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Effect of surface functionalization of Fe₃O₄ nano-enabled electrodes on the electrochemical reduction of nitrate

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21 **Abstract**

22 Nitrate is a noxious and persistent oxyanion in drinking waters. It is themed as one of the most
23 common water quality violations worldwide. Nitrate electrocatalytic reduction appears to be a viable
24 solution. However, the use of platinum group elements (PGEs) as electrocatalysts must be avoided due
25 to their high cost and limited availability. In this study, earth-abundant nano-Fe₃O₄ electrodes were
26 synthesized to surpass those implementation barriers. Surface functionalization has demonstrated to
27 impact performance of inner sphere catalytic transformations but has been seldomly explored in the
28 context of nitrate remediation. To understand the effect of the functionalization of Fe₃O₄ surfaces, Fe₃O₄
29 nano-enabled electrodes were functionalized with amine and carboxylic acids groups. After 360 min, the
30 most promising results were obtained when the Fe₃O₄ surface was modified with carboxylic groups. The
31 nitrate conversion obtained was ~90%, selectivity towards ammonia of ~55% and an electric energy per
32 order (EE/O) of 37 kWh m⁻³ order⁻¹. This EE/O value is ~2x lower, when compared to an experiment
33 using a bare Fe-plate. Therefore, nano-Fe₃O₄ electrodes hold the potential of providing a green resource
34 recovery process to treat nitrate pollution while recovering ammonia for its reuse as enriched water for
35 crops irrigation.

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41 *Keywords:* nano-enabled electrodes; functionalized magnetite; water denitrification; nitrate
42 electroremediation; mineral iron oxide

43

44 **1. Introduction**

45 Nitrate is one of the top ten drinking water contaminants worldwide causing major environmental and
46 health concerns [1–5]. Exposure to levels higher than $10 \text{ mg NO}_3^- \text{-N L}^{-1}$ relate to a wide range of human
47 ailments, such as: cancer, thyroid problems, and methemoglobinemia (blue baby syndrome) [2,6,7].
48 Nitrate concentration in natural waters has increased dramatically due to anthropogenic nitrogen-based
49 fertilizer runoff from agricultural lands, animal manure, and sewage discharges [8,9]. In the United
50 States, over 40 million people rely on private groundwater wells that may contain nitrate concentrations
51 above regulated limits [10,11]. Easy to operate technologies that can locally treat nitrate polluted water
52 sources is a need to enhance water quality for all [12].

53 Conventional nitrate removal technologies are based on ion exchange and biological processes
54 [13,14]. However, these technologies generate brines or sludge and cannot be easily deployed as
55 decentralized treatment systems [15,16]. Electrochemical reduction of nitrate (ERN) emerges as a
56 promising technology for water denitrification. Product selectivity is necessary for the implementation
57 of ERN technologies as fit-for-purpose applications. Nitrate can be reduced to nitrogen gas (N_2) or
58 ammonia (NH_3) as suitable final products in water treatment applications. Nitrogen gas is inert and it is
59 the preferred product for drinking water treatment [17,18]. However, there is an increasing interest for
60 the product selectivity towards ammonia as a valuable commodity chemical [19,20]. Besides reducing
61 the environmental burden of nitrate pollution, the treated water streams by ERN can be used in agriculture
62 irrigation decreasing the need of NH_3 production from the energy intensive Haber-Bosch process [16].
63 The selectivity and kinetics of the ERN process are strongly influenced by the choice of electrocatalytic
64 materials. Previous works have focused on the study of charge transfer processes on platinoid metals
65 (*i.e.*, Pt and Pd) [21]. Despite of their stability and excellent catalytic performance, the use of platinum
66 group elements may prevent the commercialization of electrochemical decentralized treatment units
67 because of their high cost, limited availability that identifies them as endangered elements, and the

68 adverse environmental impacts related to extraction and purification of these scarce metals [18]. Thus,
69 replacement of platinoid metals by earth-abundant, low cost and efficient ERN electrocatalysts is of great
70 interest and must be explored [22].

71 Non-precious transition metal electrocatalysts have been used as replacements for expensive
72 platinum-based electrodes. For instance, earth-abundant materials have shown to catalyze water splitting
73 reactions at different pH conditions [23,24] and Fe-containing electrodes have been reported as efficient
74 oxygen reduction catalysts in alkaline media [25]. Therefore, similar electrocatalytic strategies can be
75 used in ERN processes. Iron catalysts with mixed oxidation states (*i.e.*, Fe^0 , Fe^{2+} , and Fe^{3+}) have shown
76 to reduce nitrate to nitrite, ammonia, and nitrogen gas. For example, $\text{Fe}(\text{OH})_2$ has been reported to reduce
77 nitrate to ammonia under alkaline conditions. Also, soils and sediments containing Fe(II)-Fe(III)
78 hydroxides, or, greenish rust, have been reported to reduce nitrite to nitrous oxide and ammonia [26]. At
79 lower pH values, nano-sized zero-valent iron (nZVI) enhances the chemical conversion of nitrate to 95-
80 100% [27]. These studies demonstrate that Fe-based electrocatalysts can be used as alternative materials
81 to platinum group elements for ammonia electrogeneration from ERN.

82 ERN is a heterogeneous process that occurs at the surface of the electrode. Thus, modifications and
83 changes at the electrode material, structure or its interface may affect the catalytic performance and
84 selectivity. The aim of this work is to evaluate the competitiveness of magnetite-based electrodes as
85 alternatives to commonly used Pt catalysts for water denitrification and ammonia electrogeneration. In
86 that regard, understanding the effect of the surface functionalization of nano-enabled Fe_3O_4 electrodes,
87 such as amine-functionalized Fe_3O_4 (3-amino propyl triethoxy silane, APTES, $\text{pK}_a = 10.8$), and
88 carboxylic acid-functionalized Fe_3O_4 (polyacrylic acid, PAA, $\text{pK}_a = 4.5$), on the nitrate reduction
89 mechanism, product selectivity (*i.e.*, N_2 vs NH_3) and engineering figures of merit become important.
90 Evaluating the influence of surface acidity/basicity on the initial adsorption step of nitrate onto the
91 electrode surface, it is still barely explored in the literature. Additionally, the use of cost-effective

92 electrodes that rely on earth-abundant materials hold the promise to become a paradigm shift to enable
93 competitive implementation of electrochemically driven technologies.

94

95 **2. Experimental**

96 *2.1. Chemicals*

97 Iron (III) chloride of analytical grade was used as the metal precursor for the synthesis of magnetite,
98 and it was purchased from Sigma-Aldrich. Amino termination was obtained through functionalization
99 with 3-aminopropyl triethoxy silane (APTES) provided by Sigma-Aldrich. Poly acrylic acid, ammonium
100 acetate, and ammonium hydroxide (28-30%) were obtained from Fischer Scientific. Ethanol (99.5%) and
101 other organic solvents were obtained from Acros Organics. Analytical-grade sodium sulfate (99 %,
102 Sigma-Aldrich) was used as the supporting electrolyte. Reagent grade sodium nitrate, sodium nitrite, and
103 ammonia sulfate (> 99 %) were supplied by Sigma-Aldrich. Solutions were prepared with nano-pure
104 water obtained from a Millipore Milli-Q system with resistivity >18.2 MΩ cm at 25 °C.

105

106 *2.2. Synthesis of functionalized magnetite nanoparticles*

107 Magnetite particles were prepared following a hydrothermal synthesis method [28]. In a round bottom
108 flask, 0.68 g of FeCl₃·6H₂O (2.5 mmol) were dissolved in 60 mL of ethylene glycol. Then, 3.8 g of
109 NH₄Ac (50 mmol) was added under continuous magnetic stirring until a clear solution was formed. The
110 resulting mixture was transferred to a 100 mL Teflon-lined autoclave vessel and maintained at 200 °C
111 for 12 h after which a black precipitate of Fe₃O₄ was formed. The solid was recovered by magnetic
112 separation, and sequentially washed with milliQ water (x 3) followed by ethanol (x 3), and finally dried
113 under vacuum at 60 °C for 6 h. The dried solid was ground into uniform powder using an agate mortar
114 until the material appeared homogenous.

