successfully prepared by dissolving the combustible
524 waste slag in nitric acid. The photocatalytic activity of the prepared samples was found to

525 obey the pseudo-first-order rate constant, having a k -value of $(4.1 \pm 0.1) \times 10^{-2} \text{ min}^{-1}$ for
526 sample N5-50-800 in the photo-Fenton process. The k -value increased to
527 $(1.4 \pm 0.1) \times 10^{-1} \text{ min}^{-1}$ for the same sample after controlling the initial pH to 11. The
528 sample prepared by the melt-quenching method using the same slag has a maximum k
529 value of $(2.2 \pm 0.1) \times 10^{-2} \text{ min}^{-1}$ under the same conditions, which illustrates the
530 effectiveness of the method used in this study. The obtained results of photocatalytic
531 activity are correlated to the amount of hematite in each sample, as detected by XRD and
532 ^{57}Fe Mössbauer measurements. It was found that the HNO_3 concentration and heat
533 treatment temperature have a large impact on both hematite content and the surface area
534 of the prepared samples and, consequently, on the methylene blue degradation ability.
535 The optimum conditions for practical usage of the samples are using sample N5-50-800
536 in the photo-Fenton reaction with 0.35 M of H_2O_2 , a catalyst (iron silicate powder)
537 loading of 4 g L^{-1} , MB initial concentration $20 \text{ }\mu\text{M}$ and initial pH of 11.

538 **CRedit author statement:**

539 **Ahmed Salah Ali:** Conceptualization, Methodology **Irfan Khan:** Writing-Reviewing
540 and Editing **Bofan Zhang:** Methodology **Kiyoshi Nomura:** Software **Homonnay**
541 **Zoltan:** Writing-Reviewing and Editing **Erno Kuzmann:** Writing-Original draft **Alex**
542 **Scrimshire:** Software **Paul Bingham:** Methodology **Stjepko Krehula:** Visualization
543 **Svetozar Music:** Data curation **Kazuhiko Akiyama:** Data curation **Shiro Kubuki:**
544 Supervision.

545

546 **Declaration on conflict of interests**

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

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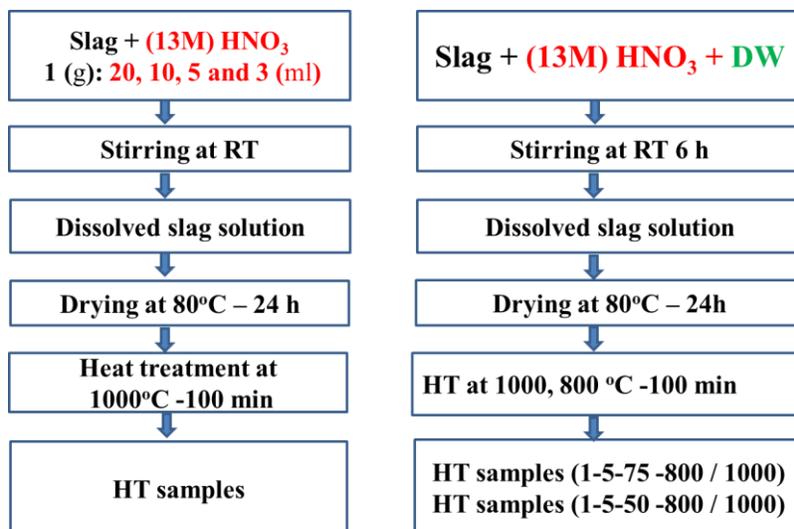
555 **References**

- 556 [1] Ferronato N, Torretta V (2019) Waste mismanagement in developing countries: A
557 review of global issues. *Int. J. Environ. Res. Public Health* 16:1–28
- 558 [2] Mary Joseph A, Snellings R, Heede P V d, Matthys S, Belie N.D (2018) The use of
559 municipal solid waste incineration ash in various building materials: A Belgian point
560 of view. *Materials* 11:1–30
- 561 [3] Yildirim I Z, Prezzi M (2011) Chemical, mineralogical and morphological properties
562 of steel slag. *Adv. Civ. Eng.* 2011:1–13
- 563 [4] Perrot J F, Alison Subiantoro A (2018) Municipal waste management strategy review
564 and waste-to-energy potentials in New Zealand. *Sustainability* 10:1–12
- 565 [5] Ishikawa S, Kobzi B, Sunakawa K, Nemeth S, Lengyel A, Kuzmann E, Homonnay
566 Z, Nishida T, Kubuki S (2017) Visible-light activated photocatalytic effect of glass
567 and glass ceramic prepared by recycling waste slag with hematite. *Pure Appl. Chem.*
568 89: 535–554
- 569 [6] Fujishima A, Honda K (1972) Electrochemical photolysis of water at a
570 semiconductor electrode. *Nature* 238:37-38
- 571 [7] Koehl M, Philipp D, Lenck N, Zundel M (2009) Development and application of a
572 UV light source for PV-module testing. *Proc. of SPIE* 7412:1–7
- 573 [8] Aramyan S, Moussavi M (2017) Advances in Fenton and Fenton Based Oxidation
574 Processes for Industrial Effluent Contaminants Control-A Review. *Int. J Environ.*
575 *Sci. Nat. Res.* 2:1–18
- 576 [9] Iida Y, Akiyama K, Kobzi B, Sinkó K, Homonnay Z, Kuzmann E, Ristić M, Krehula
577 S, Nishida T, Kubuki S (2015) Structural analysis and visible light-activated
578 photocatalytic activity of iron-containing soda lime aluminosilicate glass. *J. Alloys.*
579 *Comp.* 645:1–6
- 580 [10] Khan I, Nomura K, Kuzmann E, Homonnay Z, Sinkó K, Ristić M, Krehula S,
581 Musić S, Kubuki S (2020) Photo-Fenton catalytic ability of iron-containing
582 aluminosilicate glass prepared by sol-gel method. *J. Alloys. Comp.* 816:1–7

