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Earth-abundant elements a sustainable solution for electrocatalytic reduction of nitrate

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► To cite this version:

Ana S Fajardo, Paul Westerhoff, Carlos M Sánchez-Sánchez, Sergi Garcia-Segura. Earth-abundant elements a sustainable solution for electrocatalytic reduction of nitrate. *Applied Catalysis B: Environmental*, 2021, 281, pp.119465. <10.1016/j.apcatb.2020.119465>. <hal-02953421>

HAL Id: hal-02953421

<https://hal.science/hal-02953421v1>

Submitted on 30 Sep 2020

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Abstract

Platinum group elements (PGEs) are widely-used electrocatalysts. However, the low abundance of PGEs in the earth's crust and high environmental impacts to be acquired result in high costs, limiting their use in drinking water treatment. Identifying sustainable alternatives to PGEs is a major barrier in applying electrocatalysis for nitrate reduction. By moving up the periodic table, this study provides a framework for selecting promising earth-abundant elements that can electrocatalytically degrade nitrate in water to innocuous by-products. We benchmarked platinum (Pt) against less-endangered elements for electrodes by quantifying nitrate reduction rates, by-product selectivity, and energy efficiencies. Carbon (as boron-doped diamond) and tin had the highest average selectivity towards nitrogen gas evolution (55% and 64%, respectively) outperforming Pt, which only had 1% selectivity, and had comparable electrical energy per order removal of nitrate. Thus, earth-abundant elements for electrocatalysis hold tremendous promise as innovative, low-cost, and sustainable processes for the water treatment marketplace.

Keywords: water treatment; advanced reduction processes; electrochemical technologies; cathodic materials; selectivity towards nitrogen

1. Introduction

Ensuring access to safe water and sanitation is essential to health and a human right[1]. Nitrate pollution is one of the top ten most common water quality violations reported worldwide[2–5]. The World Health Organization (WHO) and United States Environmental Protection Agency set maximum concentration levels in drinking water of $\sim 10 \text{ mg NO}_3^- \text{-N L}^{-1}$. [6,7] Elevated NO_3^- levels in drinking water can cause cancer, thyroid problems, and adverse respiratory effects[8–11]. As a consequence of anthropogenic nitrogen fertilizer inputs, nitrate concentrations in surface and groundwater have dramatically increased during the last century[12]. There are ~ 45 million people in the United States that rely on unregulated private groundwater wells, many of which have nitrate above regulated limits[2,13]. In addition, many municipal water supplies are impacted by nitrate and are commonly treated using costly ion exchange technology[14–19]. Thus, there is a pressing need for efficient nitrate removal technologies suitable for large-scale water treatment systems as well as very small point-of-use (POU) treatment systems within homes[20,21]. In a comprehensive review, we recently summarized how electrocatalytic reduction of nitrate (ERN) can selectively reduce NO_3^- to innocuous dinitrogen (N_2) and serves as a viable drinking water treatment technology[22]. Because electrode cost dominates the capital cost of electrochemical systems, a thorough revision on the state of the art with detailed description of the electrodes applied to (ERN) was performed as well[22–24]. The majority of publications on ERN utilized platinumoid materials (i.e., Pt and Pd)[25–34]. Platinum electrodes are excellent electrocatalysts for nitrate reduction in the water-energy nexus due to its corrosion resistance [35–37]. Unfortunately, platinum group elements (PGEs) are labeled as expensive and endangered elements due to their high cost and limited availability as resources in our planet[38]. Lifecycle analysis pinpoints adverse environmental impacts related to extraction and purification of these endangered elements[39–42]. Scientific and engineering challenges lie on uncovering alternative electrocatalysts based in high-efficient earth-abundant elements.

62 Earth-abundant alternatives to PGE electrodes likely exist but have been barely explored.
63 Analogues for electrocatalytic responses using non-endangered substitutes to PGE might be
64 identified by moving up the periodic table. This research aimed to provide a framework for
65 selecting promising earth-abundant elements to electrocatalytically degrade nitrate in drinking
66 water. To the best of our knowledge, this is the first time a paper explored, under identical
67 experimental conditions, a direct comparison of PGE-based electrodes against electrodes fabricated
68 from earth-abundant elements of the first row transition metal d-block elements (e.g., Ti, Fe, Co, Ni,
69 Cu, Zn) plus carbon (C) and tin (Sn). Operating conditions were selected to minimize side reactions
70 with other electroactive species that may impact the fundamental understanding of the
71 electrochemical transformations. Nitrate degradation rates, formation of aqueous intermediates
72 (nitrite and ammonium ion), and selectivity towards gaseous by-products were quantified. Nitrogen
73 gas is the preferred nitrate reduction by-product because (a) nitrite remains toxic to humans, (b)
74 ammonia has odor and potential human health concerns, (c) ammonia reacts with chlorine
75 disinfectants, and (d) nitrogen gases are permanently removed from solution. Engineering figures of
76 merit were used to evaluate operational requirements for electrical energy per order (E_{EO}) and
77 efficient use of electron delivered in terms of Faradaic efficiency. Results are discussed for relative
78 cost and efficiency of earth-abundant elements as alternatives to Pt electrocatalysts.

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2. Materials and methods

81

2.1 Electrochemical experiments

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Electrochemical nitrate reduction was conducted using an open, undivided cylindrical glass batch reactor containing 200 mL of non-deaerated 100 mg NO_3^- -N L^{-1} solutions with 50 mM Na_2SO_4 (pH = 5.86 ± 0.07 and conductivity = 7.74 ± 0.08 mS cm^{-1}) at 25 °C. Reagent grade sodium nitrate, sodium nitrite, and ammonia sulfate (>99%) were purchased from Sigma-Aldrich. Analytical-grade sodium sulfate (99%, Sigma-Aldrich) was used as the supporting electrolyte. All

87 solutions were prepared with ultrapure water with resistivity $>18.2 \text{ M}\Omega \text{ cm}$ at $25 \text{ }^\circ\text{C}$ (Millipore
88 Milli-Q system).