115 Amino terminated magnetite ($\text{Fe}_3\text{O}_4\text{-NH}_2$) was obtained by modifying the surface with APTES. The
116 pristine magnetite particles (1.0 g) were dispersed by ultrasonication in 250 mL EtOH/ H_2O (1:1 volume)
117 for 30 min under inert N_2 atmosphere. Thereafter, 2.5 mL of APTES were added to the mixture while it
118 was vigorously stirred under a nitrogen atmosphere at 40 °C for 4 hours. The functionalized material was
119 recovered using a magnet and washed with milliQ water (x 3) followed by ethanol washing (x 3). The
120 product was dried at room temperature under vacuum for 24 h.

121 Carboxylic acid terminated magnetite ($\text{Fe}_3\text{O}_4\text{-COOH}$) was obtained by modifying the surface with
122 polyacrylic acid. Briefly, the pristine magnetite particles (1.0 g) were dispersed by ultrasonication in 300
123 mL of milliQ water. Then, 100 mL of a 15 wt.% polyacrylic acid solution was added dropwise to the
124 suspension. The mixture was kept under stirring at 75 °C for 4 h, then the solid was recovered by magnetic
125 separation and washed with milliQ water (x 3) followed by ethanol washing (x 3). The product was dried
126 under vacuum at room temperature for 24 h.

127

128 *2.3. Electrode preparation and electrochemical set-up*

129 Magnetite electrodes were prepared by drop-casting the sample ink onto carbon paper (GDL EC-20-
130 10 from FuelCell Store) for both electrolysis and cyclic voltammetry experiments. In 3 mL scintillation
131 vial, 5 mg of magnetite nanoparticles and 2.5 mg of carbon black (MSE supplies LLC) were dispersed
132 in a mixture of 1.0 mL of isopropanol and 4.5 μL of Nafion® to form the ink. The suspension was
133 sonicated for 15 min to obtain a homogenous dispersion. The ink was loaded into a micropipette and was
134 carefully evenly drop casted onto a 1.5 x 2.5 cm area of carbon paper substrate. After 500 μL were
135 carefully drop-casted onto the carbon paper, it was left to dry on a hot plate at 50 °C for 1 h. Blank
136 electrodes were prepared following the same procedure without the addition of magnetite nanoparticles
137 to the ink.

138 The electrochemical nitrate reduction was performed in a 150 mL open undivided batch glass reactor
139 using one anode (Ti/IrO₂, DeNora) and one cathode (magnetite electrodes previously synthesized)
140 connected to a TENMA 72-2720 power supply. The electrodes were flat with a geometric area exposed
141 of 3 cm² (area delimited with Teflon tape) and an intergap distance of 1 cm. Under open air conditions,
142 a constant current intensity of 0.12 A (40 mA cm⁻², a common value used for ERN) was provided to the
143 system to treat 100 mL of a solution containing 100 mg NO₃⁻-N L⁻¹ [29–31] in 50 mM of Na₂SO₄ (pH =
144 5.81±0.06 and conductivity = 9.50±0.28 mS cm⁻¹) at 25 °C during 360 min. The solution was
145 continuously mixed using magnetic stirring at 700 rpm to reduce mass transport limitations between the
146 bulk and the electrode surfaces.

147 To verify the possible re-oxidation events within the undivided electrochemical cell, individual blank
148 experiments with nitrite (100 mg NO₂⁻-N L⁻¹) and ammonia (100 mg NH₃-N L⁻¹) in 50 mM of Na₂SO₄
149 were performed. According to Fig. SM-1, nitrite can be partially re-oxidized on the surface of the anode
150 because some nitrate was detected. However, no ammonia oxidation nor volatilization were noticed.

151

152 2.4. Analytical techniques

153 The crystalline structure of the synthesized materials was analyzed by X-ray powder diffraction using
154 an *p*-XRD Empyrean 2 PANanalytical diffractometer with a Cu K α (λ = 1.5418 Å) radiation source
155 equipped with a PIXcel [3D] detector with a diffractogram scanning window of 20 - 80°. Fourier-
156 transform infrared spectroscopy (FTIR) was conducted with an Agilent Cary 630 FT-IR spectrometer
157 operated in transmittance mode between 500 cm⁻¹ to 4000 cm⁻¹. Scanning electron microscopy (SEM)
158 images were recorded using a XL30 ESEM-FEG at 10 kV.

159 Contact angle measurements were carried out with 4.0 μ L of a solution containing 10 mM NaNO₃ in
160 0.1 M Na₂SO₄ using Attention – Theta Biolin Scientific equipment, during 10 s to evaluate the surface

161 of carbon paper, Fe₃O₄, Fe₃O₄-NH₂ and Fe₃O₄-COOH electrode materials. Tests were performed in
162 quadruplicates.

163 All prepared electrodes were evaluated by cyclic voltammetry (CV) in a three-electrode conventional
164 electrochemical cell and used as working electrodes. Graphite rod was used as the counter electrode, and
165 Ag/AgCl (3.5 M) was used as the reference electrode. Solutions were de-aerated by bubbling N₂ gas
166 during 20 min and keeping a N₂ atmosphere during electroanalysis. Experiments were operated with an
167 Autolab M204 potentiostat (Metrohm). CVs were measured in 0.1 M Na₂SO₄ solution in presence and
168 absence of 10 mM NaNO₃ at 50 mV s⁻¹.

169 During the electrochemical reduction of nitrate, the pH and conductivity parameters were monitored
170 using Hanna Instruments HI 322 and VWR Scientific Products - EC Model 2052 m, respectively.
171 Samples were withdrawn over time, and the concentration of N-species was analyzed by TNT 835, 839
172 and 830 HACH kits for NO₃⁻-N, NO₂⁻-N, and NH₃-N, respectively, using HACH DR6000 UV-vis
173 equipment.

174 Nitrate conversion was calculated using Eq. (1).

$$\text{Nitrate conversion (\%)} = \frac{C_{\text{nitrate},i} - C_{\text{nitrate},t}}{C_{\text{nitrate},i}} \times 100 \quad (1)$$

175 where $C_{\text{nitrate},i}$ corresponds to the nitrate concentration at time zero, and $C_{\text{nitrate},t}$ to the nitrate
176 concentration at time (t), both in mg NO₃⁻-N L⁻¹.

177 During ERN, N-volatile species, such as N₂, NO, NO₂ or N₂O, may be produced. In this work, it was
178 assumed that the N-gas species formed were most likely corresponding to N₂ and its evolution was
179 determined by mass balance. The risk of ammonia volatilization due to gas evolution at the electrodes
180 was disregarded from the blank experiments shown in Fig. SM1b. The selectivity (S_x) towards N₂ and
181 NH₃ was calculated using Eq. (2).

$$S_X(\%) = \frac{C_X}{C_{nitrate,i} - C_{nitrate,t}} \times 100 \quad (2)$$

182

183 where C_X represents the concentration (mg N L^{-1}) of a species X produced at time t . Nitrate reduction
 184 was evaluated in terms of Faradaic efficiency (FE , Eq. (3)), which determines the number of electrons
 185 consumed in an electrochemical reaction relative to the expected theoretical conversion ruled by
 186 Faraday's law.

$$FE(\%) = \frac{n F N_i}{3600 I t} \times 100 \quad (3)$$

187

188 where n is the number of electrons required per mol of product (mol), F is the Faraday constant ($96\,487$
 189 C mol^{-1}), N_i is the amount (mol) of product generated during the electrolysis, I is the applied electric
 190 current (A), t is the electrolysis time (h), and 3600 is a unit conversion factor (3600 s h^{-1}).

