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Aksana Atrashkevich, Ana Sofia Fajardo, Paul Westerhoff, W. Shane Walker, Carlos M Sánchez-Sánchez, et al.. Overcoming barriers for nitrate electrochemical reduction: By-passing water hardness. *Water Research*, 2022, 225, pp.119118. 10.1016/j.watres.2022.119118 . hal-03790519

HAL Id: hal-03790519

<https://hal.sorbonne-universite.fr/hal-03790519>

Submitted on 28 Sep 2022

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**Overcoming barriers for nitrate electrochemical reduction: by-passing
water hardness**

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Article submitted to be published in Water Research

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20 **Abstract**

21 Water matrix composition impacts water treatment performance. However, matrix composition
22 impacts have rarely been studied for electrochemical water treatment processes, and the correlation between
23 the composition and the treatment efficiency is lacking. This work evaluated the electrochemical reduction
24 of nitrate (ERN) using different complex water matrices: groundwater, brackish water, and reverse osmosis
25 (RO) concentrate/brine. The ERN was conducted using a tin (Sn) cathode because of the high selectivity
26 towards nitrogen evolution reported for Sn electrocatalysts. The co-existence of calcium (Ca^{2+}), magnesium
27 (Mg^{2+}), and carbonate (CO_3^{2-}) ions in water caused a 4-fold decrease in the nitrate conversion into innocuous
28 nitrogen gas due to inorganic scaling formation on the cathode surface. XRF and XRD analysis of fouled
29 catalyst surfaces detected brucite ($\text{Mg}(\text{OH})_2$), calcite (CaCO_3), and dolomite ($\text{CaMg}(\text{CO}_3)_2$) mineral scales
30 formed on the cathode surface. Surface scaling created a physical barrier on the electrode that decreased
31 the ERN efficiency. Identifying these main sources of ERN inhibition was a key to devising potential
32 fouling mitigation strategies. For this reason, the chemical softening pre-treatment of a real brackish water
33 was conducted and this significantly increased nitrate conversion and faradaic efficiency during subsequent
34 ERN treatment, leading to a lower electric energy consumption per order. Understanding the ionic foulant
35 composition responsible for influencing electrochemically-driven technologies are the first steps that must
36 be taken to move towards niche applications such as decentralized ERN. Thus, we propose either direct
37 ERN implementation in regions facing high nitrate levels in soft waters, or a hybrid softening/nitrate
38 removal system for those regions where high nitrate and high-water hardness appear simultaneously.

39

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42 *Keywords: Electrochemical water treatment; Electrocatalysis; Nitrate reduction; Water hardness;*
43 *Scaling; brackish waters*

44

45 **1. Introduction**

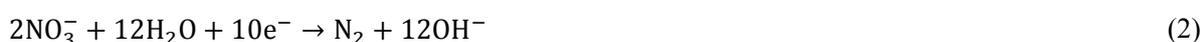
46 Electrochemically-driven technologies for water treatment are emerging as competitive solutions
47 for centralized and decentralized treatment given their high adaptability, compact reactor designs, and the
48 possibilities of transforming pollutants into products of added value (Chaplin, 2019; Martínez-Huitle et al.,
49 2015). The high relevance that electrified water purification will have in the near future is undeniable.
50 Electrochemical processes can achieve effective removal of organics through electrochemical advanced
51 oxidation processes (dos Santos et al., 2021; Moreira et al., 2017; Villanueva-Rodríguez et al., 2012),
52 inactivation of pathogens through electrodisinfection (Garcia-Segura et al., 2021; Martínez-Huitle and
53 Brillas, 2021), and even abatement of oxyanions such as nitrate by electrochemical advanced reduction
54 processes (Sergi Garcia-Segura et al., 2018; van Langevelde et al., 2021).

55 Nitrate is one of the top ten water pollutants that commonly violate water quality regulations
56 worldwide (Allaire et al., 2018; Rupert, 2008). The dramatic increase in nitrate concentration in water
57 sources mainly located in rural areas is related to the extensive use of fertilizers in agriculture due to
58 growing anthropogenic activities (Li et al., 2021). The World Health Organization (WHO) has set a
59 maximum concentration level (MCL) of 10 mg NO₃⁻ defined in terms of mass of N per liter (NO₃—N L⁻¹)
60 given the hazardous effects of nitrate for drinking water (WHO, 2016). Exposure to higher concentrations
61 of nitrate above the suggested MCL has been associated to adverse respiratory effects (i.e.,
62 methemoglobinemia), thyroid problems, and cancer (Temkin et al., 2019; Torres et al., 2020). Water
63 sources that violate the quality standards because of high nitrate levels result in the shutdown of water wells,
64 limiting access to clean water, causing additional stressors for vulnerable populations.

65 Conventional treatment of nitrate polluted water requires in most cases the implementation of
66 physical separation technologies (*i.e.*, ionic exchange, reverse osmosis) that generate undesired nitrate-rich
67 brines (Amma and Ashraf, 2020; Liu et al., 2021). Other alternatives consider delicate biologic anammox
68 treatment that requires specialized management and has a large physical footprint, both factors limiting
69 widespread utilization in decentralized settings (Abdelfattah et al., 2020; Crittenden et al., 2012).
70 Electrocatalytic reduction of nitrate (ERN) appears as a feasible solution given promising results reported

71 in literature on the study of synthetic solutions of nitrate (van Langevelde et al., 2021; Werth et al., 2021).
72 Most research in these works have focused on the discovery of electrocatalytic materials that overcome
73 sluggish nitrate reduction kinetics as well as control product selectivity in matrix-free solutions (Lim et al.,
74 2021; Sanjuán et al., 2020; Y. Zhang et al., 2021). Very few examples addressing the impact on ERN
75 performance of a complex matrix such as the one present in nuclear (Katsounaros et al., 2009) and textile
76 (Su et al., 2017) wastewater effluents can be found in the literature.

77 The ERN mechanism for producing either ammonia (NH₃) or nitrogen gas (N₂) presents a common
78 initial reduction step, the reduction of nitrate to produce nitrite (NO₂⁻), which thereafter separates in two
79 independent reaction pathways leading to each final product (i.e., NH₃ and/or N₂). Nitrate reduction towards
80 ammonia following Reaction (1) can be a resourceful approach for sustainable nitrogen recovery for
81 agriculture applications (Gabriel Antonio Cerrón-Calle et al., 2022; Katsounaros, 2021; van Langevelde et
82 al., 2021). The nitrate reduction towards innocuous nitrogen gas by Reaction (2) is of utmost importance
83 for drinking water purposes (Flores et al., 2022).