- 583 [11] Ali A S, Nomura K, Homonnay Z, Kuzmann E, Scrimshire A, Bingham P A,
584 Krehula S, Ristić M, Musić S, Kubuki S (2019) The relationship between local
585 structure and photo-Fenton catalytic ability of glasses and glass-ceramics prepared
586 from Japanese slag. *J. Radioanal. Nuc. Chem.* 322:751–761
- 587 [12] Melnikov P, Nascimento V A, Arkhangelsky I V, Zanoni Consolo L Z, de Oliveira L
588 C S (2014) Thermal decomposition mechanism of iron (III) nitrate and
589 characterization of intermediate products by the technique of computerized
590 modeling. *J Therm. Anal. Calorim.* 115:145–151
- 591 [13] Machulek A, Quina F, Gozzi F, Silva V, Friedrich L, Moraes J (2012) In: Puzyn T
592 (ed) *Organic pollutants ten years after the Stockholm convention—environmental
593 and analytical update*, 1st edn. Intechopen, London
- 594 [14] Akcil A, Karshigina Z B, Bochevskaya Ye G, Abisheva Z S (2018) Conditions of
595 nitric acid treatment of phosphorus slag from REMs recovery and production of
596 precipitated silicon. *Metallurgy* 2:28–38
- 597 [15] Du C, Gao X, Ueda S, Kitamura S (2016) Effects of Cooling Rate and Acid on
598 Extracting Soluble Phosphorus from Slag with High P₂O₅ Content by Selective
599 Leaching. *ISIJ International* 510:1–10
- 600 [16] Zhang Y, He P, Chen H (2018) A novel CdO/graphene alkali-activated steel slag
601 nanocomposite for photocatalytic degradation of dye wastewater. *Ferroelectrics*
602 522:1–8
- 603 [17] Kang L, Zhang Y, Wang L, Zhang L, Zhang K, Liu L (2015) Alkali-Activated steel
604 slag-based mesoporous material as a new photocatalyst for degradation of dye from
605 wastewater. *Integr. Ferroelectr.* 162:8–17
- 606 [18] Zeynolabedin R, Mahanpoor K (2017) Preparation and characterization of nano-
607 spherical CoFe₂O₄ supported on copper slag as a catalyst for photocatalytic
608 degradation of 2-nitrophenol in water. *J. Nanostruct. Chem.* 7:67–74
- 609 [19] Salgado S Y A, Pérez A A M, López M S, Zamora R M R (2016) Evaluation of
610 metallurgical slag as a Fenton-type photocatalyst for the degradation of an
611 emerging pollutant: Diclofenac. *Catal. Today* 266:126–135

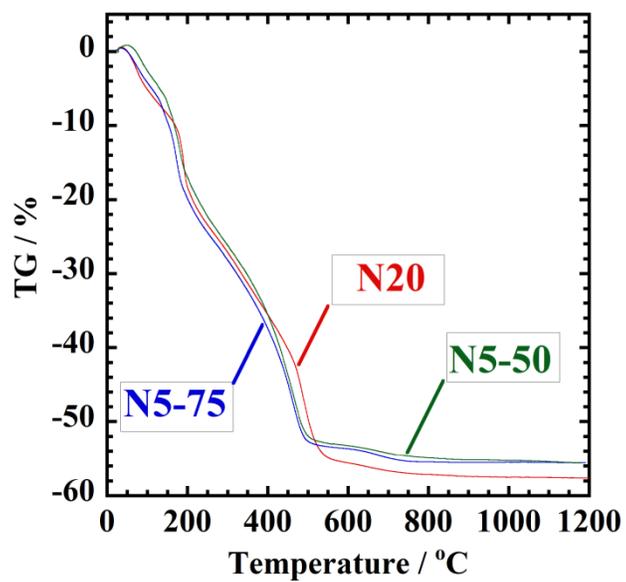
- 612 [20] Gong X, Jia F, Liu R, Ye F, Guan H, Wang R, Guo G (2014) Study on preparation
613 and photocatalytic activity of photocatalyst made from Ti-bearing blast furnace slag.
614 *Appl. Mech. Mater.* 526:33–39
- 615 [21] Sun Y, Zhang J, Wang Y, Li Q (2016) Inhibitory Effect of Thioacetamide On CdS
616 Dissolution During Photocatalytic Oxidation of 2,4-Dichlorophenol. *Rare Metal*
617 *Technology* 1:87-88
- 618 [22] Saleh R, Taufik A (2019) Degradation of methylene blue and congo-red dyes using
619 Fenton, photoFenton, sono-Fenton, and sonophoto-Fenton methods in the presence
620 of iron (II,III) oxide/zinc oxide/graphene (Fe₃O₄/ZnO/graphene) composites. *Sep.*
621 *Purif. Technol.* 210:563-573
- 622 [23] Guo S, Zhang G, Wang J (2014) Photo-Fenton degradation of Rhodamine B using
623 Fe₂O₃-Kaolin as heterogeneous catalyst: Characterization, process optimization
624 and mechanism. *J. Colloid Interf. Sci.* 433:1-8
- 625 [24] Nasuh N, Ismail S, Hameed H (2016) Activated electric arc furnace slag as an
626 effective and reusable Fenton-like catalyst for the photodegradation of methylene
627 blue and acid blue 29. *J. Taiwan Inst. Chem. E.* 67:235–243
- 628 [25] Reza K M, Kurny A S W, Gulshan F (2017) Parameters affecting the photocatalytic
629 degradation of dyes using TiO₂: a review. *Appl. Water Sci.* 7:1569–1578
- 630 [26] Abdellah M H, Nosier S A, El-shazly A H, Mubarak A A (2018) Photocatalytic
631 decolorization of methylene blue using TiO₂/UV system enhanced by air sparging.
632 *Alex. Eng. J.* 57:3727–3735
- 633 [27] Soltani N, Saion E, Hussein M Z, Erfani M, Abedini A, Bahmanrokh G, Navasery
634 M, Vaziri P (2012) Visible light-induced degradation of methylene blue in the
635 presence of photocatalytic ZnS and CdS nanoparticles. *Int. J. Mol. Sci.*, 13:12242–
636 12258
- 637 [28] Gajbhiye S B (2012) Photocatalytic degradation study of methylene blue solutions
638 and its application to dye industry effluent. *IJMER* 2:1204–1208
- 639 [29] Okamoto K, Yamamoto Y, Tanaka H, Tanaka M, Itaya A (1985) Heterogeneous
640 Photocatalytic Decomposition of Phenol over TiO₂ Powder. *Bull. Chem. Soc. Jpn.*
641 58: 2015-2022