191 Electrical energy per order (EE/O), was used as an engineering figure of merit to benchmark the
 192 electric energy required to reduce NO_3^- -N concentration by one order of magnitude in a unit volume
 193 calculated from Eq. (4) for batch operation mode.

$$EE/O(\text{kWh m}^{-3} \text{ order}^{-1}) = \frac{E_{cell} I t}{V_s \log \log (C_0/C_t)} \quad (4)$$

194

195 where E_{cell} is the average of the cell potential (V), I is current intensity (A), t is time (h), V_s is solution
 196 volume (L), and C_0 and C_t are the initial and final concentration after one order of magnitude reduction.
 197 Considering the relationship $\log(C_0/C_t) = 0.4343 t k_1$, where k_1 represents first-order kinetics constant (s^{-1})

198 ¹), the *EE/O* expression can be simplified assuming according to Eq. (5) where 6.39×10^{-4} is a conversion
199 factor:

$$EE/O(kWh\ m^{-3}\ order^{-1}) = \frac{6.39 \times 10^{-4} E_{cell} I}{V_s k_1} \quad (5)$$

200 Experiments were run in duplicate, and the samples withdrawn were analyzed in duplicate to test the
201 precision of the measurement. Deviations between runs were always lower than 5% for all
202 determinations.

203

204 Brief note: Electroanalysis is used to qualitatively study the fundamentals of a reaction/characterization of
205 an electrode material; while the electrolysis is considered a real application of these systems to
206 treat/convert pollutants. Hence, the concentrations used in both approaches were specific for the analysis
207 that was being performed within the parameters found in literature.

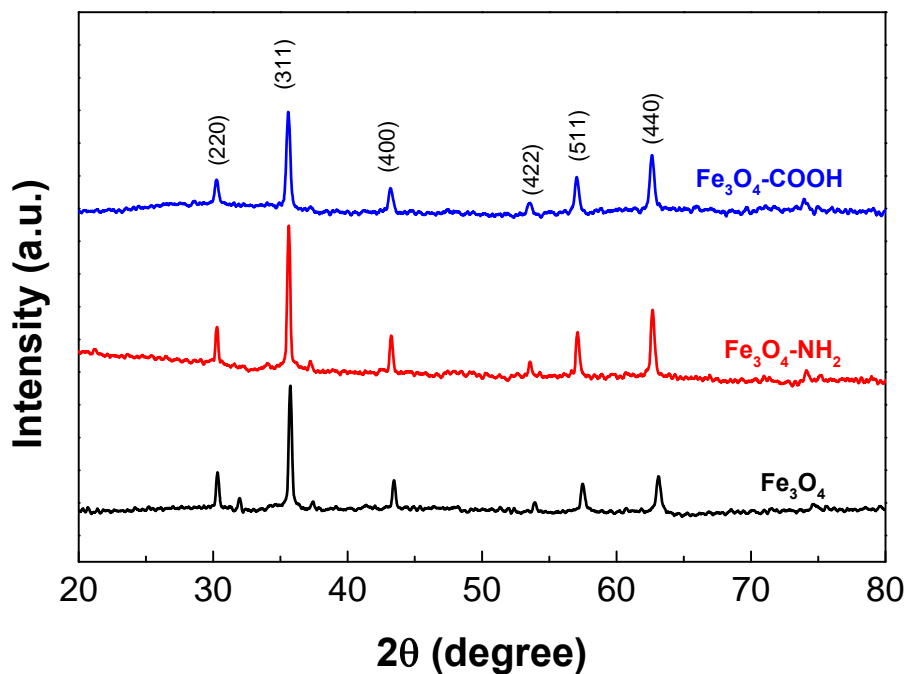
208

209 **3. Results and discussion**

210 *3.1. Physical characterization of the magnetite particles*

211 The synthesized magnetite nanoparticles were characterized through *p*-XRD in order to assess their
212 crystallinity and through FTIR in order to prove the surface functionalization. The size and morphology
213 of the nanoparticles were determined through SEM. Fig. 1 shows the powder X-ray diffraction (*p*-XRD)
214 pattern of the pristine and functionalized Fe₃O₄ samples. The *p*-XRD patterns were obtained in a 2θ range
215 from 20 to 80 degrees. The diffraction pattern for Fe₃O₄ nanoparticles was indexed according to JCPDS
216 card no. 19-629. The crystallographic planes (220), (311), (400), (422), (511) and (440) were observed
217 at 2θ = 30.4, 35.8, 37.4, 43.4, 53.7, 57.2 and 62.8°, respectively. The -NH₂ and -COOH functionalized

218 Fe_3O_4 nanoparticles show the same diffraction patterns which are consistent with crystalline magnetite
219 structures.

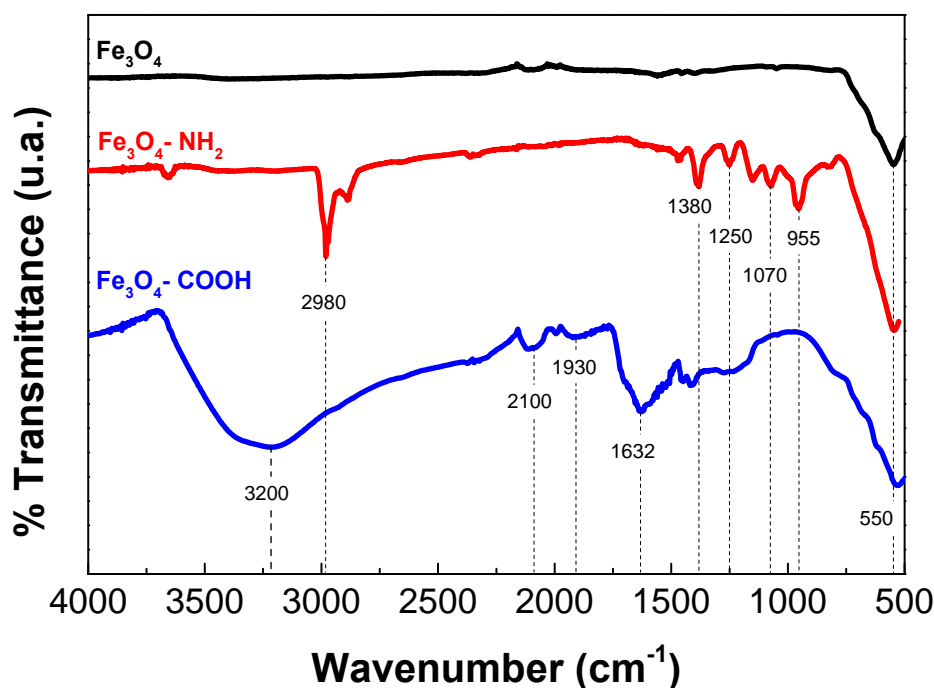


220
221 **Fig. 1** – *p*-XRD pattern of pristine Fe_3O_4 structure (bottom); NH_2 -functionalized Fe_3O_4 (middle); and
222 COOH -functionalized Fe_3O_4 (top).

223
224 The crystallite size of the nanoparticles was calculated using the Scherrer equation. The full width at
225 half maximum (FWHM) of each diffraction pattern was calculated from the (311) peak for the three
226 samples. The estimated crystallite sizes are: 5.7, 4.5, and 6.6 nm for bare Fe_3O_4 , $\text{Fe}_3\text{O}_4\text{-NH}_2$ and $\text{Fe}_3\text{O}_4\text{-}$
227 COOH , respectively. The average crystallite size for the three Fe_3O_4 samples is within the same order of
228 magnitude since the same synthetic procedure was followed prior to surface functionalization.