84 Because of concerns regarding availability, cost, and supply chains associated with platinum group
85 metals (PGMs) or rare earth elements, significant advances are being conducted to develop competitive
86 electrocatalysts based on earth-abundant materials such as tin (Sn), copper (Cu), and cobalt (Co) (G.A.
87 Cerrón-Calle et al., 2022b; Fajardo et al., 2021; Katsounaros, 2021; X. Zhang et al., 2021). High
88 competitiveness of Sn electrodes that enable fast nitrate reduction kinetics with a very high selectivity
89 towards N₂ has been demonstrated (Ambrosioni et al., 2014; Fajardo et al., 2021; Katsounaros et al., 2012;
90 Tada and Shimazu, 2005). Understanding interfacial effects that may condition the long-term sustained
91 performance of this electrodes it is relevant to advance technology readiness level of competitive ERN
92 systems. However, the promising results of ERN electrocatalysts have been at fundamental level while
93 exploring performance of the systems in ultrapure solutions and not in real water matrices polluted with
94 nitrate such as groundwater, brackish waters, brines, wastewaters, and others (Garcia-Segura et al., 2020a).

95 Co-existence of different ions may be detrimental for sustained long-performance of these promising
96 electrocatalytic materials. Co-existing species may compete with the target pollutant causing a decrease in
97 treatment efficiency or decrease the operational life of the electrode as result of material aging, fouling,
98 and/or scaling. Besides water composition, the pH is one of the most critical water quality parameters when
99 considering water use for drinking purpose. The speciation of many compounds depends on the solution
100 pH. Water distribution systems aim to maintain pH near to circumneutral conditions to avoid pipe corrosion
101 but also to ensure potable characteristics when reaching the end user. It is generally reported that ERN
102 treatment results in an increase of water pH given the reduction of nitrate according to Reactions (1) and
103 (2). Most works in literature conduct electrolysis in pure water matrices without controlling pH, which
104 reaches values close to 9–11 (Fajardo et al., 2021; Nobial et al., 2007). Water treatment should ideally
105 provide clean water with a pH ranging from 6-9, which may be ensured by the presence of pre-existing
106 buffers in solution (i.e., carbonate system) or other pH controlling techniques. Therefore, understanding the
107 major influential factors on the ERN are essential to develop preemptive strategies that enable successful
108 technology transfer into challenging real conditions.

109 Groundwater is especially impacted with high nitrate concentrations in regions of high agricultural
110 activity. Nevertheless, groundwater of non-agricultural regions may be polluted with nitrate over MCL, but
111 considered as a nitrate-poor water source (e.g., nitrate below 30 mg NO₃-N L⁻¹). A possible solution already
112 suggested in the literature is to concentrate the nitrate and all other ions in solution prior to ERN using
113 separation technologies such as reverse osmosis, ionic exchange, or capacitive deionization (van
114 Langevelde et al., 2021; Werth et al., 2021; Yang et al., 2013). This pre-concentration approach will
115 produce electrolyte compositions close to the ones displayed by either brackish or brine streams. For this
116 reason, real water samples from brackish and brine streams are studied herein, besides synthetic water. The
117 amount of nitrate added as contaminant in all three types of water source studied has been kept constant
118 (30 mg NO₃-N L⁻¹) in order to reach a fair comparison. Treatment of groundwater with either decentralized
119 or centralized electrochemically-driven technologies can be a suitable solution for purification of waters
120 with nitrate content over MCL. However, groundwater, brackish, and brine have complex water matrices

121 that were barely explored in literature while studying the electrochemical treatment. The effect of co-
122 existing electrolytes during ERN should be addressed (Sergi Garcia-Segura et al., 2018; Katsounaros and
123 Kyriacou, 2008). Understanding the impact of ionic species of environmental relevance is an urgent need
124 to assess the competitiveness of emerging technologies under real conditions (Flores et al., 2022; Werth et
125 al., 2021).

126 This work aims to elucidate common anions/cations in real water matrices which might become a
127 barrier to the efficient ERN. Especial attention is driven to understand scaling induced by water hardness
128 ions, as the generation of physical barrier demonstrated to deleteriously affect performance of ERN. The
129 effect of complex water matrices is assessed exploring the treatment of realistic multiple ion solute samples
130 of ground, brackish, and brine waters. These water sources with elevated nitrate level have been identified
131 as possible niche applications for decentralized electrified technologies (Hansen et al., 2017; Maxwell et
132 al., 2020). The research showed which water matrices may benefit from implementing pre-treatment
133 systems prior to electrochemical nitrate reduction. Therefore, feasible alternatives to overcome challenges
134 associated to specific species are proposed and evaluated. In particular, chemical softening of brackish
135 water prior to the ERN treatment was conducted. Implementation of management strategies should be
136 considered when exploring real world treatment scenarios.

137

138 **2. Materials and methods**

139 *2.1 Chemicals and solutions*

140 Sodium nitrate (NaNO_3), calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), magnesium sulfate
141 heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), sodium bicarbonate (NaHCO_3), sodium chloride (NaCl), sodium phosphate
142 monobasic monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$), sodium fluoride (NaF), and sodium metasilicate nonahydrate
143 ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) compounds, with purity > 99%, were purchased from Sigma-Aldrich to evaluate single
144 component effects as well as to verify their interaction together by mimicking groundwater matrices.
145 Sulfuric acid (H_2SO_4 96%, Sigma Aldrich) and sodium hydroxide (NaOH 99%, Sigma Aldrich) solutions
146 were used to adjust the pH when required. Table 1 summarizes the analytical characterization of the

147 different water matrices treated by the ERN. Synthetic aqueous solutions containing 30 mg NO₃⁻-N L⁻¹ (133
148 mg NO₃⁻ L⁻¹) were prepared with distilled water (pH = 5.8 ± 0.1; conductivity 10 ± 5 μS cm⁻¹) and they
149 correspond to entries from A to I in Table 1. This nitrate concentration was selected since it is within the
150 common ranges found in groundwaters (WHO, 2016). Sodium sulphate (Na₂SO₄, > 99% purity, Sigma-
151 Aldrich) was used as a supporting electrolyte; the “Blank” (or control) matrix listed in Entry A is a brackish
152 ternary solution containing 25 meq L⁻¹ of sodium sulfate and 2.14 meq L⁻¹ of sodium nitrate. Entry B is a
153 complex synthetic brackish water prepared according to the NSF-challenge water recipe from the National
154 Sanitation Foundation (NSF International) which is a model for natural groundwater and has already been
155 applied in many other studies (Gröhlich et al., 2017; Usman et al., 2018). The groundwater recipe emulates
156 the real representative concentrations of electrolytes found in environmental samples. Thus, the effect of
157 coexisting ions was explored using the meaningful concentration of each species as reported for the
158 composition of Entry B but considering only single solute compositions. In Table 1, Entries C through I are
159 brackish quaternary solutions that include the constituency of Entry A with the addition of a single cation,
160 anion, or silica; the concentration of each of these constituents was selected in basis of the general
161 compositions reported for groundwaters (defined by Entry B). Entries J and L correspond to real brackish
162 groundwater and reverse osmosis (RO) concentrate/brine water collected in Texas (USA), respectively,
163 where a constant amount of nitrate pollutant (30 mg NO₃⁻-N L⁻¹) is added.