89 Batch reactor experiments were continuously mixed using magnetic stirring at 700 rpm to
90 reduce mass transport limitations between the bulk solution and the electrode surfaces. The
91 electrochemical cell was equipped with commercial sheet parallel electrodes of $2.5 \text{ cm} \times 2.4 \text{ cm}$
92 with a defined geometrical area of 6.0 cm^2 (area delimited with Teflon, back part and sides). The
93 interelectrode gap distance was 1.5 cm. A Ti/IrO₂ (DeNora) anode, and different cathodes were
94 tested: titanium (99.9%, McMaster-Carr), stainless steel (as iron element, Victor Monteiro), cobalt
95 (99.9%, Fine Metals), nickel (99.6%, Trudsafe), copper (99.9%, CynKen), zinc (99.9%, Filzinc),
96 carbon cloth (99.5% carbon content, Fuel Cell Store), carbon felt (99.0% carbon content, Fuel Cell
97 Store), synthetic boron-doped diamond (BDD; Adamant Technologies), tin (99.9%, McMaster-
98 Carr), and a polycrystalline platinum (99.9 %, Stanford Advanced Materials). The electrocatalysts
99 were rinsed with ultrapure water before use. The carbon-based materials (see specifications in
100 Supplementary Information (SI) Table S1) were activated in a solution containing 50 mM of
101 Na₂SO₄ at 100 mA cm^{-2} for 120 min.

102 Experiments were conducted galvanostatically using a TENMA 72-13610 DC power
103 supply under constant applied current density of 20 mA cm^{-2} . To evaluate the possible re-oxidation
104 of reduction by-products to nitrate, control experiments with Sn were performed using initial
105 solutions of $100 \text{ mg L}^{-1} \text{ NO}_2^- \text{-N}$ or $100 \text{ mg L}^{-1} \text{ NH}_3 \text{-N}$ solutions with 50 mM Na₂SO₄, the details are
106 shown in SI, Figure S1a and S1b, respectively. It was detected that a slight oxidation of nitrite to
107 nitrate may occur on the surface of the anode. However, that re-oxidation did not seem meaningful
108 when compared to nitrite's reduction to nitrogen gas (Figure S1a). No ammonia oxidation was
109 observed (Figure S1b). Because the oxidation reactions occur at the anode and the electrode
110 material was always the same, only one control was needed. Samples were collected over time and
111 analyzed for aqueous nitrogen species, conductivity, and pH. Experiments were run in triplicate,
112 and deviations between them were lower than 5% for all trials.

113

114 **2.3 Analytical techniques**

115 The pH and conductivity were measured over time using a 2 Hanna Instruments HI 322 and
116 VWR Scientific Products - EC Model 2052 meters, respectively. Nitrate and nitrite were quantified
117 using ionic chromatography. Sample aliquots of 20 μL were injected in Thermo Dionex ICS-
118 5000DC equipment coupled to a conductivity detector AERS 500, fitted with a high capacity
119 hydroxide-selective anion-exchange column Dionex Ionpac AS18 (2 mm \times 250 mm) column at 30
120 $^{\circ}\text{C}$. A 10–45 mM KOH gradient solution at 0.25 mL min^{-1} was used as mobile phase per EPA 300
121 method[43]. Aqueous ammonia was measured according to Hach Method 10205, a salicylate-based
122 ammonia chemistry that is equivalent to EPA 350.1, EPA 351.1, and EPA 351.2. Measurements
123 used HACH DR6000 UV-vis equipment at 694 nm applying TNT 830 HACH kits. Reproducible
124 NO_3^- -N, NO_2^- -N, and NH_3 -N concentrations were obtained with an accuracy of 1%. Nitrate removal
125 (NR) was calculated using Eq. (1)[44].

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

126 where $C_{\text{nitrate},i}$ is the nitrate concentration in mg NO_3^- -N L^{-1} at time zero, and $C_{\text{nitrate},t}$ is the nitrate
127 concentration at time (t).

128 Some publications quantified specific N-volatile species (N_2 , NO, NO_2 or N_2O) that were
129 generated during the electrocatalytic reduction of nitrate. However, most of the works report all the
130 obtained gas was N_2 . Therefore, in this work, the evolution of gaseous nitrogen species determined
131 from mass balances on aqueous nitrogen species assumed noted as N-gas, but likely corresponds
132 mostly to N_2 . We do report ammonium ion concentrations, and near or above the pKa of 9.25 for
133 $\text{NH}_4^+/\text{NH}_3$ some ammonia volatilization can occur but the Henry's constant is not very large and
134 such losses from solution of ammonia gas would be highly depending upon mixing or gas-purging
135 conditions. The selectivity (S_X) towards N-gas evolution and ammonia was calculated using Eq.
136 (2)[45].

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

137 where C_X represents the concentration (mg N L⁻¹) of a species, X, produced over time.

138 The NO₃⁻-N decay followed pseudo-first order reaction kinetics and was fitted ($R^2 > 0.95$) by
 139 a rate constant (k_1 , s⁻¹). Because the electrode surface area (6 cm²) was the same for all experiments,
 140 k_1 (s⁻¹) can be directly converted to a surface-normalized area ($k_1/6$ s⁻¹cm²). Nitrate reduction was
 141 evaluated in terms of Faradaic efficiency (FE, Eq. (3)), which determines the number of electrons
 142 consumed in an electrochemical reaction relative to the expected theoretical conversion ruled by
 143 Faraday's law[22].

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

144 where n is the amount of electrons required per mol of product (mol), F is the Faraday constant (96
 145 487 C mol⁻¹), N_i is the amount (mol) of product generated during the electrolysis, I is the applied
 146 electric current (A), t is the electrolysis time (h), and 3600 is a unit conversion factor (3600 s h⁻¹).

147 Electrical energy per order (E_{EO}), was used as an engineering figure of merit to benchmark
 148 the electric energy required to reduce NO₃⁻-N concentration by one order of magnitude in a unit
 149 volume calculated from Eq. (4) for batch operation mode[46].

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

150 where E_{cell} is the average of the cell potential (V), I is current intensity (A), t is time (h), V_s is
 151 solution volume (L), and C_0 and C_t are the initial and final concentration after one order of
 152 magnitude reduction.