- 642 [30] Al-Sayyed G, D'Oliveira J, Pichat P (1991) Semiconductor-sensitized
643 photodegradation of 4-chlorophenol in water. *J. Photochem. Photobiol. A: Chem.* 58:
644 99–114
- 645 [31] Hu Q, Liu B, Zhang Z, Song M, Zhao X (2014) Temperature effect on the
646 photoeatalytic degradation of methyl orange under UV-vis Light irradiation. *Journal*
647 *of Wuhan University of Technology-Mater. Sci. Ed.* 25:210-213
- 648 [32] Kaur J, Bansal S, Singhal S (2013) Photocatalytic degradation of methyl orange
649 using ZnO nanopowders synthesized via thermal decomposition of oxalate precursor
650 method. *Physica, B Condens. Matter* 416:33–38
- 651 [33] Tang Z W, Huang C P (1995) Inhibitory Effect of Thioacetamide on CdS
652 Dissolution During Photocatalytic Oxidation of 2, 4-Dichlorophenol. *Chemospher*
653 30:1385–1399
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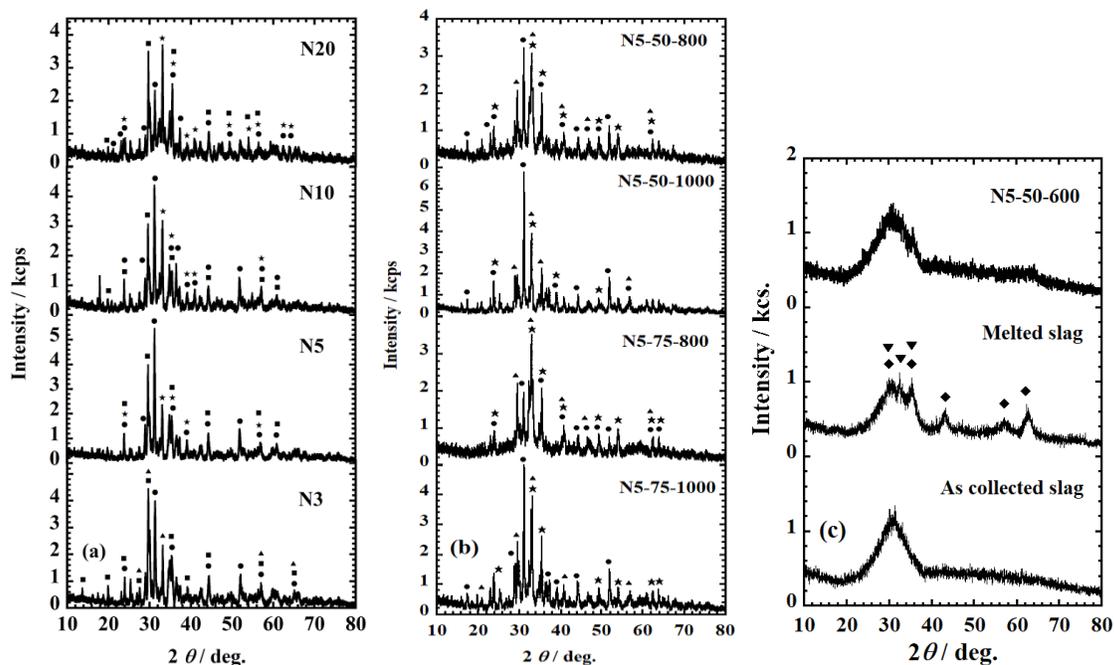
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A. S. Ali *et al.*, Scheme 1