164 **Table 1.** Characterization of the brackish water matrices tested in this work (all prepared with 30 mg NO₃⁻
 165 -N L⁻¹).

Entry	Water matrices	Initial pH	Conductivity (mS cm ⁻¹)	Cations (mg L ⁻¹)				Anions (mg L ⁻¹)					Silica (mg SiO ₂ L ⁻¹)	
				Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NO ₃ ⁻	HCO ₃ ⁻	Cl ⁻	F ⁻	PO ₄ ³⁻		SO ₄ ²⁻
A	Blank	5.95	3.1	-	-	625	-	133	-	-	-	-	1201	-
B	Synthetic Brackish Groundwater	6.22	3.85	41	12	749	-	133	183	72	1	0.12	1347	20
C	Ca ²⁺	5.95	3.1	41	-	625	-	133	-	-	-	-	1299	-
D	Mg ²⁺	5.95	3.1	-	12	625	-	133	-	-	-	-	1249	-
E	Si ₂ O	5.95	3.1	-	-	632	-	133	-	-	-	-	1201	20
F	HCO ₃ ⁻	5.95	3.1	-	-	693	-	133	183	-	-	-	1201	-
G	Cl ⁻	5.95	3.1	-	-	671	-	133	-	72	-	-	1201	-
H	F ⁻	5.95	3.1	-	-	626	-	133	-	-	1	-	1201	-
I	PO ₄ ³⁻	5.95	3.1	-	-	625	-	133	-	-	-	0.12	1201	-
J	Real Brackish Groundwater*	7.90	4.5	130	30	725	13	133	99	135 2	1	n.m.	269	n.m.
L	Real RO Brine*	8.10	20	567	157	3268	74	133	417	552 2	4	n.m.	1218	n.m.

* Identification and quantification of water composition was conducted by ionic chromatography. "n.m." – not measured.

166

167 2.2 Electrochemical experiments

168 The electrochemical reduction of nitrate was conducted under galvanostatic operating mode
 169 applying a constant current intensity of 120 mA (i.e., current density $j = 40 \text{ mA cm}^{-2}$) using a power supply
 170 TENMA 72-2710. The undivided electrochemical glass batch cell was equipped with a tin cathode plate
 171 (Sn, 99.99% purity from McMaster-Carr/USA). Electrodes of Sn have shown excellent electrocatalytic
 172 activity for ERN with outstanding selectivity towards N₂ (Dortsiou et al., 2013; Fajardo et al., 2021). The
 173 electrochemical cell was completed with a DSA® Ti/IrO₂ (DeNora/USA) mesh anode. Both electrodes had
 174 a geometric area of 3 cm² delimited with Teflon tape and were located with a 1.0 cm electrode gap distance
 175 within the electrochemical cell. Solutions of 100 mL were treated under magnetic stirring at 550 rev min⁻¹
 176 to ensure transport of electroactive species towards/from the electrode. Samples were withdrawn over time
 177 and analyzed for aqueous nitrogen species, conductivity, and pH. Experiments were performed in triplicate,
 178 and deviations between them were lower than 5% for all trials. Statistical paired *t*-test analysis was
 179 conducted for experimental results using Minitab® statistical software considering an $\alpha = 0.05$.
 180 Experiments conducted while maintaining constant the pH ($5.5 < \text{pH} < 6.4$), small quantities of 0.1 M

181 H₂SO₄ (< 3 μL) were gradually added every 7-8 min during the 360 min of reaction. For the case of
 182 carbonate buffer, pure CO₂ gas was bubbled in the solution during the experiment. Statistically significant
 183 difference between experiments was evaluated based on *p*-value.

184

185 2.3 Analytical techniques

186 The pH and conductivity were measured with a Thermo Scientific Orion Star A221 pH-meter and
 187 an A322 conductivity meter, respectively. The concentrations of NO₃⁻-N, NO₂⁻-N and NH₃-N species were
 188 quantified using the HACH kits TNT 835, TNT 839 and TNT 830, respectively, by an HACH DR 6000
 189 UV-vis spectrophotometer. From experimental quantification of nitrate concentration over electrolysis time
 190 the nitrate conversion was calculated according to Equation (3). The selectivity (*S_x*) of nitrogen gas was
 191 estimated from Equation (4).

$$192 \text{ Nitrate conversion (\%)} = \frac{C_{\text{nitrate},i} - C_{\text{nitrate},t}}{C_{\text{nitrate},i}} \times 100\% \quad (3)$$

$$193 S_{N_{\text{gas}}} (\%) = \frac{C_{N_2,t}}{C_{\text{nitrate},i} - C_{\text{nitrate},t}} \times 100\% \quad (4)$$

192 where *C_{nitrate,i}* is the nitrate concentration at the beginning of the treatment (*t* = 0 min) in mg NO₃⁻-N L⁻¹,
 193 and *C_{nitrate,t}* is the nitrate concentration at time *t* in mg NO₃⁻-N L⁻¹, and *C_{N₂,t}* is the concentration of a
 194 nitrogen gas in mg N₂ – N L⁻¹ at time *t*.

195 The efficient use of electrons delivered to promote nitrate reduction was evaluated in terms of
 196 Faradaic efficiency (FE) as defined by Equation (5). The FE is an electrocatalytic figure of merit that defines
 197 the number of electrons consumed for nitrogen gas evolution reaction relatively to the total charge delivered
 198 according to Faraday's law. The FE shows the effectiveness of the actual charge transfer during the reaction
 199 of interest.

$$200 FE(\%) = \frac{Q_{\text{reaction}}}{Q_{\text{total}}} \times 100\% = \frac{n F N_i}{3600 I t} \times 100\% \quad (5)$$

200 where *Q_{reaction}* is the empirical charge consumed in the reaction of interest (C), *Q_{total}* is the total charge
 201 consumed during electrochemical process (C), *n* is the amount of electrons required per mole of product

202 (10 mol e⁻/mol N₂), F is the Faraday constant (96 487 C eq⁻¹), N_i is the amount of product generated during
 203 the electrolysis (mol N₂), I is the applied current intensity (A), t is the time (h), 3600 is a unit conversion
 204 factor (s h⁻¹). To evaluate the energy requirements of ERN, the engineering figure of merit electric energy
 205 per order (EE/O) was computed according to Equation (6) (Bolton et al., 2001; Marcos-Hernández et al.,
 206 2022).

$$EE/O(kWh\ m^{-3}\ order^{-1}) = \frac{E_{cell}\ I\ t}{V_s \log\left(\frac{C_{nitrate,i}}{C_{nitrate,t}}\right)} \quad (6)$$

207 where E_{cell} is the average of the cell potential (V) and V_s is the volume of the treated solution (L). Assuming
 208 that the electrochemical reduction of nitrate in the experiments follows a *pseudo*-first order kinetics
 209 (Equation (7)) the EE/O can be simplified as Equation (8).

$$\log\left(\frac{C_{nitrate,i}}{C_{nitrate,t}}\right) = 0.4343k_1t \quad (7)$$

$$EE/O(kWh\ m^{-3}\ order^{-1}) = \frac{6.39\ 10^{-4}E_{cell}\ I}{V_s\ k_1} \quad (8)$$

211 where, k_1 is the *pseudo*-first order kinetics constant (s⁻¹).