229 The FTIR spectra of the three Fe_3O_4 samples are shown in Fig. 2. The three spectra show a sharp peak
230 corresponding to the Fe-O stretch at 550 cm^{-1} which corroborates the iron oxide nature of all the
231 nanomaterials considered. The FTIR spectrum of bare Fe_3O_4 nanoparticles do not show any additional

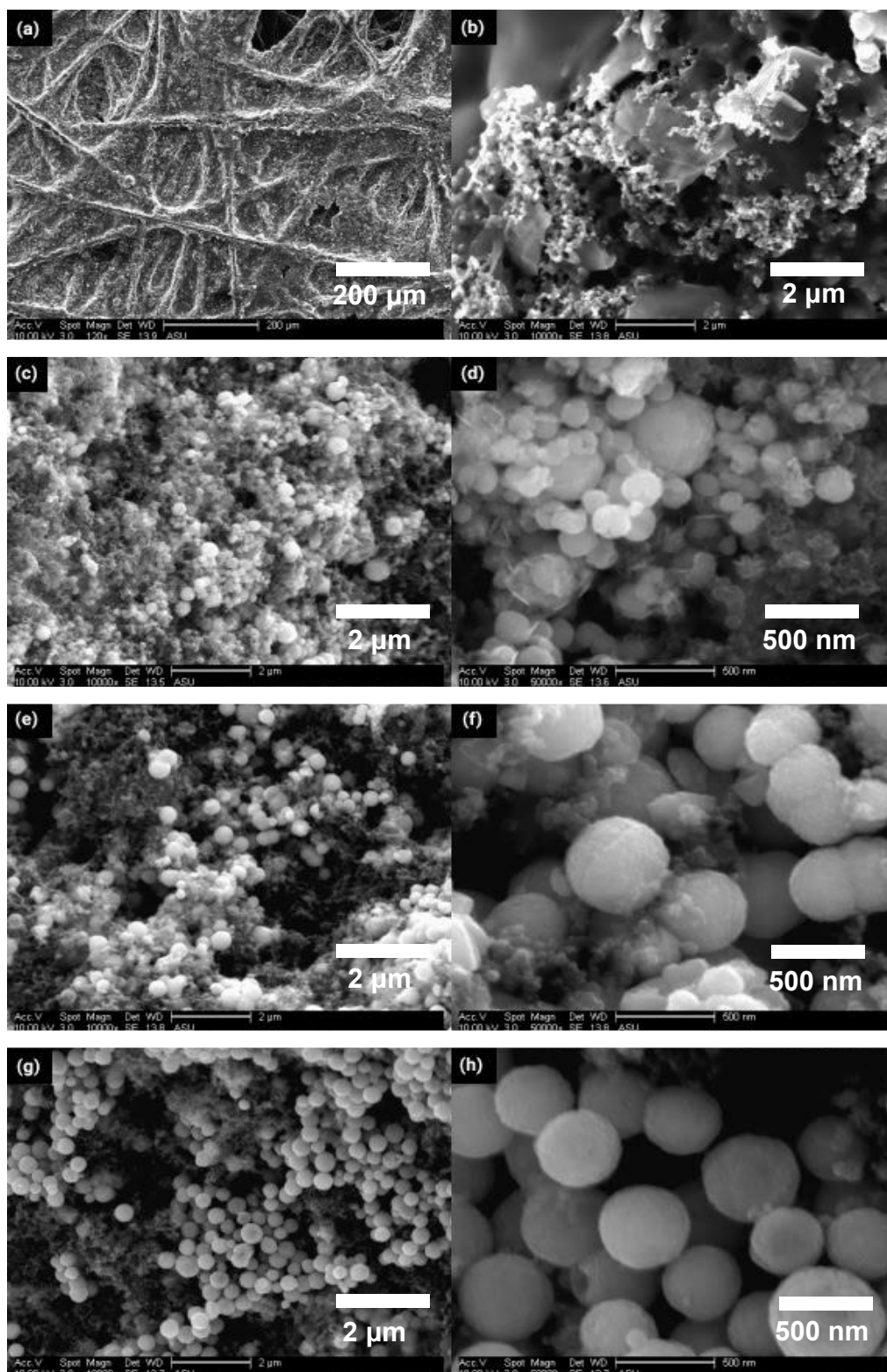
232 significant peak. The second spectrum corresponding to Fe₃O₄ functionalized with APTES (Fe₃O₄-NH₂)
233 show the characteristic peaks corresponding to the Si-O stretching at 955 cm⁻¹ and SiO-H stretching at
234 1070 cm⁻¹, which allow inferring the successful surface modification and coordination of APTES to the
235 Fe₃O₄ surface. This conclusion is further supported by the two peaks corresponding to N-H stretching
236 observed at 1420 and 2980 cm⁻¹. The peak at 2890 cm⁻¹ corresponds to a HC-H vibration associated to
237 the alkyl chain. Finally, the spectrum corresponding to the Fe₃O₄ functionalized with poly-acrylic acid
238 (Fe₃O₄-COOH) shows a peak at 1632-1930 cm⁻¹ associated to the C=O bond of the carboxyl group,
239 demonstrating the successful surface functionalization of the nanoparticles. The broad signal centered at
240 3200 cm⁻¹ is assigned to the O-H bond stretch from the hydroxyl groups.



241
242 **Fig. 2** – FTIR overlay spectra of pristine Fe₃O₄ (top), NH₂-functionalized Fe₃O₄ (middle) and COOH-
243 functionalized Fe₃O₄ (bottom).

244

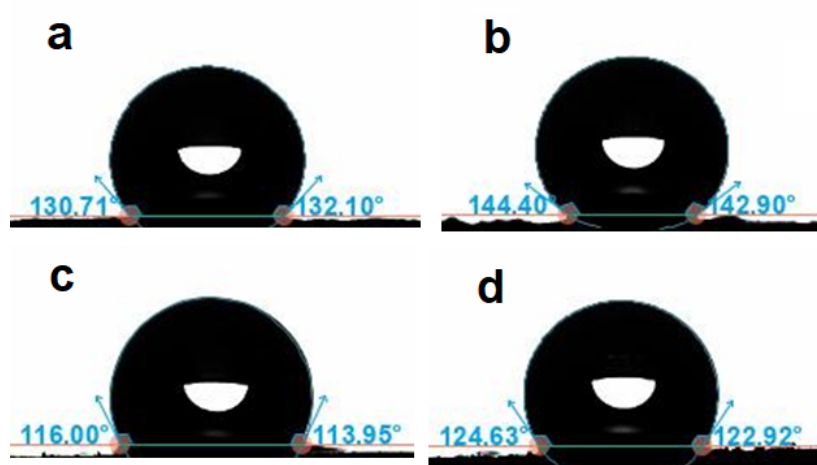
245 Scanning electron microscopy images were obtained to observe the morphology and the size of the as
246 prepared Fe₃O₄ nanoparticles and the bare carbon paper substrate. Fig. 3 depicts the two different
247 magnifications that were used to study each material. The surface morphology of bare carbon paper in
248 Fig. 3a shows folds and creases that become clearer at higher magnification in Fig. 3b. Bare Fe₃O₄
249 nanoparticles loaded onto the carbon paper substrate have a spherical shape and a size distribution of 250
250 nm and show some aggregation according to Figs. 3c and 3d. Spherical NH₂-functionalized Fe₃O₄ loaded
251 onto the carbon paper substrate have an average size of 350 nm in diameter and are shown in Fig. 3e and
252 f. These nanoparticles are less aggregated compared to the bare Fe₃O₄ due to the amine functionalization.
253 The micrographs corresponding to the Fe₃O₄-COOH electrodes (Fig. 3g and 3h) exhibit similar spherical
254 morphology with a diameter of \approx 500 nm. These COOH-functionalized Fe₃O₄ particles are less
255 aggregated when compared to the bare and to the NH₂-functionalized nanoparticles. There is a size
256 increase in the diameter of the nanoparticle after functionalization. This is due to the PAA and APTES
257 molecules surrounding the spheres.
258



260 **Fig. 3** – SEM images corresponding to (a,b) carbon paper, (c, d) carbon paper + Fe₃O₄, (e, f) carbon
261 paper + Fe₃O₄-NH₂ and (g, h) carbon paper + Fe₃O₄-COOH, at 120X (a), 10,000X of magnitude (b, c, e
262 and g) and at 50,000X of magnitude (b, d, f and h).

263

264 Hydrophobic interactions of the electrode surface between the solution and the surface of the
265 catalyst/electrode can affect the electrochemical reduction process of nitrate. Fig. 4 shows the contact
266 angle of the model solution which is in an average of $133^\circ \pm 5^\circ$, $141^\circ \pm 4^\circ$, $121^\circ \pm 8^\circ$ and $124^\circ \pm 3^\circ$ for
267 carbon paper, Fe₃O₄, Fe₃O₄-NH₂, Fe₃O₄-COOH, respectively, showing that materials are mainly
268 hydrophobic. The functionalized Fe₃O₄ electrodes show a decrease in the contact angles (and
269 hydrophobicity) compared to the bare Fe₃O₄ electrodes which likely enhances the interaction between
270 their surface and the aqueous solutions. solvent.