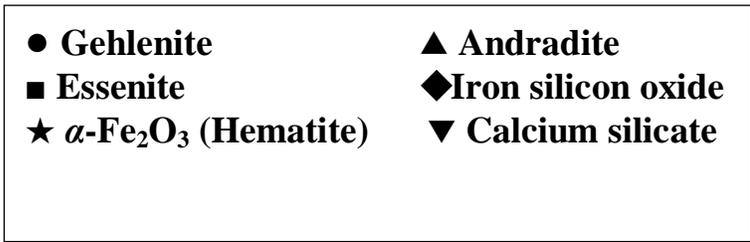


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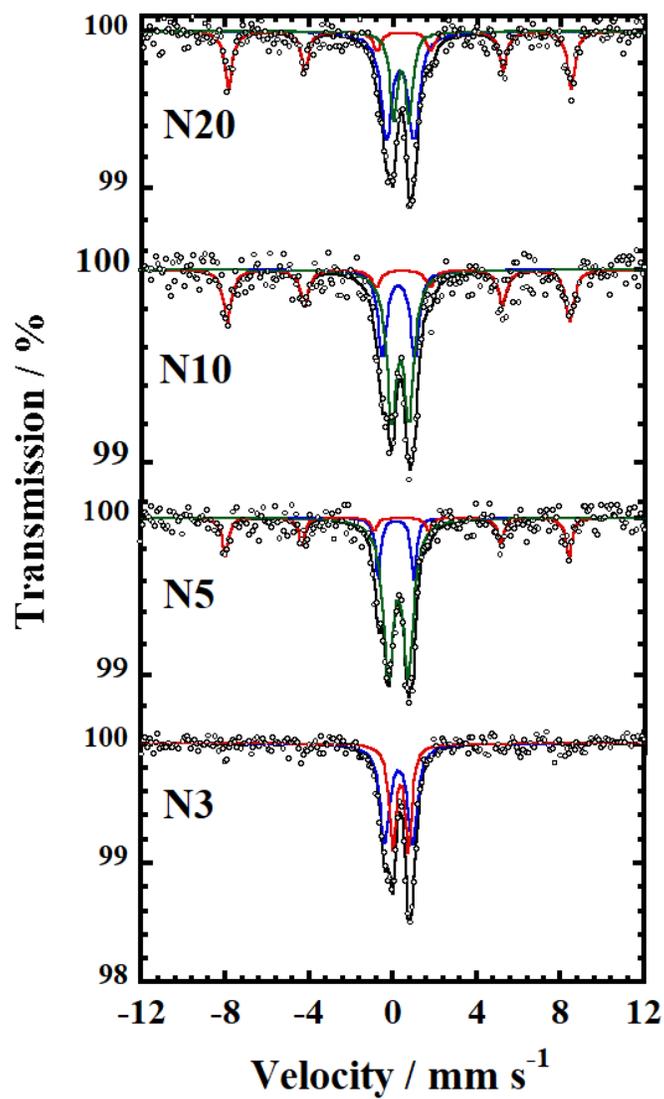
A. S. Ali *et al.*, Fig. 1



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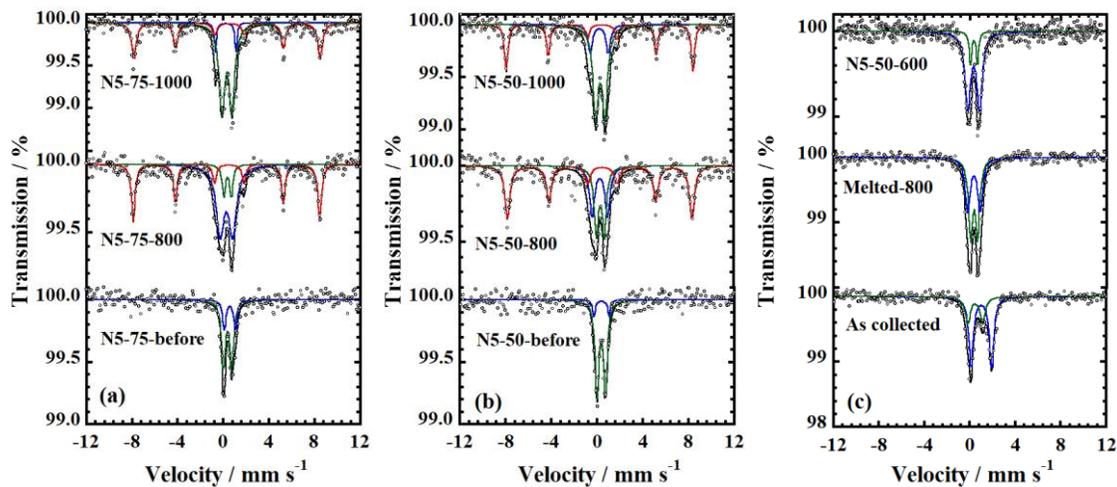