212 The concentrations of inorganic ions present in the real brackish and RO brine waters were
 213 quantified with a Thermo Scientific simultaneous cation and anion ion chromatography (IC) system. Cation
 214 concentrations were analyzed with a DIONEX Aquion with an IonPac CS16 (5x250 mm) column, a 10 µL
 215 sample injection volume, and 47 mmol L⁻¹ methanesulfonic acid (MSA) as eluent with an eluent flow rate
 216 of 1 mL min⁻¹. Anions were analyzed with a DIONEX Integrion HPIC with an IonPac AS18-Fast-4µm
 217 column, a 10 µL sample injection volume, 30 mmol L⁻¹ of potassium hydroxide as eluent, and an eluent
 218 flow rate of 1 mL min⁻¹.

219 Chemical precipitation is one of the more common methods used to soften water (Chao and
 220 Westerhoff, 2002). The lime-soda softening method was used to decrease water hardness of brackish water
 221 prior ERN treatment. The chemicals used were lime (calcium hydroxide, Ca(OH)₂) and soda ash (sodium
 222 carbonate, Na₂CO₃). Lime was applied to remove chemicals that cause carbonate hardness, while soda ash
 223 was used to remove chemicals that cause non-carbonate hardness. When lime and soda ash were added,

224 hardness-causing species formed insoluble precipitates such as calcium carbonate (CaCO_3) and magnesium
225 hydroxide ($\text{Mg}(\text{OH})_2$). Solid-liquid separation was performed to recover the liquid sample first by gravity
226 separation and after through filtration using 0.45 μm filter.

227 Analysis of the surface of the cathode included its elemental composition, determined by x-ray
228 fluorescence (XRF) using a Thermo Scientific PTS22163. Electrodes were gently rinsed with ultrapure
229 water to ensure that measurements corresponded to scaled solid deposited on the surface of the electrode
230 during water treatment and not result of electrolyte evaporation. The crystalline structure of collected solids
231 deposited on the electrode surface was analyzed by the X-ray diffraction (XRD) using a PANalytical AERIS
232 X-ray diffractometer within 2θ range from 10° to 100° with a step of 0.01° .

233

234 **3. Results and discussion**

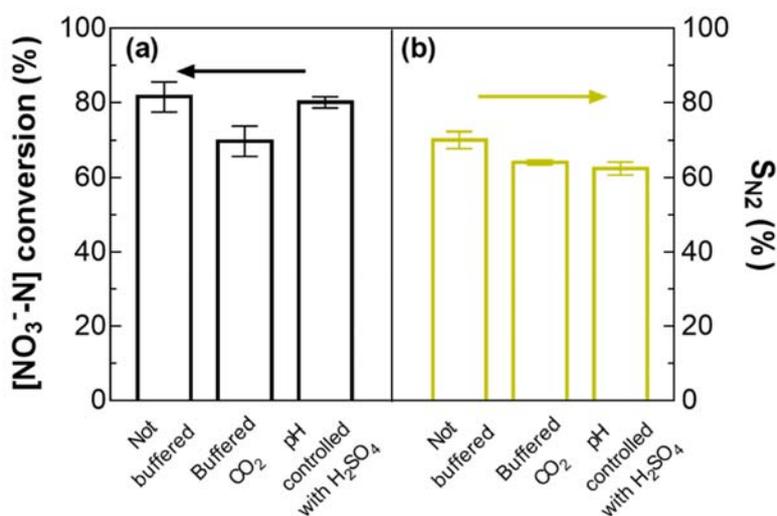
235 *3.1 Effect of pH control on the electrochemical reduction of nitrate*

236 The effect of nearly constant bulk water pH conditions on treatment performance was explored to
237 evaluate the impact in nitrate conversion and product selectivity. Figure 1 shows that the ERN during the
238 treatment of 30 mg NO₃⁻-N L⁻¹ using Sn electrode attained predominantly electrocatalytic selectivity
239 towards N₂. The high product selectivity towards innocuous N₂ (ca. 70%) is one of the most promising
240 characteristics of Sn as an electrode material for the ERN and is explained by the intrinsic electrocatalytic
241 properties of the electrode. During the blank experiments conducted using an unbuffered solution, the
242 nitrate conversion achieved 82% and nitrate concentration diminished to 5.5 mg NO₃⁻-N L⁻¹, which is below
243 the MCL level of 10 mg NO₃⁻-N L⁻¹. The pH of unbuffered solution increased from 5.95 up to 10.15, which
244 is a commonly observed feature in many other studies, regardless of electrode materials (Fuladpanjeh
245 Hojaghan et al., 2019; Szyrkowicz et al., 2006). The pH increase is explained by the release of hydroxyl
246 anions during reduction processes described in Reaction (1) and (2). During electrochemical processes, the
247 generation of OH⁻ ions is promoted on the surface of the cathodes, causing the solution pH to increase over
248 time. The results of unbuffered pH were used to benchmark the performance of pH-controlled systems
249 through: (i) CO₂ bubbling, and (ii) active pH control through acid addition (i.e., H₂SO₄).

250 The pH control by carbonate buffer through CO₂ bubbling is a common practice at water treatment
251 plants to lower water pH, especially after softening processes. Note that CO₂ is an acid gas that when
252 dissolved in water forms carbonic acid (Cerrón-Calle et al., 2022a). Here CO₂ bubbling was employed to
253 control solution pH during ERN. The CO₃²⁻ concentration was controlled through the gas-liquid equilibria
254 in an open system. Statistical paired *t*-test analysis showed similar nitrate removal values for the blank and
255 CO₂ bubbling experiments (ca. 70%) without statistically significant difference based on obtained *p*-value
256 of 0.208. Moreover, the selectivity towards N₂ (ca. 64%) remained the same with high reproducibility (*p*-
257 value = 0.166). These results suggest that a possible small content of dissolved oxygen within the
258 electrochemical cell was not significant to inhibit nor compete with the nitrate reduction Reactions (1) and

259 (2). Therefore, ERN treatment may be conducted in principle under unbuffered conditions without
260 detriment on performance in the pH range between 6 and 11.