153 Considering the relationship $\log(C_0/C_t) = 0.4343 \cdot t \cdot k_1$, the E_{EO} expression can be simplified
 154 assuming first-order kinetics according to Eq. (5) where 6.39×10^{-4} is a conversion factor:

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

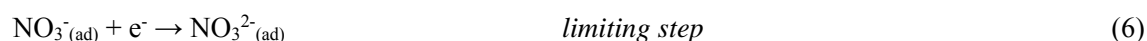
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3. Results and discussion

3.1 Platinum electrode performance as reference electrocatalyst for nitrate reduction

158 Electrochemical reduction of nitrate has been focused mostly on the study of platinum as
 159 standard cathodic material[47–49], therefore Pt is used herein to benchmark alternative electrodes
 160 based on more sustainable elements. Figure 1 shows nitrate reduction and evolution of nitrite
 161 intermediates as ammonium ion and nitrogen gas by-products. A pseudo-first order rate constant
 162 (k_1) fits well the observed nitrate degradation ($k_1 = 3.7 \times 10^{-5} \text{ s}^{-1}$; $R^2 = 0.996$). The sluggish reduction
 163 kinetics on Pt is controlled by the first charge transfer reaction as limiting step (Eq. (6)). Bimetallic
 164 electrodes on PGEs are often required to reduce this barrier[50–54], but this was beyond the scope
 165 of this study. The initial reduction of nitrate towards nitrite follows a three-step electrochemical-
 166 chemical-electrochemical (ECE) mechanism described by Eqs. (6)-(8)[22].



167

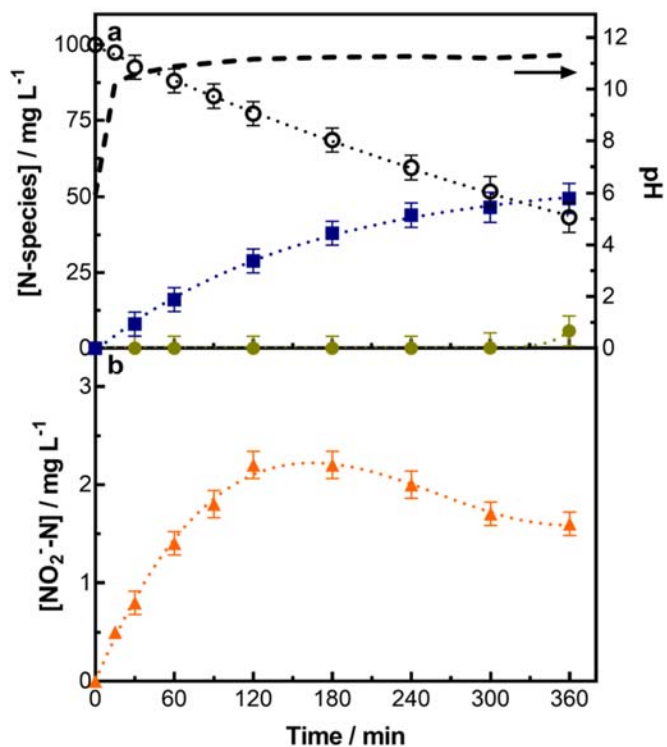
168 Nitrate reduction by-products kinetics did not show appreciable accumulation of NO_2^-
 169 intermediates; a maximum concentration of 2.2 mg NO_2^- -N L^{-1} was reached at 120 min (Figure 1b).
 170 The observed trend occurs due to the high electrocatalytic activity of Pt reducing nitrite to nitrogen
 171 gas and/or ammonia following reactions (9) and (10), respectively [55,56]. The net reduction of
 172 nitrate presented takes into account that nitrite yielded may be re-oxidized at the anode in the
 173 undivided cell (see Fig. S1a). According to reactions (9) and (10), hydroxide ions (i.e., consumption
 174 of protons during nitrate reduction) are also generated, increasing the pH from 5.86 ± 0.07 to
 175 11.3 ± 0.1 over time as shown in Figure 1a (dashed line). In this pH range, N_2 and $\text{NH}_3/\text{NH}_4^+$ are the
 176 thermodynamically most stable forms of nitrogen according to Frost-Ebsworth diagrams[22,57].
 177 Note that ammonia volatilization was not observed in blank experiments. Fundamental
 178 electrochemical studies typically do not buffer pH, and effects of constant pH and other water

179 quality parameters (e.g., alkalinity, ion composition) could be evaluated in a second-tier framework
180 study. Note that during the reduction of nitrate higher amount of OH⁻ is yielded by electron (1.3
181 OH⁻/1e⁻ for nitrogen gas and 1.2 OH⁻/1e⁻ for ammonia) than H⁺ produced in the anodic oxidation of
182 water (1 H⁺/1e⁻). Thus, the pH change observed also allows inferring that nitrate reduction takes
183 place.



184

185 After 360 min of reaction, a 58% nitrate loss yielded 49.5 mg L⁻¹ NH₃-N and 5.8 mg L⁻¹ N₂-
186 N. The calculated selectivity towards nitrogen evolution ($S_{\text{N}_{2(\text{gas})}}$) was only 10% with preferential
187 production of ammonia ($S_{\text{NH}_3} = 87\%$). The Pt selectivity is closely related to crystallographic
188 availability at the interface[58]. Fundamental studies using monocrystalline electrodes have
189 identified Pt(100) domains as essential for selective reduction towards N₂ following the Duca-Feliu-
190 Koper mechanism[59–61]. However, synthesis of monocrystalline Pt electrodes limits the electrode
191 size to a few millimeters. Introducing defects in crystalline structure affects selectivity of Pt
192 catalysts. Nitrogen evolution can be drastically reduced by the defects in symmetry as observed at
193 Pt [(1 0 0) x (1 1 0)] and [(1 0 0) x (1 1 1)] surfaces[62]. This is evident in commercial
194 polycrystalline Pt electrodes where all crystallographic facets are present in a random distribution
195 rather than a preferential orientation such as the one reported in single crystal Pt. This is the reason
196 for reduced selectivity towards nitrogen evolution observed in polycrystalline Pt electrodes, with
197 the characteristic behavior depicted in Figure 1.