A. S. Ali *et al.*, Fig. 2 (a), (b), (c)

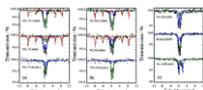


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A. S. Ali *et al.*, Fig. 3

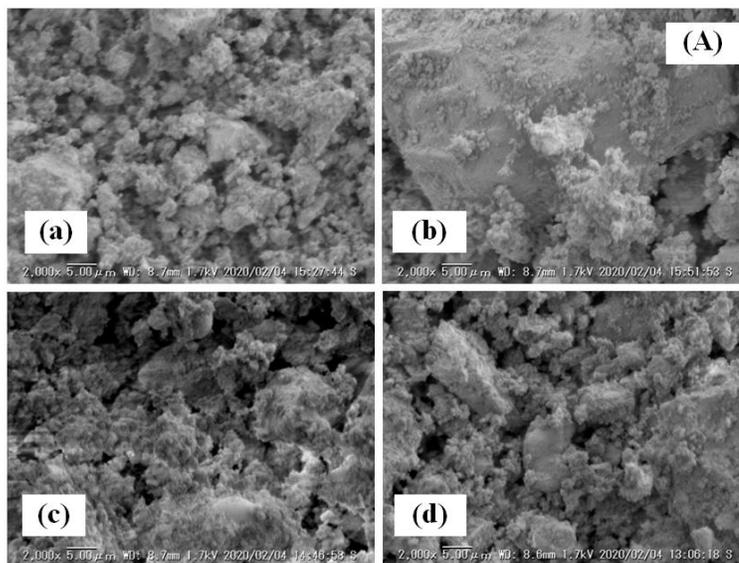


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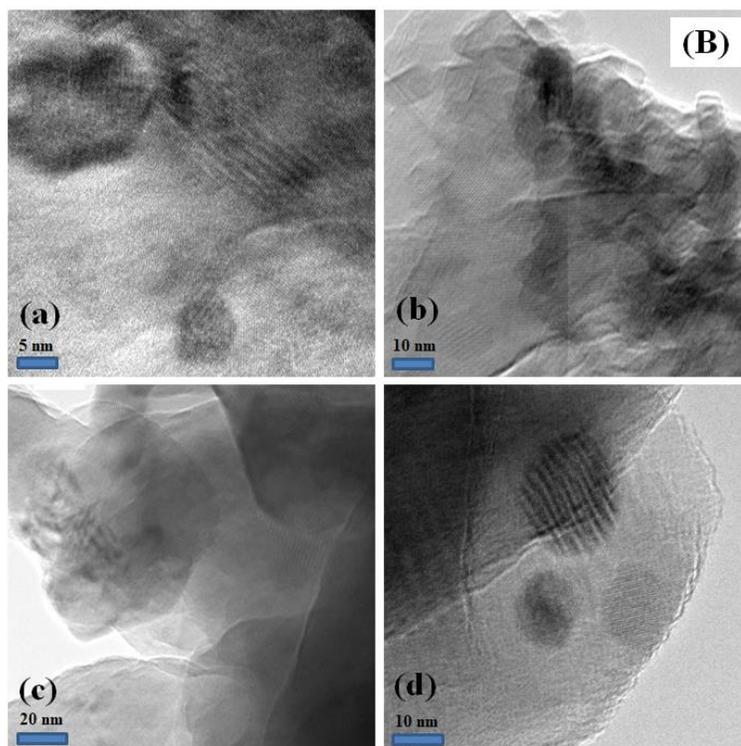


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A. S. Ali *et al.*, Fig. 4 (a), (b), (c)



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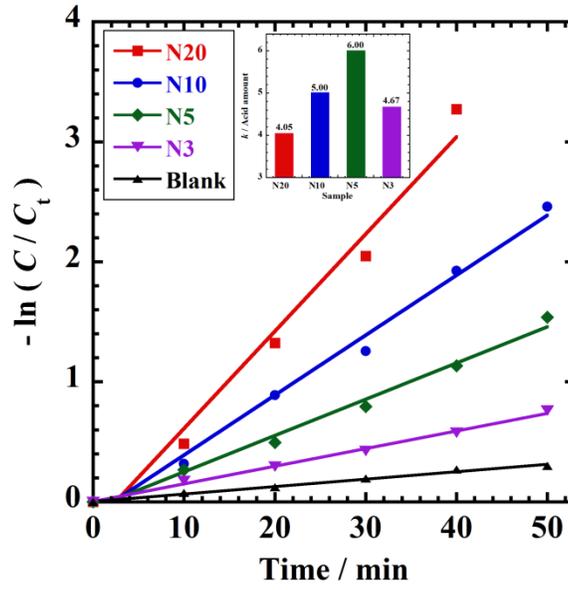
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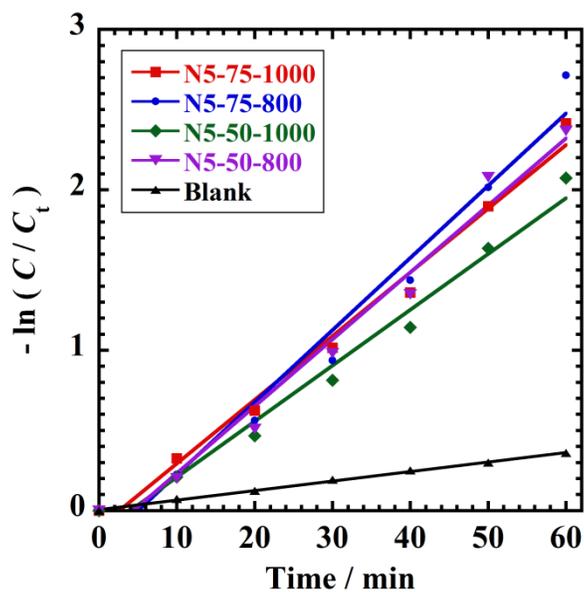
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752 A. S. Ali *et al.*, Fig. 5