261 Acidification by adding liquid reactants instead of a gas is an alternative approach to control pH
262 changes during treatment. Sulfuric acid is the most common strong acid used at water treatment plants to
263 lower pH, usually ahead of coagulation or membrane processes. Additionally, sulfuric acid was selected
264 given the inert character of sulfate anions as electrolytes in electrochemical systems. The initial pH of 5.95
265 was maintained during the ERN treatment of 30 mg NO₃⁻-N L⁻¹ nitrate solution. The experiments with
266 continuous acidification led to nitrate conversion of 80% which is not significantly different neither from
267 blank (*p*-value = 0.500) nor from buffered experiment with CO₂ (*p*-value of 0.152). The results in Fig. 1
268 allowed to infer negligible impact of pH control on the overall reduction kinetics as well as the final product
269 selectivity. Considering these outcomes, ERN treatment can be conducted without strict pH control but may
270 require pH adjustment prior its use for drinking water applications. Following sections explore the treatment
271 of natural water solutions without any pH adjustment given that this operational condition is the easiest
272 scalable approach without additional costs associated to continuous pH control.



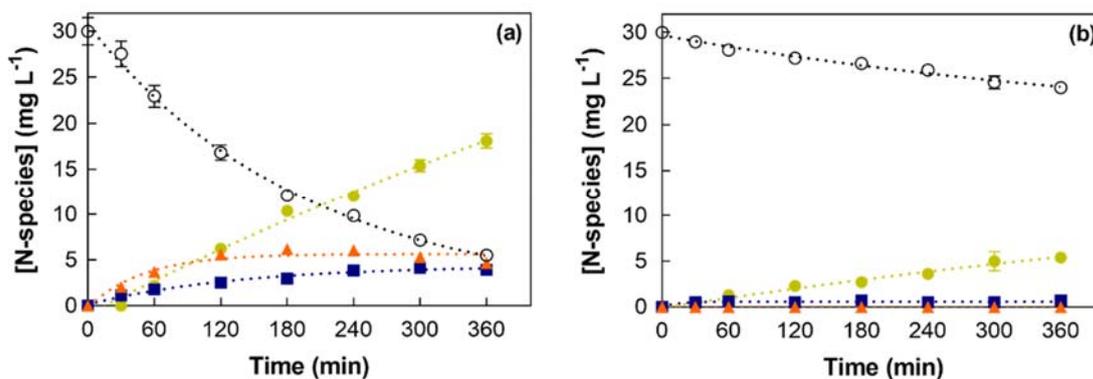
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274 **Figure 1.** *Electrocatalytic reduction of 30 mg NO₃⁻-N L⁻¹ in 12.5 mM Na₂SO₄ at 40 mA cm⁻² after*
275 *360 min of treatment in unbuffered solution, carbonate buffer through CO₂ bubbling, pH-controlled*
276 *solution by H₂SO₄ addition: a) nitrate conversion, and b) selectivity towards nitrogen gas.*

277

278 3.2 Effect of different inorganic ions on the electrochemical reduction of nitrate

279 Figure 2 illustrates a significant loss of ERN performance when comparing idealistic treatment
280 conditions of nitrate in a simple ternary brackish water solution (entry A in Table 1) with a more complex
281 synthetic brackish groundwater that contains a mixture of coexisting ionic species (entry B in Table 1).
282 Figure 2a shows the common behavior reported for nitrate electrochemical reduction in which the sluggish
283 reduction kinetics is controlled by the first charge transfer reaction as limiting step. The ERN treatment of
284 30 mg NO₃⁻-N L⁻¹ in simple ternary water solution (Table 1 – entry A) exhibited a gradual decay during
285 the first 360 min treatment time until reaching 5.5 mg NO₃⁻-N L⁻¹ (below MCL), which corresponded to a
286 nitrate conversion of 82%. This conversion fits well with a *pseudo*-first order constant (k_1) with the value
287 $k_1 = 7.8 \times 10^{-5} \text{ s}^{-1}$ ($R^2 = 99.8\%$). In contrast, the treatment of 30 mg NO₃⁻-N L⁻¹ in the complex synthetic
288 brackish groundwater (Figure 2b and Table 1 – entry B) decreases effective conversion 4-fold from 82%
289 removal down to 19%, and decreases the rate 8-fold as observed from the *pseudo*-first order rate constant
290 of $0.95 \times 10^{-5} \text{ s}^{-1}$ ($R^2 = 97.9\%$). The coexistence of other inorganic ions in the system clearly impacted the
291 ERN performance. To elucidate which ions drive such significant decrease in the treatment performance,
292 the individual effect of each ion was tested on the ERN using the same concentrations present in the
293 groundwater sample.



294
 295 **Figure 2.** Evolution of nitrogenated species, (○) NO₃⁻-N, (▲) NO₂⁻-N, (■) NH₃-N, (●) N₂-N, over
 296 time for the electrochemical reduction of groundwater at 40 mA cm⁻² with (a) blank solution (entry A in
 297 Table 1): 30 mg NO₃⁻-N L⁻¹ in 12.5 mM Na₂SO₄ (b) synthetic brackish solution (entry B in Table 1).

298 Figure 3 summarizes the effect on nitrate conversion of single ionic species in solution assuming
 299 that Na⁺ and SO₄²⁻ are inert electrolytes on nitrate conversions in the electrochemical systems (ions also
 300 present in the blank as supporting electrolyte). Anionic species commonly found in natural waters (PO₄³⁻,
 301 HCO₃⁻, F⁻ and Cl⁻) had slight effects on the ERN performance where the nitrate conversion attained was
 302 statistically the same. The treatment attained desired residual concentrations of nitrate below recommended
 303 MCL after ERN treatment in all instances. Nitrate removal in presence of different anionic species has
 304 negligible effect because these species are not susceptible of being reduced under these operation
 305 conditions, which would explain the low impact on ERN. Dissolved silica (*e.g.*, SiOH₄; pK_a=10.4) is found
 306 in groundwaters between 5 to 50 mg SiO₂ L⁻¹, but its evaluation demonstrated negligible impact on ERN
 307 performance. The coexistence of these ionic species (PO₄³⁻, HCO₃⁻, F⁻ and Cl⁻) does not seem to explain the
 308 drastic loss in performance observed on ERN in Figure 2b.