198

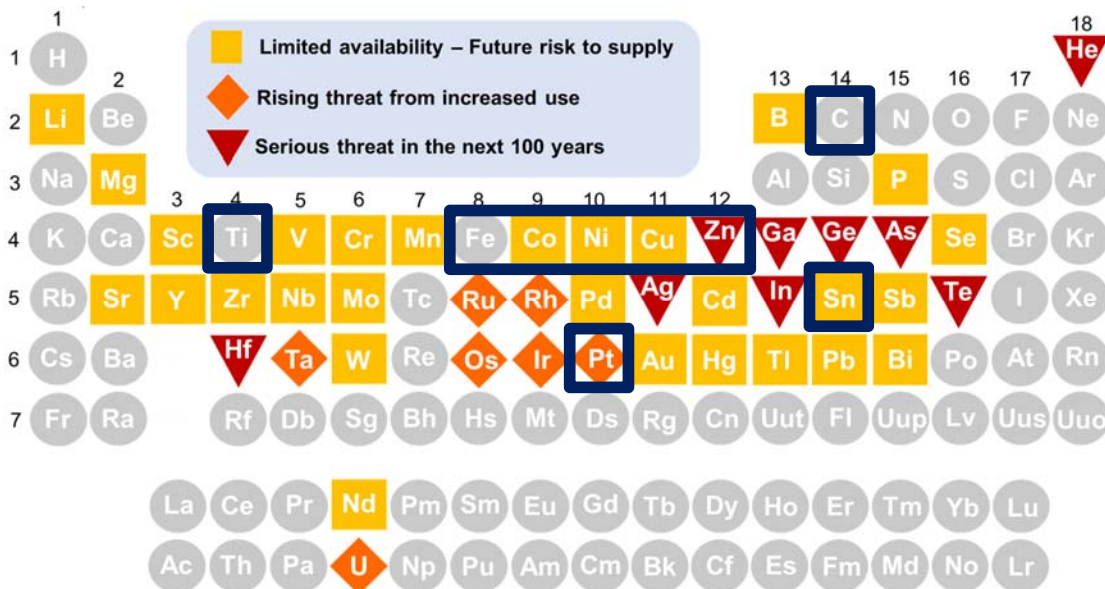
199 **Figure 1.** (a) Evolution of the nitrogenated species ((O) NO₃⁻-N, (■) NH₃-N, and (●) N₂-N) and
 200 pH (long-dashed line) over time for the electroreduction of 100 mg L⁻¹ NO₃⁻-N in 50 mM Na₂SO₄ at
 201 20 mA cm⁻², using Pt as cathode material. (b) Evolution of nitrite ((▲) NO₂⁻-N) over time.

202

203 3.2 Nitrate reduction kinetics of electrocatalysis materials upon moving up the periodic table

204 Figure 2 shows the periodic table and identifies “endangered elements”, which reflect their
 205 relative earth abundance[38]. While platinum is considered a standard in electrocatalysis due to its
 206 excellent properties, it is unfortunately an endangered element because of its limited abundance and
 207 increasing use in products or processes[38]. The high electrocatalytic activity of Pt is associated
 208 with the unclosed d-orbital shells of the metal, which contributes to the charge injection to the
 209 lowest unoccupied molecular π* orbital of nitrate[22,63]. Transition metals resembling the electron
 210 configuration of Pt are suitable for nitrate reduction but have not been the focus of comparative
 211 studies. Thus, we compared the performance of transition metals for nitrate removal. By “moving

212 up the periodic table”, catalysts using transition metals are more earth abundant and lower cost than
 213 Pt. The elements from the fourth period of the periodic table accomplish that requirement.



214
 215 **Figure 2.** The periodic table’s endangered elements (adapted from open source[38]). Elements
 216 availability: (●) high abundance, (■) limited availability, (◆) rising threat, (▼) serious threat in
 217 next 100 years.

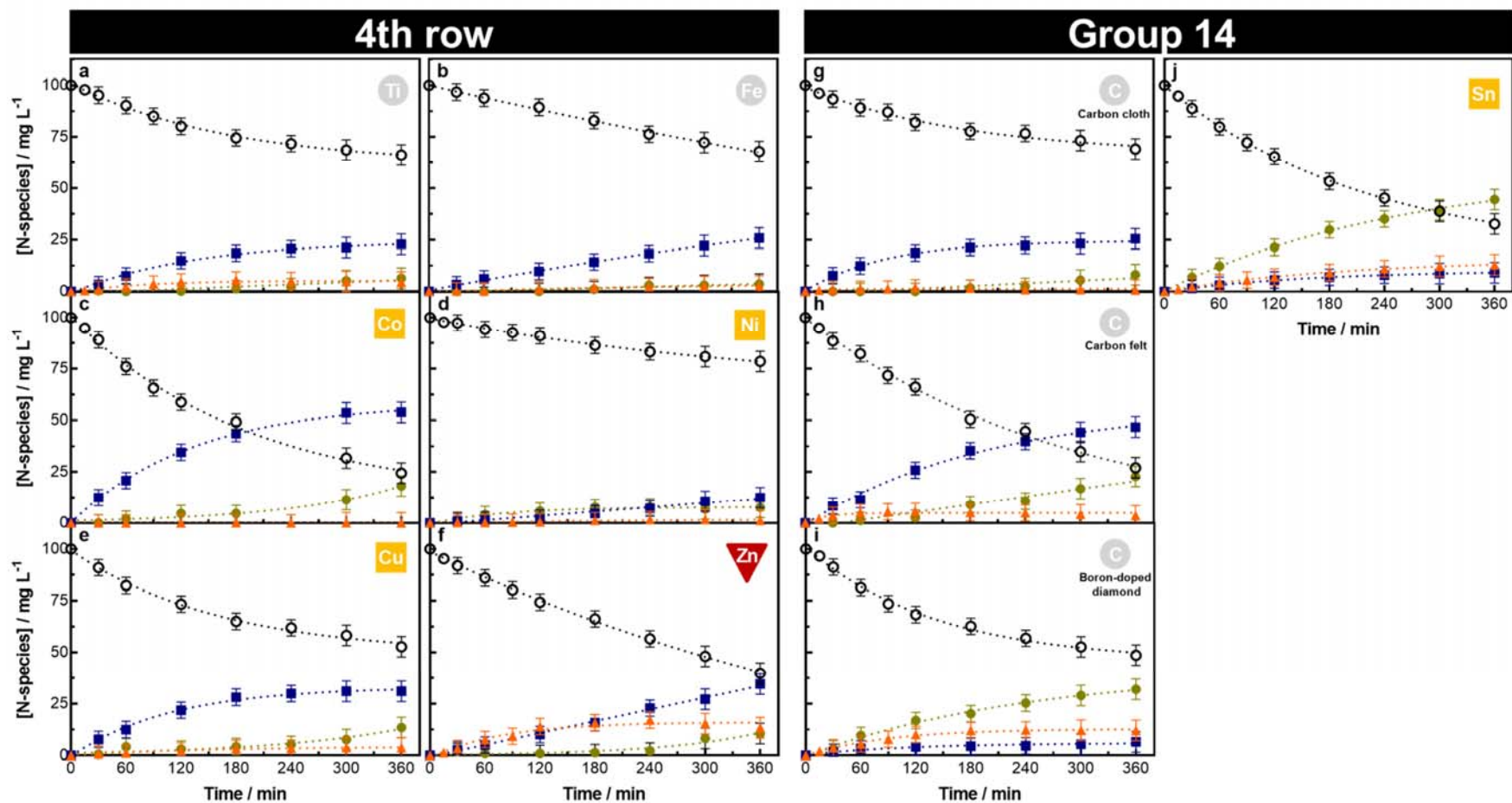
218
 219 Figure 3 depicts the performance of several transition metals materials to reduce nitrate
 220 under the same operating conditions. Fitted k_f values fell within a narrow range (1.3 to $6.6 \times 10^{-5} \text{ s}^{-1}$)
 221 (statistical fit details shown in SI, Figure S2). The low variability suggests a possible mass transfer
 222 rate limit that can be overcome through reactor engineering design.