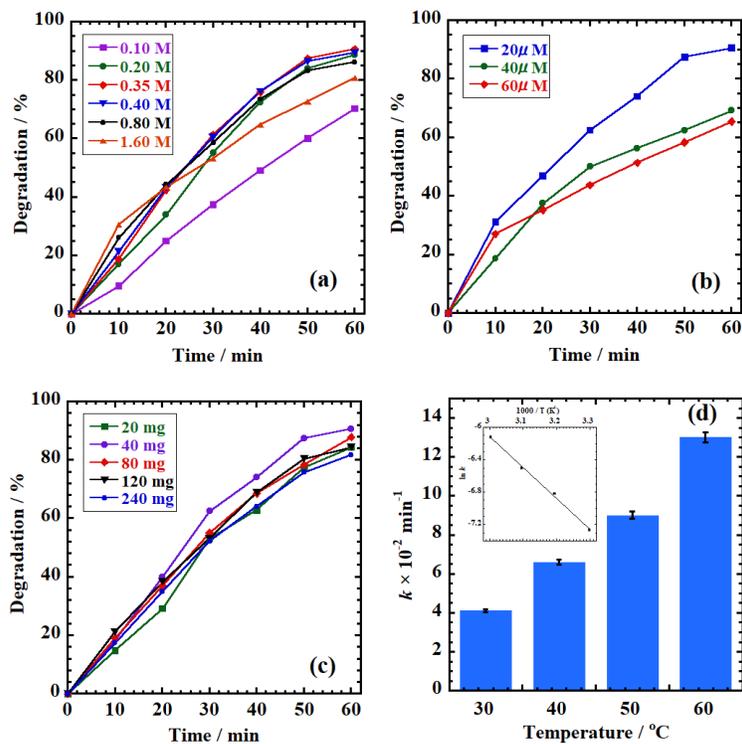
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A. S. Ali *et al.*, Fig. 6



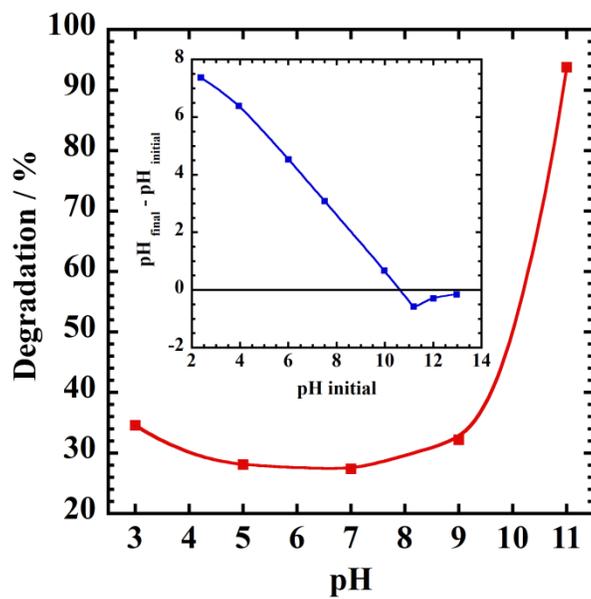
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A. S. Ali *et al.*, Fig. 7



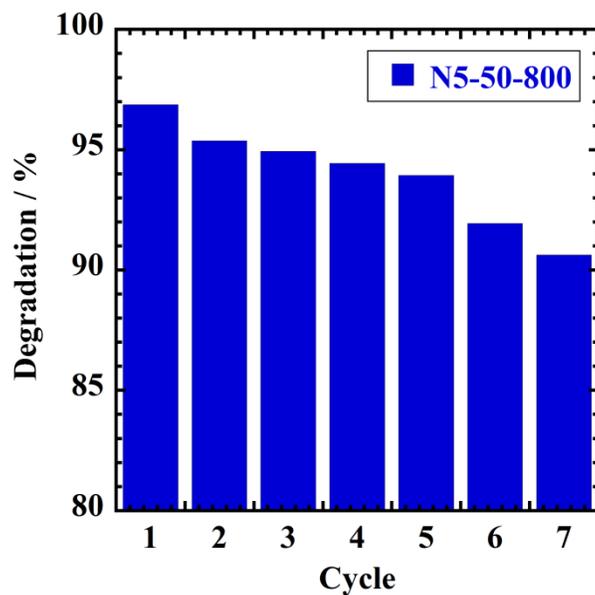
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A. S. Ali *et al.*, Fig. 8 (a), (b), (c), (d)



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A. S. Ali *et al.*, Fig. 9



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835 A. S. Ali *et al.*, Fig. 10

836 **Figure Captions**

837 **Scheme 1** Schematic diagram of the sample preparation using concentrated HNO₃ (left)
838 and diluted HNO₃ (right)