271

272 **Fig. 4** – Contact angle images for droplets of 10 mM NaNO₃ in 0.1 M Na₂SO₄ on: (a) carbon paper, (b)
273 carbon paper + Fe₃O₄, (c) carbon paper + Fe₃O₄-NH₂ and (d) carbon paper + Fe₃O₄-COOH.

274

275 *3.2. Electrochemical characterization of the nano-enabled electrodes*

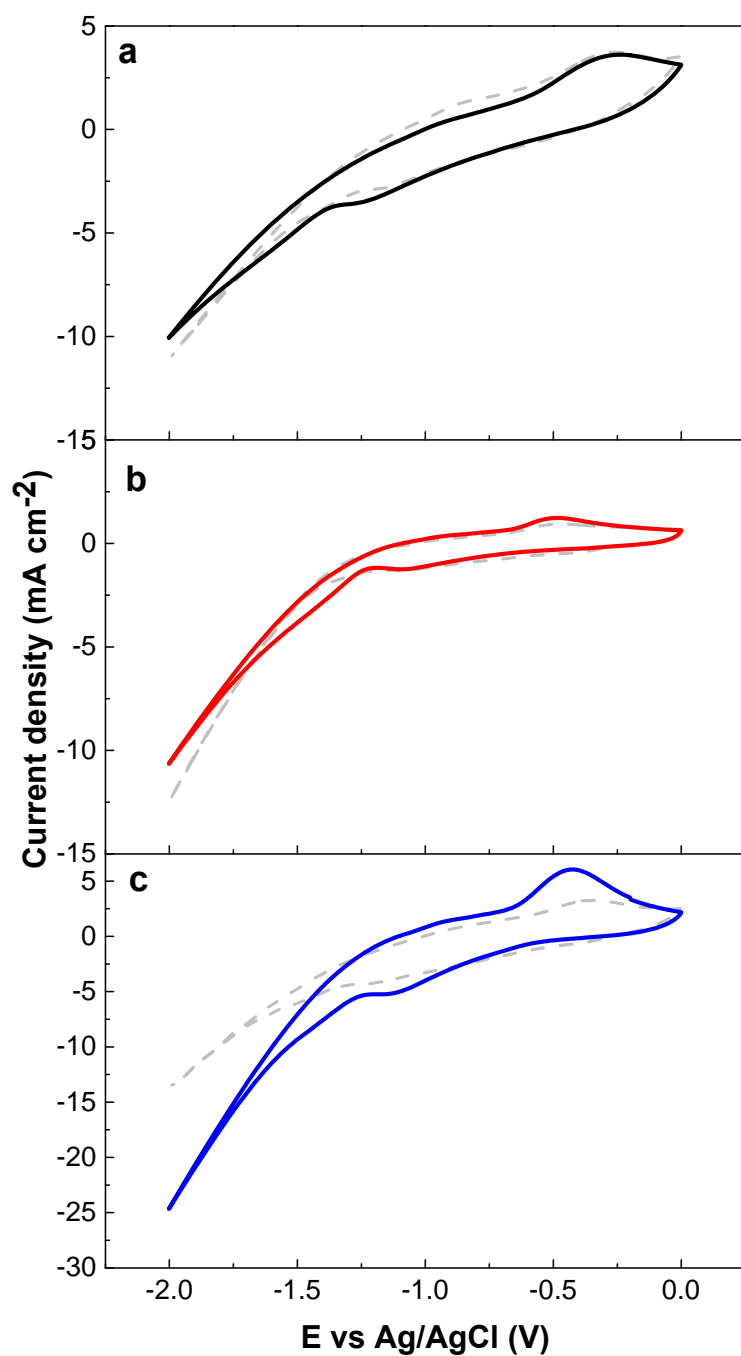
276 The electrochemical behavior of the nano-enabled electrodes was evaluated in 0.1 M Na₂SO₄ with
277 and without 10 mM NaNO₃ using cyclic voltammetry (CV) (Fig. 5). The solution resistance observed in
278 CV shape corresponds to electrode-electrolyte resistance corresponding with the contact angle results, a
279 higher resistance for Fe₃O₄ and lower resistance for Fe₃O₄-NH₂.

280 For the three electrodes, an oxidation peak (-0.25 V) and reduction peak (-1.2 V) are associated to the
281 oxidation and reduction of iron species contained in Fe₃O₄ as previously reported in literature [32–34].
282 In absence of nitrate, the reduction current density increases starting from -1.25 V due to hydrogen
283 evolution reaction (HER). By comparing the current density displayed in presence and absence of nitrate,
284 it can be concluded that the larger current density displayed in the presence of nitrate in all 3 cases might
285 be attributed to two coexisting processes, nitrate reduction and HER.

286 The functionalization of Fe₃O₄ nanoparticles with APTES presents a similar electrochemical behavior
287 than Fe₃O₄ nanoparticles. Despite the contact angle indicates more wettability and better contact of water
288 molecules with electrode surface, it does not provide information related to nitrate transport from/towards
289 the metal oxide surface where the charge transfer takes place. The Fe₃O₄ surface linked APTES is a large
290 group that can hinder the transport of NO₃⁻ due to steric effects or due to the occupation of catalytic sites
291 by the Si-O-Fe bond.

292 In the case of Fe₃O₄-COOH, the electrochemical behavior shows a considerable increment of current
293 density than other electrodes, this could be that carboxyl group promotes the HER [35]. Besides, the
294 results correspond to contact angle result that reported a better interaction of electrolyte and surface than
295 Fe₃O₄ nanoparticles.

296



297

298 **Fig. 5** – Cyclic voltammetry recorded at 50 mV s⁻¹ with (a) Fe₃O₄, (b) Fe₃O₄-NH₂, and (c) Fe₃O₄-
 299 COOH in 0.1 M Na₂SO₄ (dash line) and with the presence of 10 mM NaNO₃ (solid line). Solutions
 300 previously purged with N₂ during 20 min.

301

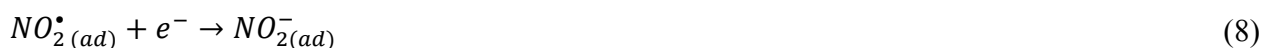
302 The electrochemical reduction of nitrate requires the transport of nitrate from the bulk solution to the
303 electrode surface and its subsequent adsorption and it is proposed to occur via inner-sphere electron
304 transfer mechanism. Recent studies suggest the contribution of outer sphere reduction mechanisms that
305 involve the participation of a redox mediator (*i.e.*, H_{ads} , H_2) [36–38]. The electroanalytical results
306 displayed in Fig.5 show only slight differences in the CV between the three magnetite-based catalysts.
307 This suggests that the functionalized surface of Fe_3O_4 electrodes does not control the interaction
308 electrode-electrolyte.

309

310 3.3. Electrocatalytic reduction of nitrate with iron and magnetite electrodes

311 The magnetite-based electrodes in this study were benchmarked against a pure Fe plate. Fig. 6a shows
312 the nitrate reduction over time and the evolution of nitrite as well as nitrogen gas and ammonium
313 employing the Fe-plate as cathode. This Fe electrode has a pollutant conversion rate that fits a pseudo
314 first-order reaction with k_1 of $5.7 \times 10^{-5} \text{ s}^{-1}$ ($R^2=0.998$) and a maximum of 71% of NO_3^- -N transformation,
315 after 360 min. These results are consistent to previous studies on Pt and other materials surfaces [22],
316 where the nitrate reduction kinetics on the electrode is controlled by the first charge transfer reaction as
317 limiting step (Eq. 6). The conversion of nitrate to nitrite is based on a three-step electrochemical-
318 chemical-electrochemical (ECE) mechanism as described by Eqs 6 – 8. During the treatment process,
319 the maximum concentration of NO_2^- -N was 0.23 mg L^{-1} at 30 min. According to Eq. 9 and Eq.10, the
320 reduction of nitrite generates hydroxide ions which increases the pH of the solution over time from
321 5.81 ± 0.06 to 11.05 ± 0.04 after 360 min of electrolysis. In this pH range, N_2 and NH_3/NH_4^+ are the
322 thermodynamically most stable forms of nitrogen according to Frost-Ebsworth diagrams [18,39]. The
323 highest accumulation of nitrite reduction products was obtained after 360 min with concentration values
324 of N_2 -N = 37.9 mg L^{-1} and NH_3 -N = 35.9 mg L^{-1} . Table 1 summarizes key fitted and calculated parameters

325 from all the experiments and it shows that the Fe-plate electrode led to a conversion of nitrate of 51% to
 326 nitrogen gas (S_{N_2}), and of 49% to ammonia (S_{NH_3}). Despite the previously reported ability of Fe cathodes
 327 to obtain ammonia as the major by-product [40,41], under the specific operating conditions applied in
 328 this work, it was observed a balanced selectivity towards ammonia and nitrogen gas. The use of Fe plate
 329 yielded a decrease in the nitrate concentration (28.7 mg L⁻¹ NO₃⁻-N) after treatment; however, it did not
 330 fall below the maximum contamination level of 10 mg NO₃⁻-N L⁻¹.