223 Titanium (Ti) and iron (Fe) are widely available elements without a close depletion risk
 224 (Figure 2), but few direct comparisons of nitrate removal exist in the literature. Figures 3a and 3b
 225 illustrate that Ti ($k_f = 2.8 \times 10^{-5} \text{ s}^{-1}$, $R^2=0.993$) and Fe ($k_f = 1.8 \times 10^{-5} \text{ s}^{-1}$, $R^2=0.997$) electrodes both
 226 have ~2.0-fold slower nitrate reduction kinetics when compared with Pt. Table 1 summarizes key
 227 fitted and calculated parameters from all the experiments. For the Fe electrode, nitrite
 228 concentrations peaked at $2.7 \text{ mg L}^{-1} \text{ NO}_2^- \text{-N}$ and followed trends similar to Pt. After 360 minutes of

229 reaction, the residual ammonium ion was 26 mg NH₃-N L⁻¹. S_{N_{gas}} and S_{NH₃} using Fe were about
230 11% and 80%, respectively, also similar to Pt. For Ti electrode, nitrite accumulation peaked at 5.6
231 mg L⁻¹ NO₂⁻-N at 180 min and decreased slowly to reach 4.5 mg L⁻¹ NO₂⁻-N at 360 min. Consistent
232 with the literature[55,64–66], our Ti and Fe results showed ammonia generation was
233 electrocatalytically preferential over nitrogen gas evolution.

234 Cobalt (Co), nickel (Ni), and copper (Cu) are within the group of elements with limited
235 availability and possible future supply risk (Figure 2). Nitrate kinetics for these metals are shown in
236 Figures 3c, 3d, and 3e; Table 1 summarizes associated key parameters, and Figure S3 shows pH
237 evolution over time. Co had the highest nitrate reduction kinetics (~1.8-fold higher than Pt) and
238 produced the lowest nitrite (<0.08 mg NO₂⁻-N L⁻¹) throughout the experiment. Ni electrodes
239 achieved a high S_{N_{gas}} (36%) but had amongst the slowest kinetics. Cu electrodes performed
240 between Ni and Co. Electrocatalytic reduction with Cu exhibited a slightly higher *k*₁ than Pt,
241 accumulated 3.8 mg NO₂⁻-N L⁻¹, and had S_{N_{gas}} and S_{NH₃} of 28% and 64%, respectively. Cu
242 catalyzes the initial charge injection illustrated by Eq. (6), which is a rate limiting reaction for nitrite
243 formation. However, prolonged electrolysis preferentially reduces nitrite to ammonia instead of
244 nitrogen gas.

245 Zn electrodes had slightly higher *k*₁ than Pt (Table 1) and reached 60% nitrate reduction
246 after 360 min of treatment (Figure 3f). Zn showed the highest nitrite accumulation among the
247 evaluated elements in the fourth period of the periodic table, with maximum value of 17 mg NO₂⁻-N
248 L⁻¹ at 240 min, decreasing during the following 120 min to 13 mg NO₂⁻-N L⁻¹.



249

250 **Figure 3.** Evolution of the nitrogenated species ((O) NO_3^- -N, (\blacktriangle) NO_2^- -N, (\blacksquare) NH_3 -N, and (\bullet) N_2 -N) over time for the electroreduction of $100 \text{ mg L}^{-1} \text{ NO}_3^-$ -N in
 251 $50 \text{ mM Na}_2\text{SO}_4$ at 20 mA cm^{-2} using (a) Ti, (b) Fe, (c) Co, (d) Ni, (e) Cu, (f) Zn, (g) carbon cloth, (h) carbon felt, (i) boron-doped diamond, and (j) Sn.

252

253 **Table 1.** Key fitted and calculated parameters from all the experiments for the electroreduction of
 254 100 mg L⁻¹ NO₃⁻-N in 50 mM Na₂SO₄ at 20 mA cm⁻² and 360 min of treatment time.

Electrode material	$k_t, \times 10^{-5} \text{ (s}^{-1}\text{)}$	NR (%)	$S_{N_{gas}} \text{ (%)}$	$S_{NH_3} \text{ (%)}$	Maximum (and t=360 min) nitrite (mg NO ₂ ⁻ -N L ⁻¹)
Pt	3.7±0.2	57±2	10±1	87±3	2.2±0.2 (1.6±0.3)
Ti	2.8±0.4	34±1	19±1	68±2	5.6±0.3 (4.5±0.5)
Fe	1.8±0.1	31±1	11±1	80±2	2.7±0.2 (2.7±0.2)
Co	6.6±0.5	76±3	25±2	75±1	0.08±0.01 (0.03±0.01)
Ni	1.3±0.2	21±1	36±1	58±1	1.6±0.3 (1.3±0.2)
Cu	4.2±0.3	47±2	28±2	64±3	3.8±0.4 (3.7±0.3)
Zn	4.1±0.3	60±1	18±1	59±2	17±2 (13±1)
Sn	5.4±0.4	67±3	67±3	14±1	13±1 (13±1)
Carbon					
Cloth	2.8±0.1	31±1	24±1	74±2	1.8±0.3 (0.7±0.1)
Felt	5.9±0.3	73±3	31±2	64±2	5.7±0.4 (3.6±0.3)
BDD	5.5±0.2	51±2	63±2	13±1	12±1 (12±1)

255

256 Tin (Sn) is not a 4th period d-block element in the periodic table, but it is widely reported as
 257 an electrocatalyst[22]. Figure 3l shows that the tin electrode achieved 67% nitrate removal and
 258 yielded the highest mass production of N-gases (44.5 mg N L⁻¹). Tin enhanced nitrate removal with
 259 kinetics 1.5-fold higher than Pt and achieved the highest nitrogen gas concentration among the
 260 electrode materials studied.