839 **Fig. 1** TG curves of the samples N20, N5-75 and N5-50

840 **Fig. 2** XRD patterns of samples (a) prepared using concentrated HNO₃ heat-treated at
841 1000 °C for 100 min, (b) prepared using diluted HNO₃ heat-treated at 800 and 1000 °C

842 for 100 min and (c) as collected slag, melted slag heat-treated at 800 °C for 100 min and
843 the sample prepared using diluted HNO₃ heat-treated at 600 °C for 100 min

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845 **Fig. 3** RT Mössbauer spectra of samples prepared using concentrated HNO₃ heat-treated
846 at 1000 °C for 100 min

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848 **Fig. 4** RT Mössbauer spectra of samples prepared using diluted HNO₃ (a) 75% (b) 50%
849 and (c) as collected slag, melted slag heat-treated at 800 °C for 100 min and the sample
850 prepared using diluted HNO₃ heat-treated at 600 °C for 100 min

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852 **Fig. 5** Images of (A) SEM and (B) TEM of the samples (a) N5-75-800 (b) N5-75-1000
853 (c) N5-50-800 (d) N5-50-1000

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855 **Fig. 6** Kinetic dye degradation measurements of methylene blue for the samples prepared
856 using concentrated HNO₃ heat-treated at 1000 °C for 100 min under photo Fenton the
857 inset is the ratio of k and acid amount for each sample

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859 **Fig. 7** Kinetic dye degradation measurements of methylene blue for the samples prepared
860 using diluted HNO₃ heat-treated at 800 and 1000 °C for 100 min under photo Fenton

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862 **Fig. 8** Effect of (a) H₂O₂ concentration, (b) MB concentration, (c) catalyst (iron silicate
863 powder) loading and (d) temperature on the MB degradation for the sample N5-50 heat-
864 treated at 800 °C for 100 min

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866 **Fig. 9** Influence of pH on the MB degradation for the sample N5-50 heat-treated at 800
867 °C for 100 min the inset is zero point of charge

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869 **Fig. 10** Reusability of the samples N5-50-800 for MB degradation at pH 11 under
870 catalyst loading 4 g/L, MB concentration 20 µM and H₂O₂ concentration 0.35M

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873 **Table 1** XRF compositional analysis of domestic waste slag (weight %) collected July
874 2018

	Fe ₂ O ₃	CaO	Na ₂ O	TiO ₂	MgO	P ₂ O ₅	K ₂ O
80	18.33	24.61	4.69	2.14	3.12	1.45	0.21

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899 **Table 2** Composition and identification of the samples dissolved in diluted HNO₃

Slag (g)	HNO ₃ (ml)	DW (ml)	HNO ₃ V (%)	Sample identification (Slag-Solution-HNO ₃)
1.00	3.75	1.25	75	1-5-75
1.00	2.50	2.50	50	1-5-50
1.00	1.25	3.75	25	1-5-25

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922 **Table 3** Room temperature ^{57}Fe Mössbauer fitted parameters for room temperature
923 analyses of as collected slag (not heat treated), slag melted at 1400 °C; heat treated at
924 800°C for 100 min; and concentrated HNO_3 dissolved slag samples after heat treatment at
925 1000°C for 100 min

Sample	Species	A (%)	δ (mm s^{-1})	Δ (mm s^{-1})	H_{int} (T)	Γ (mm s^{-1})
N20	$\text{Fe}^{\text{III}} T_d$	44	0.33 ± 0.02	1.30 ± 0.10	-	0.63 ± 0.05
	$\text{Fe}^{\text{III}} O_h$	23	0.39 ± 0.02	0.74 ± 0.06	-	0.40 ± 0.09
	Hem	33	0.42 ± 0.02	-0.20 ± 0.03	50.6 ± 0.1	0.42 ± 0.05
N10	$\text{Fe}^{\text{III}} T_d$	25	0.25 ± 0.03	1.55 ± 0.16	-	0.48 ± 0.17
	$\text{Fe}^{\text{III}} T_d$	46	0.34 ± 0.03	0.82 ± 0.12	-	0.56 ± 0.10
	Hem	29	0.37 ± 0.02	-0.23 ± 0.05	50.6 ± 0.17	0.48 ± 0.08
N5	$\text{Fe}^{\text{III}} T_d$	13.7	0.15 ± 0.02	1.69 ± 0.04	-	0.29 ± 0.07
	$\text{Fe}^{\text{III}} T_d$	66	0.26 ± 0.01	0.95 ± 0.03	-	0.58 ± 0.03
	Hem	20.3	0.35 ± 0.03	-0.21 ± 0.05	50.7 ± 0.2	0.35 ± 0.08
N3	$\text{Fe}^{\text{III}} T_d$	57.5	0.29 ± 0.01	1.33 ± 0.04	-	0.53 ± 0.13
	$\text{Fe}^{\text{III}} O_h$	42.5	0.38 ± 0.01	0.76 ± 0.02	-	0.37 ± 0.03
Melted slag	$\text{Fe}^{\text{III}} O_h$	55.6	0.36 ± 0.01	0.62 ± 0.06	-	0.44 ± 0.05
	$\text{Fe}^{\text{III}} T_d$	44.4	0.34 ± 0.01	1.10 ± 0.09	-	0.51 ± 0.06
As collected slag	$\text{Fe}^{\text{II}} O_h$	70.2	1.01 ± 0.01	1.81 ± 0.02	-	0.47 ± 0.03
	$\text{Fe}^{\text{III}} O_h$	29.8	0.48 ± 0.06	1.32 ± 0.09	-	0.53 ± 0.09