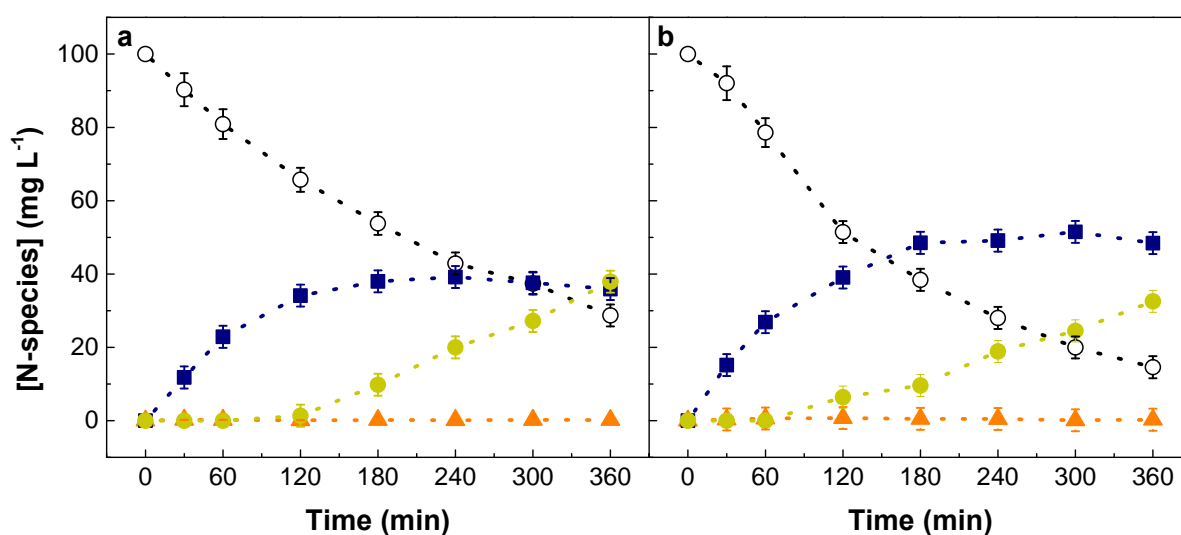


331

332 As it can be observed in Fig. 6b, using Fe₃O₄ nanoparticles deposited on carbon paper, the nitrate
 333 conversion was 85% ($k_1=8.5 \times 10^{-5} \text{ s}^{-1}$, $R^2=0.999$). The carbon paper substrate itself has no significant
 334 effect on the ERN (Fig. SM2), which highlights the excellent electrocatalytic properties of nano-enabled
 335 Fe₃O₄ electrodes for nitrate reduction in neutral and slightly alkaline aqueous solution. When using the
 336 Fe₃O₄, the maximum concentration of NO₂⁻-N generated occurred after 120 min with 0.63 mg L⁻¹,
 337 decreasing over time until 0.16 mg L⁻¹. This trend can be attributed to a higher generation of ammonia
 338 (48.5 mg L⁻¹) and nitrogen gas (32.6 mg L⁻¹), representing 59% and 40% of their selectivity, respectively.
 339 In contrast to Fe plate electrodes, the magnetite-based electrodes have a higher affinity towards ammonia
 340 generation. Nitrogen gas is the most desirable product when considering drinking water usage, but
 341 ammonia can be an added value product desirable for other applications. For example, an ammonia
 342 enriched water may be useful for agriculture irrigation given its fertilizing capabilities. Indeed, attention

343 has been given recently to the sustainable generation of ammonia by the electrochemical reduction of
 344 nitrate due to the opportunity to use that by-product as a fertilizer in crops [42,43].

345 Table 1 shows that the use of iron oxide nanoparticles has an increase of 1.2 times in the nitrate
 346 conversion when compared to the Fe plate electrode. This behavior can be attributed to the increase of
 347 active sites available in the presence of Fe₃O₄ nanoparticles. Moreover, the use of nano-Fe₃O₄ as cathodes
 348 for ERN leads to a 45% decrease in the EE/O from 72 kWh m⁻³ order⁻¹ for Fe to 41 kWh m⁻³ order⁻¹ for
 349 Fe₃O₄. EE/O values are directly related to the cell potential average (E_{cell}) and the kinetics constant for
 350 each material (Table 1). If waters with lower conductivity values were used, EE/O would have increased,
 351 since conductivity is inversely proportional to E_{cell} .



352
 353 **Fig. 6** - Evolution of the nitrogenated species ((○) NO₃⁻-N, (▲) NO₂⁻-N, (■) NH₃-N, and (●) N₂-N)
 354 over time for the electroreduction of 100 mg L⁻¹ NO₃⁻-N in 50 mM Na₂SO₄ at 40 mA cm⁻² using a) Fe-
 355 plate or b) Fe₃O₄ as cathodes.

356

357 *3.4. Influence of magnetite functionalization on the reaction mechanism and product selectivity*

358 To enhance the long-term stability of the nano-Fe₃O₄ based electrodes, the Fe₃O₄ nanomaterials were
359 surface functionalized with amino- and carboxylic groups. As the Fe₃O₄-NH₂ electrode has in its
360 composition NH₂, a blank experiment with only 50 mM Na₂SO₄ was performed as a control to verify if
361 any change occurred on the concentration of the nitrogenous compounds over time. Fig. SM3 shows that
362 null yield of N-species occurs when using Fe₃O₄-NH₂ electrodes during 360 min of electrolysis, hence
363 not affecting the performance of the process. A gradual reduction of nitrate was observed when
364 conducting electrolysis with Fe₃O₄-NH₂ cathode as seen in Fig.7a. A maximum abatement of 71% of
365 initial nitrate concentration was reached after 360 min of treatment, with a kinetic constant slightly lower
366 (~1.5x) than the one observed for Fe₃O₄ (Table 1). The NH₂ functionalization of Fe₃O₄ did not improve
367 the performance of nitrate reduction and has similar selectivity values for NH₃ (60%) and N_{gas} (38%)
368 products (Table 1). This result is consistent with the information obtained from the cyclic voltammetry
369 (cf. Fig. 5) analysis that depicted a lower electrocatalytic response of Fe₃O₄-NH₂ electrode in presence
370 of nitrate. The long APTES amine chain in the Fe₃O₄-NH₂ cathode seems to decrease the interaction
371 between the nitrate and the surface of the electrode. The lower reduction of nitrate may be associated to
372 steric effects and catalytic sites blockage that hinder the transport of nitrate towards the electrode surface,
373 making it difficult both, inner and outer sphere reduction processes. Conversely, a positive effect in
374 activity was observed for the cathode based on Fe₃O₄-COOH. The introduction of -COOH functional
375 group (Fig. 7b) led to 90% of nitrate conversion. Meanwhile, the kinetic analysis revealed a higher k_1
376 than the decay kinetic constant observed with bare Fe₃O₄ nanoparticles (~1.2x higher) (Table 1). In that
377 case, steric effects are not expected to occur given the smaller dimensions of the functional molecule
378 bonded to the bare Fe₃O₄ surface. When using the Fe₃O₄-COOH electrode, the lowest final nitrogenous
379 concentrations for NO₃⁻-N (11 mg L⁻¹, close to the MCL≈10 mg L⁻¹) and NO₂⁻-N (0.1 mg L⁻¹) were

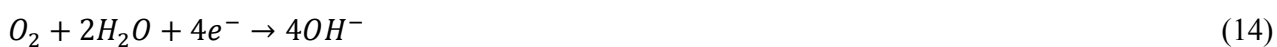
380 reached, being accompanied by the highest concentrations for NH₃-N (50 mg L⁻¹) and N₂-N (41 mg L⁻¹)
 381 species. This corresponds to $S_{NH_3}=55\%$ ($FE_{NH_3}=11\%$) and $S_{N_{gas}}=45\%$ ($FE_{N_{gas}}=5\%$). It is important to
 382 remark that besides leading to the highest decay kinetic constant for nitrate, the Fe₃O₄-COOH
 383 electrocatalyst reduced nitrate with the lowest EE/O of 37 kWh m⁻³ order⁻¹.