261 Each electrode material led to different trends for nitrate reduction and by-product
 262 formation. The mechanism by which the material transfers electrons more easily to adsorbed nitrate
 263 determines its suitability for pollutant removal. Nitrite is the first stable intermediate produced
 264 during nitrate reduction. The further electrochemical reduction of this species can yield ammonia
 265 (reaction (10)) and innocuous nitrogen gas (reaction (9)). Nitrite and ammonia are harmful to
 266 human health and cause operational problems in drinking water systems, therefore making them
 267 undesired by-products from nitrate reduction[22].

268

269 **3.2.2. Carbon-based materials**

270 Carbon is one of the most abundant elements on Earth[38]. Carbon-based materials have a
271 diversity of structures, good electrical, thermal conductivity, and high mechanical strength, making
272 carbon stand out as an electrode material[67]. Carbonaceous electrodes, such as carbon cloth and
273 carbon felt, can be 1000-fold cheaper than PGEs. Carbon cloth and felt (Figures 3g and 3h) yielded
274 a 1.8-fold lower k_1 than Pt (Table 1). Nitrite concentrations with carbon cloth reached a maximum
275 of $1.8 \text{ mg L}^{-1} \text{ NO}_2^- \text{-N}$ at 120 min and decreased to $0.73 \text{ mg L}^{-1} \text{ NO}_2^- \text{-N}$ at 360 min. Overall, carbon
276 felt performed better (higher k_1 values) than Pt, carbon cloth, and most of the transition metals. One
277 factor that may explain the superior performance of carbon felt is that its high porosity and large
278 pores formed by interlace fibers allow the electrolyte to flow through the felts, favoring the
279 reactants transport and reducing the cell resistance[68–70].

280 BDD electrodes achieved the most favorable outcomes among the carbon-based electrodes.
281 Most notably, BDD achieved the highest selectivity towards desired gaseous N by-products
282 ($S_{N_{gas}}=63\%$) while also degrading nitrate 1.5-fold faster than the Pt electrodes (Figure 3i and Table
283 1). Due to its high stability under aggressive high acidic/alkaline media[71], corrosion resistance,
284 low electrocatalytic inhibition[72], and belonging to the group of elements most available, BDD is a
285 promising electrode for the electrocatalytic reduction of nitrate (ERN).

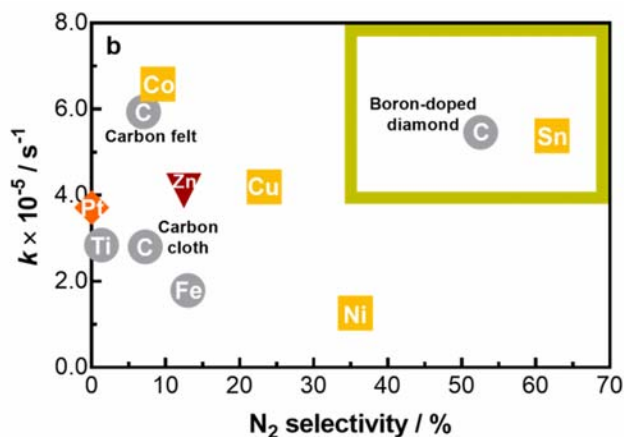
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287 **3.3. Benchmarking electrocatalysts towards higher electrokinetics and selectivity**

288 Electrochemical reduction applicability is defined by treatment kinetics and selectivity (i.e.,
289 preferential formation of N_2). Technology competitiveness in market settings will be defined by
290 techno-economic aspects related to material cost and availability, which goes beyond treatment
291 performance. While market costs are good indicators of electrode costs for some elements (e.g., Pt)
292 (see Fig. S4), the actual capital costs for low-cost elements may be further influenced by electrode
293 synthesis processes and net manufacturing costs. For example, the three carbon-based electrodes

294 demonstrated that even for a single earth-abundant element (i.e., carbon), the electrode morphology,
 295 element oxidation state, and element bonding configuration played a major factor in overall
 296 electrode performance. Manipulating the element's morphological and chemical properties
 297 influence the synthesis or manufacturing costs of electrodes. This is true for most of the elements
 298 studied herein. For example, while elemental Ti plate was used here, other researchers observed that
 299 Magneli phase of titanium oxide (e.g., Ti_4O_7) can also degrade nitrate[73]. The numerous oxidation
 300 states of many of the earth-abundant elements, compared with the almost exclusive reliance on
 301 elemental metals in application of PGE electrodes, offer a remarkable “design space” for use of
 302 non-endangered elements as electrode materials.

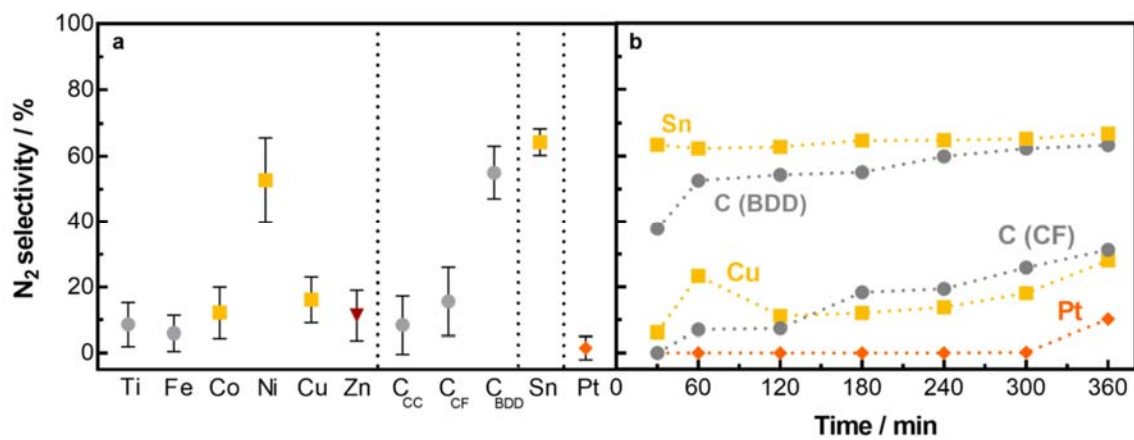
303 Figure 4 benchmarks each electrocatalyst against Pt (◆) in terms of kinetics and selectivity
 304 obtained at 20% of nitrate removal, while considering sustainability aspects of different elements.
 305 Note that several electrocatalysts (Co, Cu, Zn, carbon felt, BDD, and Sn) outperformed Pt for NO_3^-
 306 reduction kinetics, which is illustrated by their location in the upper half of Figure 4b.