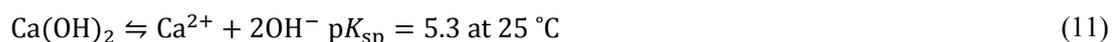
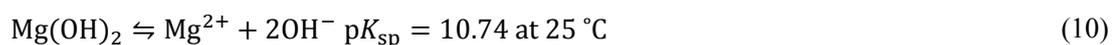
309 In contrast, divalent cations exert a stark impact on nitrate abatement. The presence of 0.5 mmol L⁻¹
 310 Mg²⁺ led to the lowest nitrate conversion with 26% with lower selectivity towards nitrogen gas. Meanwhile
 311 with dosed Ca²⁺, the nitrate reduction achieved 74% conversion, which is close to the 82% observed for the
 312 water solution containing solely nitrate and electrolyte. Analysis of equilibrium speciation of the complex

313 synthetic brackish groundwater matrix (Table 1 Entry B) with Visual Minteq v3.1 revealed that 99.3% of
314 nitrate remains not complexed, so complexation does not explain the observed decrease in denitrification.

315 Electrochemically-driven nitrate reduction takes place at the cathode surface mediated by direct
316 charge transfer processes (Flores et al., 2022; S. Garcia-Segura et al., 2018). Electrocatalytic reactions are
317 heterogeneous in nature and require an intimate interaction between the electroactive target species (*i.e.*,
318 nitrate) and catalytic sites on the electrode surface. Electrode scaling induced by the precipitation of
319 insoluble species on the vicinity of the electrode surface may result in the inhibition of mass transport
320 from/towards electrodes. It is important to remark that cathodic surfaces become, locally, alkaline due to
321 proton consumption during ERN as stated in reactions (1) and (2), as well as during the competitive
322 hydrogen evolution Reaction (9).

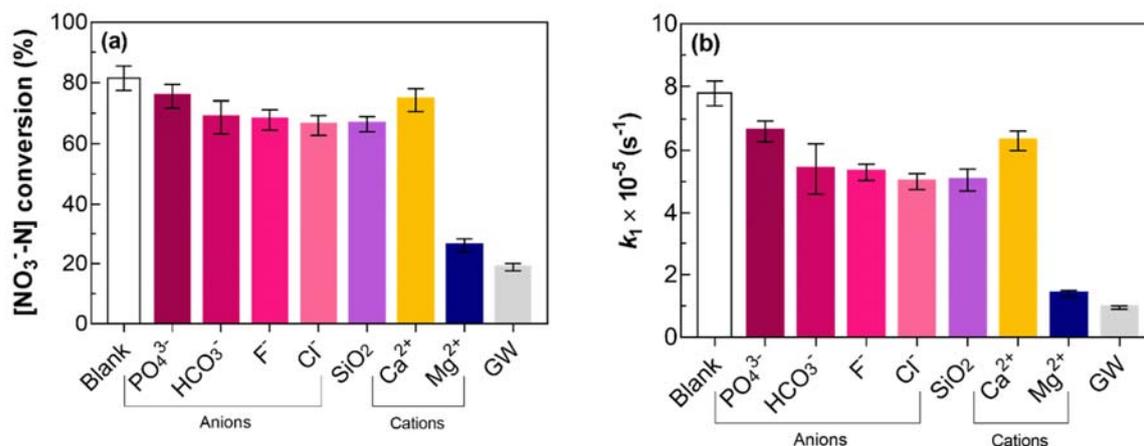


323 Interface studies report that the localized pH on the cathode surface reaches values ranging between
324 10-11, even when bulk water pH is measured as < 7 (Monteiro and Koper, 2021; Tlili et al., 2003). Figure 4a
325 illustrates the solubility diagram of Mg^{2+} and Ca^{2+} ions regarding their hydroxide insoluble salts in function
326 of the pH as defined by equilibrium Reactions (10) and (11) with thermodynamic solubility constants (K_{sp})
327 of $10^{-10.74}$ and $10^{-5.30}$ at 25 °C, respectively (Snoeyink and Jenkins, 1980). Note that precipitation of $\text{Ca}(\text{OH})_2$
328 is thermodynamically not feasible at given concentrations and localized pH condition of 10-11 at cathodic
329 surfaces given its higher solubility. Meanwhile, solubility of Mg^{2+} drastically decreases under alkaline pH
330 conditions with values as low as $10^{-2.74}$ M at pH 10 or $10^{-4.74}$ M at pH 11. Nucleation and growth of insoluble
331 $\text{Mg}(\text{OH})_2$ on the electrode surface would explain the drastic decrease on performance since the scaling acts
332 as a physical barrier inhibiting the charge transfer process at the interface.



333 It is important to remark that solutions only containing Ca^{2+} ions would hardly precipitate at given
334 conditions, which therefore does not inhibit ERN treatment (see Figure 3a). These results would pinpoint a

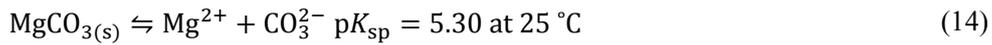
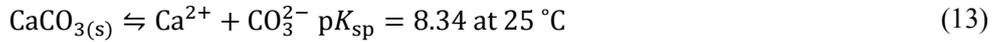
335 driving effect of Mg^{2+} as major inhibitor for sustained ERN treatment. However, Ca^{2+} ions below pH 10.5
 336 tend to precipitate not because the formation of insoluble $Ca(OH)_2$, but because of another much more
 337 insoluble species (*i.e.*, $CaCO_3$). Thus, the impact of Ca^{2+} on the ERN depends on alkalinity as the CO_3^{2-}
 338 availability in solution defines Ca^{2+} precipitation (Figure 4b).