926 *Hem.* Hematite, T_d tetrahedral, O_h octahedral, A absorption area, δ isomer shift, Δ
927 quadrupole splitting, H_{int} internal magnetic field, Γ line width

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Table 4 Room temperature ^{57}Fe Mössbauer fitted parameters for room temperature analyses of diluted HNO_3 dissolved slag samples before and after heat treatment at 600, 800 and 1000°C for 100 min

Sample	Species	A (%)	δ (mm s^{-1})	Δ (mm s^{-1})	H_{int} (T)	Γ (mm s^{-1})
N5-50-1000	$\text{Fe}^{\text{III}} T_{\text{d}}$	13.6	$0.24_{\pm 0.01}$	$1.58_{\pm 0.06}$	-	$0.46_{\pm 0.07}$
	$\text{Fe}^{\text{III}} T_{\text{h}}$	52.4	$0.32_{\pm 0.01}$	$0.80_{\pm 0.02}$	-	$0.56_{\pm 0.04}$
	Hem	34.0	$0.37_{\pm 0.01}$	$-0.23_{\pm 0.03}$	$50.7_{\pm 0.1}$	$0.35_{\pm 0.04}$
N5-50-800	$\text{Fe}^{\text{III}} T_{\text{d}}$	23.4	$0.28_{\pm 0.03}$	$1.36_{\pm 0.1}$	-	$0.52_{\pm 0.1}$
	$\text{Fe}^{\text{III}} T_{\text{d}}$	27.0	$0.32_{\pm 0.02}$	$0.69_{\pm 0.08}$	-	$0.45_{\pm 0.08}$
	Hem	49.6	$0.39_{\pm 0.02}$	$-0.23_{\pm 0.04}$	$50.1_{\pm 0.1}$	$0.53_{\pm 0.07}$
N5-50-600	$\text{Fe}^{\text{III}} T_{\text{d}}$	84.0	$0.32_{\pm 0.01}$	$1.04_{\pm 0.06}$	-	$0.58_{\pm 0.03}$
	$\text{Fe}^{\text{III}} O_{\text{h}}$	16.0	$0.35_{\pm 0.02}$	$0.62_{\pm 0.05}$	-	$0.25_{\pm 0.08}$
N5-50-bef	$\text{Fe}^{\text{III}} O_{\text{h}}$	88.7	$0.36_{\pm 0.01}$	$0.74_{\pm 0.04}$	-	$0.38_{\pm 0.04}$
	$\text{Fe}^{\text{III}} O_{\text{h}}$	10.3	$0.39_{\pm 0.05}$	$1.32_{\pm 0.14}$	-	$0.27_{\pm 0.03}$
N5-75-1000	$\text{Fe}^{\text{III}} T_{\text{d}}$	7.1	$0.20_{\pm 0.02}$	$1.81_{\pm 0.06}$	-	$0.22_{\pm 0.08}$
	$\text{Fe}^{\text{III}} T_{\text{d}}$	54.5	$0.30_{\pm 0.01}$	$0.88_{\pm 0.03}$	-	$0.60_{\pm 0.04}$
	Hem	38.3	$0.43_{\pm 0.02}$	$-0.22_{\pm 0.03}$	$50.6_{\pm 0.10}$	$0.48_{\pm 0.06}$
N5-75-800	$\text{Fe}^{\text{III}} O_{\text{h}}$	9.9	$0.36_{\pm 0.04}$	$0.65_{\pm 0.06}$	-	$0.33_{\pm 0.10}$
	$\text{Fe}^{\text{III}} T_{\text{d}}$	50.3	$0.26_{\pm 0.02}$	$1.10_{\pm 0.10}$	-	$0.81_{\pm 0.06}$
	Hem	39.8	$0.39_{\pm 0.01}$	$-0.25_{\pm 0.02}$	$50.6_{\pm 0.07}$	$0.38_{\pm 0.03}$
N5-75-bef	$\text{Fe}^{\text{III}} O_{\text{h}}$	72.4	$0.37_{\pm 0.02}$	$0.73_{\pm 0.04}$	-	$0.40_{\pm 0.05}$
	$\text{Fe}^{\text{III}} O_{\text{h}}$	27.6	$0.57_{\pm 0.04}$	$0.97_{\pm 0.08}$	-	$0.34_{\pm 0.1}$

939 Hem. Hematite, T_{d} tetrahedral, O_{h} octahedral, A absorption area, δ isomer shift, Δ
940 quadrupole splitting, H_{int} internal magnetic field, Γ line width

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947 **Table 5** Surface area and *k* values of the samples prepared using diluted HNO₃ and heat

948 treated at 800 and 1000 °C for 100 min

Sample	Surface area (m ² / g)	<i>k</i> (× 10 ⁻² min ⁻¹)
N5-50-800	2.63 ± 0.05	4.1 ± 0.1
N5-50-1000	2.16 ± 0.05	3.4 ± 0.1
N5-75-800	5.38 ± 0.10	4.5 ± 0.1
N5-75-1000	3.64 ± 0.07	3.9 ± 0.1

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