307
 308 **Figure 4.** Pseudo-first order kinetics obtained vs. selectivity towards N_2 during electrochemical
 309 reduction of $100 \text{ mg L}^{-1} NO_3^-$ -N in 50 mM Na_2SO_4 at 20 mA cm^{-2} (values set at 20% of initial NO_3^-
 310 abatement). The electrocatalysts included in the upper right quadrant present the fastest reduction
 311 kinetics and highest selectivity towards nitrogen gas. Elements earth availability color coded based
 312 upon Figure 2: (●) high abundance, (■) limited availability, (◆) rising threat, (▼) serious threat in
 313 next 100 years.

314

315 For water treatment, the viability of electrodes fabricated from different elements depends
316 strongly on by-product selectivity towards innocuous nitrogen gas rather than selectivity toward
317 nitrite or ammonia. In Figure 5a, the average of selectivity towards nitrogen is plotted with error
318 bars showing that this parameter varies minimally across the duration of the electrochemical
319 treatment for most of the elements studied. In fact, this behavior can be verified in Figure 5b, with
320 BDD and Sn attaining the highest $S_{N_{gas}}$.



321

322 **Figure 5.** (a) Average and standard deviation of the selectivity towards N_2 obtained with
323 the different cathodic materials studied during the ERN treatment. (b) Selectivity towards N_2 over
324 time for selected electrodes. Note: CC, CF, and BDD stands for carbon cloth, carbon felt, and
325 boron-doped diamond, respectively. Conditions: $100 \text{ mg L}^{-1} \text{ NO}_3^- \text{-N}$ in $50 \text{ mM Na}_2\text{SO}_4$ at 20 mA
326 cm^{-2} . Elements availability: (●) high abundance, (■) limited availability, (◆) rising threat, (▼)
327 serious threat in next 100 years.

328

329 Effective electrocatalysts should have the attributes of rapid nitrate removal (i.e., high k_t)
330 with a corresponding high selectivity towards desired N-gas by-products (i.e., high $S_{N_{gas}}$). For
331 electrode materials illustrated in Figure 4, the more effective materials are located in the upper-right
332 quadrant. Thus, Sn and carbon-based BDD would be classified as the most effective for nitrate

333 removal and are clearly superior to commercial polycrystalline Pt electrodes, which achieved only
334 1% selectivity towards N-gases.

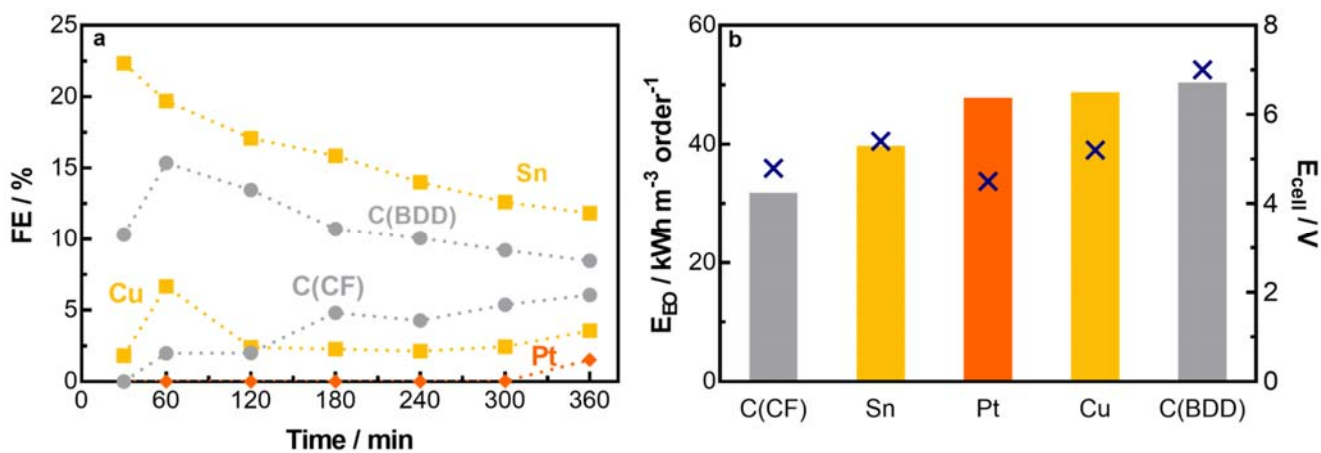
335 Other material factors can impact electrocatalyst effectiveness for use in drinking water.
336 Most notably, corrosion of some electrodes may impart regulatory concerns or long-term
337 operability challenges. Among the metals investigated, only Cu is included in primary drinking
338 water regulations, where levels above 0.8 mg L⁻¹ begin to pose health concerns. Such high levels
339 would be detrimental to the electrode itself and would therefore need to be studied in more detail.
340 Fe and Zn have similarly high secondary drinking water limits, set by aesthetics rather than health
341 limits, of 0.3 and 5 mg L⁻¹, respectively. Other metals (Ti, Co, Ni, Sn) are not regulated in drinking
342 water. While carbon is not directly regulated, numerous organic carbon compounds (e.g.,
343 polyaromatic hydrocarbons) are regulated as carcinogens, but their evolution from graphitic or
344 diamond forms of carbon are unlikely. Thus, considering drinking water contaminant limits
345 wouldn't change the above recommendation to focus on BDD- or Sn-based electrodes.