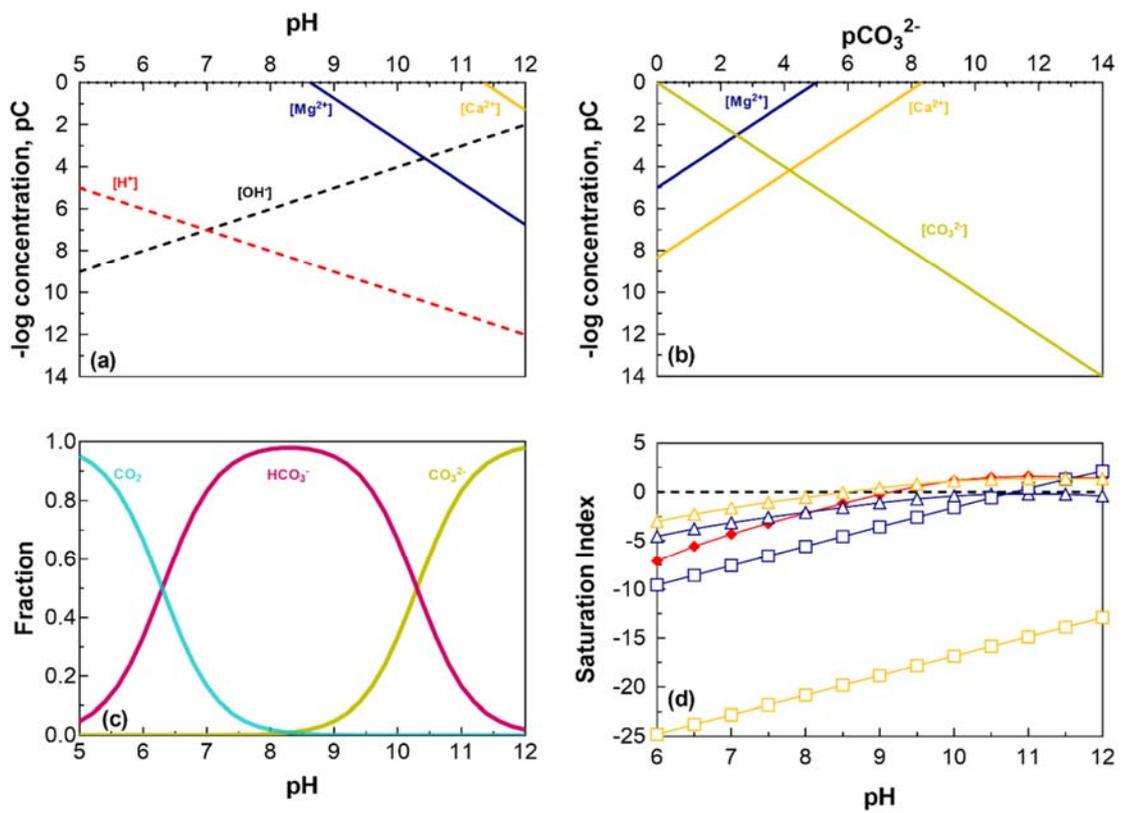
339 **Figure 3.** (a) Nitrate conversion and (b) kinetic constants after 360 min of electrocatalytic
 340 treatment with Sn cathode at 40 mA cm^{-2} in different water matrices: ultrapure water, single competitive
 341 ionic species, or synthetic complex brackish groundwater matrix (GW). Composition of the matrices is
 342 summarized in Table 1.

343 Note that carbonate species at the initial bulk solution pH is primarily bicarbonate ion (HCO_3^-), but
 344 the speciation close to the alkaline region on the cathode surface is likely carbonate ion (CO_3^{2-}) as indicated
 345 by the speciation diagram of Fig. 4c according to the acid-base equilibrium of Reaction (12) with
 346 characteristic pK_{a2} value of 10.3 (Lertratwattana et al., 2019; Snoeyink and Jenkins, 1980). The relative
 347 concentration of CO_3^{2-} and Ca^{2+} define the oversaturation conditions that may induce the precipitation of
 348 insoluble $CaCO_3$ as deduced from the solubility diagram of Figure 4b. Carbonate insoluble species are
 349 formed following Reactions (13) and (14) with K_{sp} of $10^{-8.34}$ and $10^{-5.30}$ at 25 °C, respectively (Snoeyink and
 350 Jenkins, 1980). The high concentration of Ca^{2+} ions as the main hardness species in real brackish and brine

351 water would explain the identification of calcite as predominant scalant formed on the alkaline cathodic
 352 surface in entries J and L, respectively.



353



354

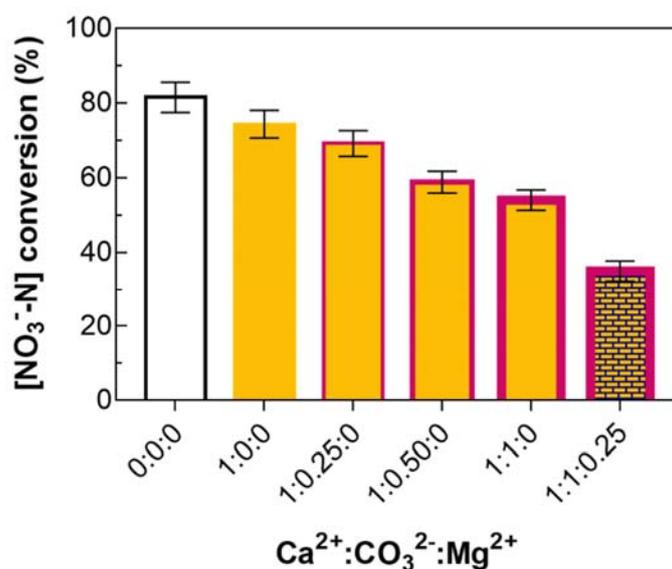
355 **Figure 4.** (a) Solubility diagram of Mg²⁺ and Ca²⁺ in function of pH considering the formation of
 356 insoluble hydroxide precipitates Mg(OH)₂ and Ca(OH)₂. (b) Solubility diagram of Mg²⁺ and Ca²⁺ in
 357 function of CO₃²⁻ concentration. (c) Speciation of carbonate in function of pH. (d) Saturation index as a
 358 function of pH of Ca(OH)₂ (yellow □), CaCO₃ (yellow △), Mg(OH)₂ (blue □), MgCO₃ (blue △) and

359 $\text{CaMg}(\text{CO}_3)_2$ (red \blacklozenge) considering a molar ratio composition of $\text{Ca}^{2+}:\text{CO}_3^{2-}:\text{Mg}^{2+}$ of 1:1:0.25 in a water
360 matrix at equilibrium for initial concentration of Ca^{2+} of 1 mM..

361
362 To mimic scaling formation under experimental electrolyte composition during ERN, saturation
363 indexes of possible precipitated solids over pH were plotted in Figure 4d for an actual water matrix
364 (considering a molar ratio composition of $\text{Ca}^{2+}:\text{CO}_3^{2-}:\text{Mg}^{2+}$ of 1:1:0.25 in a water matrix at equilibrium for
365 initial concentration of Ca^{2+} of 1 mM). The saturation index (SI) is defined as the logarithmic difference
366 between product ion activity (or activity quotient) and product solubility constant. The positive value of SI
367 illustrates that precipitation of the solids is thermodynamically favorable (supersaturated conditions), while
368 negative value of SI suggests undersaturated conditions. However, the rate of precipitation is controlled by
369 the kinetics of nucleation of solids in supersaturated conditions. Thus, solids may not be formed despite
370 being in supersaturated conditions unless nucleation and crystal growth favor precipitation conditions. The
371 kinetics of precipitation of each species can differ significantly, but nucleation and initial precipitation of
372 one solid can accelerate in cascade the rate of solid formation for all supersaturated species. As can be seen
373 in Figure 4d, simultaneous existence of non-carbonate hardness Ca^{2+} , Mg^{2+} and carbonate hardness during
374 the ERN might lead to formation of multiple solids. At pH >10.5 in water matrix $\text{Ca}^{2+}:\text{CO}_3^{2-}:\text{Mg}^{2+}$ 1:1:0.25
375 at equilibrium state, the precipitation of solids such as $\text{CaCO}_{3(s)}$, $\text{CaMg}(\text{CO}_3)_{2(s)}$, and $\text{Mg}(\text{OH})_{2(s)}$ is
376 thermodynamically favorable to occur.