384 Comparing from a global point of view the nitrate conversion (~71 - 90%) and the selectivity towards
 385 nitrogen gas (~38 - 45%) and ammonia (~55 - 60%) reached by Fe₃O₄ nanoparticles with and without
 386 functionalization were only slightly different. These results suggest that the surface driven mechanism
 387 expected for an inner sphere process is not the main driver for nitrate reduction when using Fe₃O₄-based
 388 electrocatalysts in neutral and slight alkaline aqueous solutions. To rule out the contribution of other
 389 species that may be electrogenerated during electrolysis under natural conditions, further studies were
 390 conducted to disregard impacts of side-reactions such as oxygen reduction reactions (ORR) according to
 391 Eqs. (11) – (16) [44].

Acidic electrolyte



Alkaline electrolyte



392

393 The ORR is commonly observed in carbonaceous electrodes [45], and it was detected in aerated cyclic
 394 voltammetry (data not shown). ORR is a competitive reaction taking place simultaneously to ERN during
 395 electrolysis, which can reduce Faradaic efficiency and yield other electroactive species that can act as

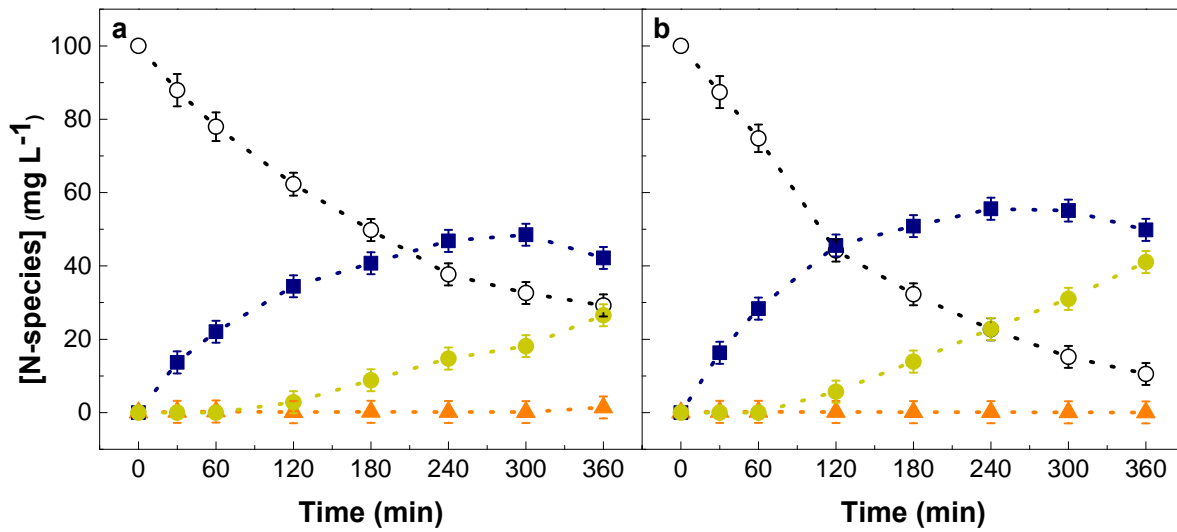
396 redox mediators for nitrate reduction. Therefore, a bulk electrolysis for nitrate removal was conducted in
 397 a de-aerated solution bubbling N₂ to avoid ORR. No notorious differences in nitrate conversion were
 398 observed when compared to the initial experiments without N₂ bubbling, so the effect of the ORR during
 399 ERN was discarded. Additional blank experiments were conducted to evaluate the impact of coexisting
 400 Fenton and Fenton-like reactions through reactions (17) and (18), respectively. These reactions that can
 401 be catalyzed by the iron species of the magnetite catalyst yield reactive oxygen species such as hydroxyl
 402 radical ($\bullet\text{OH}$) and superoxide radical ($\text{O}_2\bullet^-$) that can engage in different charge transfer reactions
 403 [25,26,46]. Nitrate solutions of 100 mg L⁻¹ NO₃⁻-N in 50 mM Na₂SO₄ were exposed to 12.5 mM of H₂O₂
 404 during 360 min without affecting the initial nitrate concentration nor N-species distribution (no reduction
 405 observed). Similarly, no variation on the time-course of nitrate concentration was observed when
 406 exposing the same solution to a Fenton reaction in presence of 12.5 mM of H₂O₂, 0.5 mM of Fe²⁺ and an
 407 initial pH of 3.0 for 360 min. From these results, the effect of ORR and other reactive oxygen species
 408 that may act as redox mediators were completely excluded as drivers of nitrate reduction.



409

410 The fact that nitrate reduction occurred overlapped with hydrogen evolution reaction (Fig. 5) and the
 411 small differences observed for different Fe₃O₄-functionalized electrocatalysts suggest that hydrogen may
 412 play a role in the reduction of nitrate during ERN and the NO₃⁻ (Eq. 6) adsorption and first electron
 413 transfer is not the rate determining reaction step in the mechanism.

414 Thus, ERN occurs through two co-existing pathways on Fe₃O₄ nanoparticles: (1) an inner sphere
 415 process where adsorption is the most likely limiting step, and (2) an outer sphere process through a
 416 hydrogen based redox mediator species electrogenerated at negative potentials on the Fe₃O₄ surface.



417

418 **Fig. 7** - Evolution of the nitrogenated species ((○) NO_3^- -N, (▲) NO_2^- -N, (■) NH_3 -N, and (●) N_2 -N)

419 over time for the electroreduction of $100 \text{ mg L}^{-1} \text{NO}_3^-$ -N in $50 \text{ mM Na}_2\text{SO}_4$ at 40 mA cm^{-2} using a)

420 $\text{Fe}_3\text{O}_4\text{-NH}_2$ or b) $\text{Fe}_3\text{O}_4\text{-COOH}$ materials as cathodes.

421

422 **Table 1** – Average of the cell potential and key fitted/calculated parameters from all the experiments for

423 the electroreduction of $100 \text{ mg L}^{-1} \text{NO}_3^-$ -N in $50 \text{ mM Na}_2\text{SO}_4$ at 40 mA cm^{-2} and 360 min of treatment

424 time.