346

347 **3.4 Energy-based figures of merit considerations**

348 Beyond performance (i.e., nitrate removal rates and by-product formation), energy
349 efficiency will also contribute to electrode element selection. Electrochemical reduction
350 effectiveness is commonly evaluated in terms of Faradaic efficiency (FE, Eq. (3)) for N₂ evolution.
351 Figure 6a shows FE over time for selected electrocatalysts and demonstrates competitive
352 alternatives to conventional Pt electrodes in terms of superior kinetics and selectivity.
353 Electrocatalysts with low selectivity for N₂ (i.e., Pt, Cu, carbon felt) accordingly had low FE,
354 ranging between 0% and 7%. Meanwhile, promising BDD and Sn electrodes had FEs between 10
355 and 22%. Both BDD and Sn showed an analogous decrease in FE over electrolysis time. This
356 behavior can be related to the nitrate concentration decrease over time, whereas the electric current
357 is the same. Consequently, the kinetics of parasitic reactions, such as hydrogen evolution, may be
358 enhanced[72,74], resulting in a lower final FE.

359 Engineering figures of merit provide a different, practical method to assess process energy
 360 efficiency across multiple options. Because the WHO recommends $\sim 11 \text{ mg L}^{-1}$ as NO_3^- -N and our
 361 experiments had initial nitrate concentrations of 100 mg NO_3^- -N, the E_{EO} is shown for one order of
 362 magnitude decrease in nitrate ($\text{kWh m}^{-3} \text{ order}^{-1}$, Figure 6b). Under identical electrochemical cell
 363 reactor configurations, E_{EO} ranged between 30 and $50 \text{ kWh m}^{-3} \text{ order}^{-1}$. For the two most effective
 364 materials from Figure 4 (i.e., Sn and BDD), E_{EO} was 39 and $49 \text{ kWh m}^{-3} \text{ order}^{-1}$, respectively. E_{EO} at
 365 a given applied current is controlled by two main factors: (a) nitrate reduction rate k_1 and (b) the cell
 366 potential (E_{cell}). Although Sn and BDD had a comparable kinetic constant for nitrate removal, the
 367 cell potential average (E_{cell}) for each is different. The E_{cell} was 5.4 V for Sn and 7.0 V for BDD,
 368 which resulted in a higher E_{EO} for the BDD cathode. The interdependence between k_1 and E_{cell}
 369 explain why the E_{EO} for Pt ($47 \text{ kWh m}^{-3} \text{ order}^{-1}$) is between the ones for Sn and BDD. Other
 370 research shows that E_{EO} can be decreased by >10 -fold from the observed values through
 371 engineering design of electrode morphology, electrode spacing, and hydrodynamics[22,23,73]. For
 372 example, flow-through electrodes are superior to flow-by electrodes because the former exhibits
 373 lower mass transfer limitations for target pollutants/by-products towards/from the electrode surface.
 374 Fortunately, many of the elements, including BDD and Sn, can be engineered into almost any
 375 integrated electrode and reactor configuration.
 376



377

378 **Figure 6.** (a) Faradaic efficiency (FE) over time, (b) energy consumption per order (bars) and cell
379 potential average (\times) for the electroreduction of 100 mg L⁻¹ NO₃⁻-N in 50 mM Na₂SO₄ at 20 mA
380 cm⁻², using Cu, C-CF, C-BDD, Sn, and Pt as cathode materials. Note: CF and BDD stand for carbon
381 felt and boron-doped diamond, respectively. Elements availability: (●) high abundance, (■)
382 limited availability, (◆) rising threat, (▼) serious threat in next 100 years.

383

384 **4. Conclusions**

385 This work applies a framework for screening earth-abundant electrode materials under
386 identical operating conditions to obtain figures of merit suitable to identify more sustainable
387 electrocatalytic systems that can remove nitrate from drinking waters. Platinum (Pt), a well-studied
388 electrocatalyst in the literature, was selected as a benchmark electrode representing the PGEs.
389 Electrokinetic pseudo first-order nitrate degradation rates (k_1) were slightly better (~50% larger k_1)
390 for Cu-, C-, and Sn-based electrodes relative to Pt. The difference in selectivity towards the
391 preferential by-products (i.e., N-gases) showed tremendous promise for more earth-abundant
392 elements, being up to 7-fold more selective ($S_{N_{gas}}$ of 55% and 64% for BDD and Sn, respectively)
393 than the PGE-based electrode ($S_{N_{gas}} \sim 1\%$ for Pt). Degradation rates and selectivities impacted
394 Faradaic efficiency and E_{EO} . No adverse effects were shown on these figures of merit when
395 transitioning electrode material from PGE to more sustainable elements (e.g., Sn, BDD).

396 Each element used in the electrodes has a commodity market cost (\$ kg⁻¹). The structure of
397 catalytic materials, with crystallites of different sizes and orientations, are critical to maximize the
398 selectivity towards the preferred by-product species (N₂ gas). Electrode manufacturing to transform
399 the base element into the plethora of electrode architectures (e.g., high porosity electrodes) will add
400 to the cost of the final electrode. For example, while carbon is the cheapest commodity element, the
401 three carbon-based electrodes showed that different morphologies, oxidation states, and crystallites
402 can lead to very different reaction outcomes. Thus, while acknowledging it may be premature to

403 draw a specific selection of electrodes in terms of performance-cost analysis, this work provides an
404 initial roadmap on expected cost depending on the element source. A complete techno-economic
405 analysis will be conducted in a well-developed electrocatalytic system considering electrode life
406 and its manufacturing associated costs.

407 The above framework identified the application of earth-abundant materials, which global
408 availability is not endangered, to electrochemical nitrate reduction. This represents a game changer
409 for developing low-cost electrocatalytic-based treatment water systems, where Pt-based catalysts
410 have been shown to be cost prohibitive (e.g., [40,41]). Sn-based and carbonaceous electrodes (i.e.,
411 BDD) were recognized as viable earth-abundant electrocatalysts alternatives to endangered
412 elements. Innovations in electrode manufacturing are still needed to reduce capital costs and E_{EO} by
413 optimizing mass transport. This may occur by maximizing surface area of the more reactive and
414 stable surfaces of earth-abundant elements as electrodes. Future research using nanotechnology with
415 earth-abundant materials can exploit opportunities[75], enabling catalytic sites that specifically
416 tailor nitrate reduction towards innocuous nitrogen gas, further increasing the competitiveness of
417 POU systems.

418

419 **Acknowledgments**

420 This project has received funding from the European Union's Horizon 2020 research and
421 innovation program under the Marie Skłodowska-Curie grant agreement No 843870. This work was
422 partially funded by the National Science Foundation (NSF) through the Nanotechnology-Enabled
423 Water Treatment Nanosystems Engineering Research Center under project EEC-1449500. Laurel
424 Passantino provided technical editing.

425

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