Electrode material	E_{cell} (V)	$k_1 \times 10^{-5}$ (s^{-1})	NC (%)	$S_{\text{N}_{\text{gas}}}$ (%)	S_{NH_3} (%)	$FE_{\text{N}_{\text{gas}}}$ (%)	FE_{NH_3} (%)	EE/O ($\text{kWh m}^{-3} \text{ order}^{-1}$)
Fe-plate	5.35	5.7	71	51	49	5	8	72
Fe_3O_4	4.78	8.9	85	40	59	4	10	41
$\text{Fe}_3\text{O}_4\text{-NH}_2$	5.25	6.1	71	38	60	4	9	66
$\text{Fe}_3\text{O}_4\text{-COOH}$	4.91	10.3	90	45	55	5	11	37

425

426

427 **4. Conclusions**

428 In this work, earth abundant Fe₃O₄ nanoparticle-based electrodes were synthesized and tested as model
429 mineral iron oxide for the electrochemical reduction of nitrate (ERN) under easy-to-handle experimental
430 conditions. The effect of the functionalization of the Fe₃O₄ nanoparticles, with amine and carboxylic
431 acids groups, was studied to identify sustainable electrocatalytic systems that can remove nitrate from
432 drinking waters. Initially, bare Fe₃O₄ nanoparticle-based electrodes were benchmarked against a Fe-
433 plate, being demonstrated the superiority of using cathodes with iron nanoparticles because of the
434 increase of active sites. In fact, Fe₃O₄ nanoparticle-based electrodes increased ~1.2x nitrate conversion
435 and led to a decrease in the electric energy per order of ~45%. Regarding the functionalization of Fe₃O₄
436 with organic groups, there were slightly differences when applying these materials to the ERN. While
437 Fe₃O₄-NH₂ did not improve the performance of the reduction process, Fe₃O₄-COOH led to the best
438 results in 360 min, with 90% nitrate conversion ($k_1=10.3\times 10^{-5} \text{ s}^{-1}$, $R^2=0.999$), 55% selectivity towards
439 ammonia, 11% faradaic efficiency for NH₃ generation and the lowest electric energy per order with 37
440 kWh m⁻³ order⁻¹. According to the results, the surface functionalization of Fe₃O₄ demonstrated that nitrate
441 adsorption and first electron transfer is not the rate determining reaction step in the electrocatalytic
442 reduction of nitrate mechanism on Fe₃O₄ nanoparticles in neutral-alkaline pH solution. An outer sphere
443 process occurring through the hydrogen based redox mediator species electrogenerated on the cathode
444 surface seems to be the dominant process in the ERN.

445 This work reveals that mineral Fe₃O₄ particles can be potentially useful as electrode material for nitrate
446 reduction in natural water sources, representing a green water denitrification treatment option and a
447 sustainable method to recover ammonia to be used as enriched water for crop field irrigation.

448

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457

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596 **Effect of surface functionalization of Fe₃O₄ nano-enabled electrodes on the**
597 **electrochemical reduction of nitrate**

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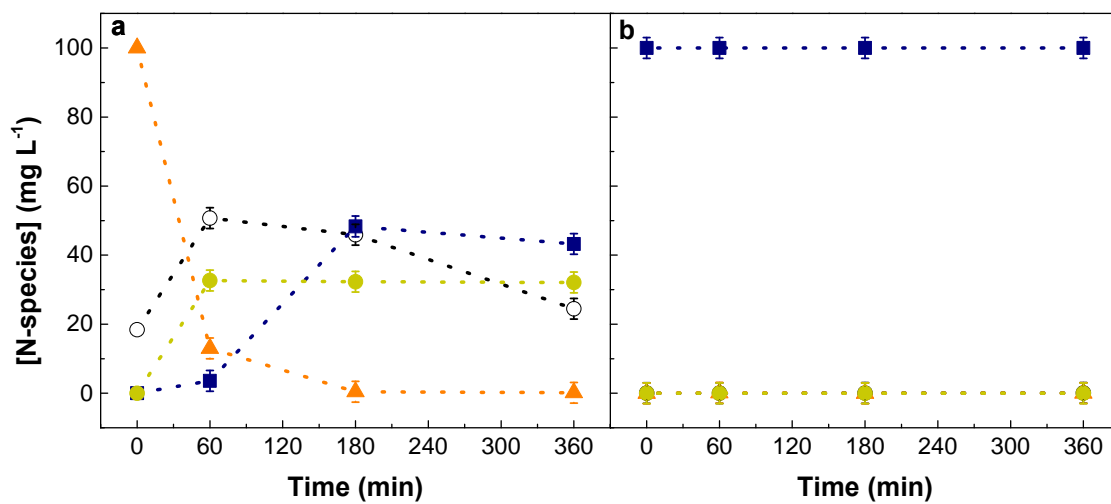
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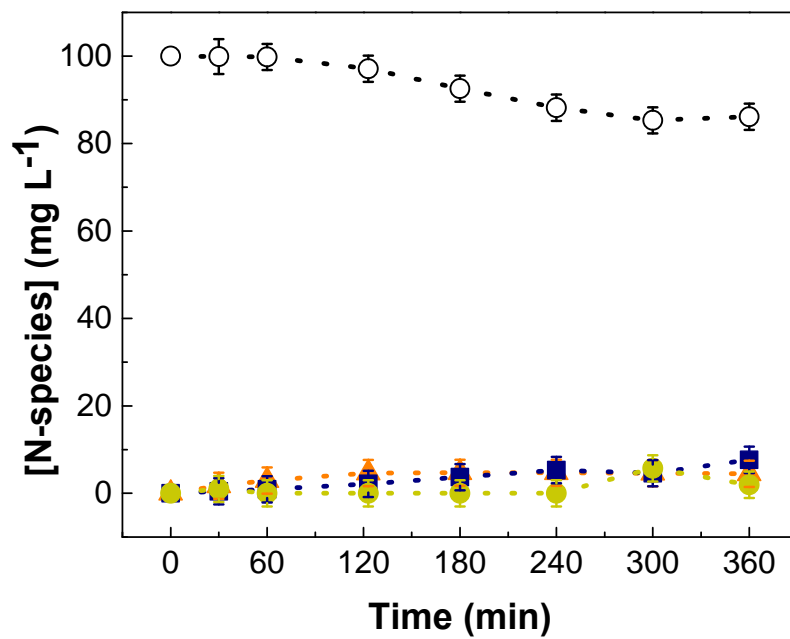
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617 **Fig. SM1** – Evolution of the nitrogenated species ((○) NO₃⁻-N, (▲) NO₂⁻-N, (■) NH₃-N, and (●) N₂-
 618 N) over time for the electroreduction of a) 100 mg NO₂⁻-N L⁻¹ and b) 100 mg NH₃-N L⁻¹ in 50 mM
 619 Na₂SO₄ at 40 mA cm⁻² using Fe₃O₄-COOH as cathode.

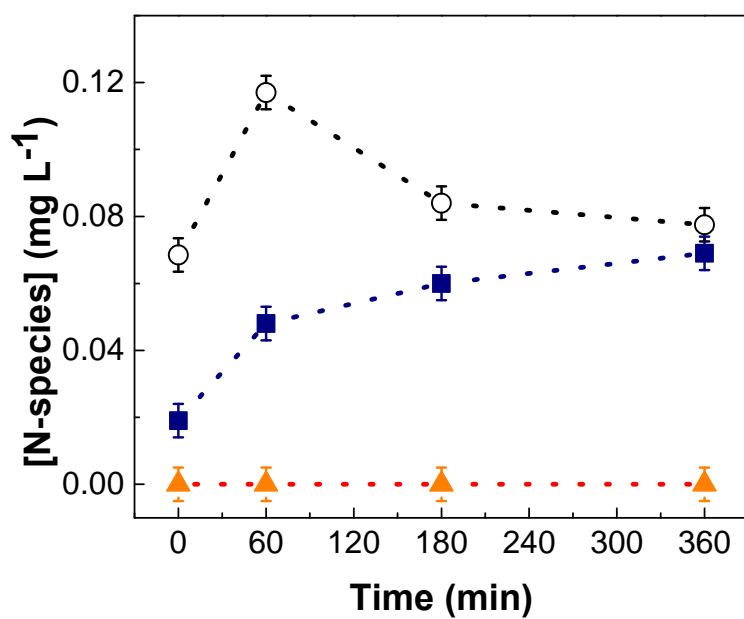
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622 **Fig. SM2** - Evolution of the nitrogenated species ((○) NO₃⁻-N, (▲) NO₂⁻-N, (■) NH₃-N, and (●) N₂-N)
 623 over time for the electroreduction of 100 mg L⁻¹ NO₃⁻-N in 50 mM Na₂SO₄ at 40 mA cm⁻² using carbon
 624 paper as cathode.

625



626

627 **Fig. SM3** - Evolution of the nitrogenated species ((○) NO₃⁻-N, (▲) NO₂⁻-N and (■) NH₃-N over time

628 for the electrolysis of 50 mM Na₂SO₄ at 40 mA cm⁻² using Fe₃O₄-NH₂ as cathode.

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