377 Figure 5 evaluates the impact of co-existing CO_3^{2-} at the given initial Ca^{2+} concentration in the
378 ground water matrix of 1 mM Ca^{2+} . Increasing concentration of CO_3^{2-} decreases nitrate reduction, which
379 can be explained by the enhanced insolubility of Ca^{2+} species driven by the precipitation of CaCO_3 . The
380 initial nitrate reduction of 74% observed in the simple quaternary brackish solution containing only Ca^{2+}
381 (Table 1 Entry D with $\text{Ca}^{2+}:\text{CO}_3^{2-}:\text{Mg}^{2+}$ 1:0:0) is almost equivalent to the one obtained in the blank solution
382 without Ca^{2+} (Table 1 Entry A with 0:0:0). In contrast, the ERN performance decreased to 54% in the
383 presence of equimolar concentration of Ca^{2+} and CO_3^{2-} (1:1:0). It is important to note that solubility
384 diagrams describe the thermodynamic trend to precipitate in supersaturated conditions, but they do not

385 specify how fast the precipitation reaction will occur because if supersaturated conditions are reached,
386 precipitation depends on kinetics of nucleation and crystal growth. Figure 5 illustrates also how a small
387 content of Mg^{2+} of 0.25 mM (1:1:0.25) strongly impacted nitrate reduction performance by further
388 decreasing nitrate removal to 35%. These results illustrate the relevance of synergistic effect of hardness
389 ions, which induce electrode scaling and inhibit the ERN treatment.



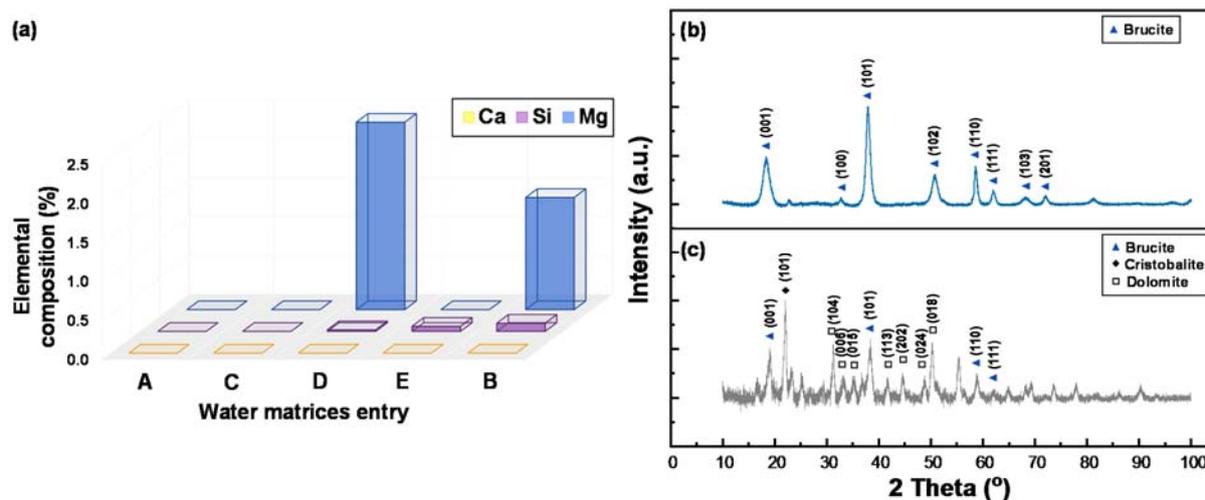
390
391 **Figure 5.** Impact of coexisting calcium, carbonate, and magnesium ions on nitrate conversion after
392 360 min of ERN on Sn cathode at 40 mA cm⁻². The graph illustrates impact of different molar ratios
393 Ca²⁺:CO₃²⁻:Mg²⁺ for initial concentration of Ca²⁺ of 1 mM.

394
395 X-ray fluorescence spectroscopy (XRF) is a non-destructive and fast surface analysis that provides
396 information on elemental composition. XRF measurements provide a holistic view of the impact on the
397 electrode surface of coexisting ions that might be associated to undesired scaling. When Sn electrodes
398 (cathodes) were analyzed before electrolysis, the XRF only identified Sn as the solely elemental
399 composition of pristine electrodes. Figure 6a shows the XRF analysis of the same cathodes after the
400 treatment of pure nitrate solution (blank), the synthetic brackish groundwater, and solutions with individual
401 cations, entries A, B, and C to E in Table 1, respectively. The XRF analysis did not detected calcium in any

402 case, but identified magnesium and silicon on the electrode surface after ERN for water samples described
403 in entries D and B. The quantification of these elements may suggest the incrustation of SiO₂ particles as
404 well as the precipitation of insoluble Mg²⁺ species. The treatment of nitrate in presence of solely silica salts
405 (entry E in Table 1) resulted in a lower quantity of Si detected, which may be justified by the role of Mg²⁺
406 precipitate that form inorganic scaling on the electrode surface and might simultaneously co-precipitate
407 silica. Meanwhile, an increase in percentage of Mg on the surface was observed for solutions containing
408 solely nitrate and Mg²⁺ (entry D in Table 1).

409 The visually whitish solid formed on the cathode surface during the treatment of water sample
410 described in entry D was collected, dried at 60 °C, and analyzed by XRD. The diffractogram of Fig. 6b
411 shows the characteristic peaks of magnesium hydroxide with the hexagonal crystallographic structure of
412 brucite (Mg(OH)₂) (Donneys-Victoria et al., 2020; Pang et al., 2011). The crystallographic planes with
413 Miller indices of (001), (100), (101), (102), (110), (111), (103), and (201) were observed at 2θ angles of
414 18.3, 32.8, 37.9, 50.8, 58.6, 61.9, 68.2 and 72.0, respectively. The precipitation of brucite can be explained
415 by the high alkaline localized pH near the cathode surface that induces supersaturation conditions of Mg²⁺,
416 and therefore the nucleation of this insoluble species on the Sn cathode surface. The XRD analysis of the
417 whitish solid formed on the cathode after ERN of water sample described in entry B (synthetic brackish
418 groundwater) showed that besides brucite more complex inorganic salts were formed such as dolomite
419 (CaMg(CO₃)₂) and cristobalite (SiO₂). At the 2θ angle of 22, the crystallographic plane with Miller index
420 of (101) of tetragonal cristobalite was detected, and at the 2θ angle of 31.3, 33.2, 35.1, 41.6, 44.5, and 50.3
421 the crystallographic planes of hexagonal dolomite were observed with Miller indexes of (104), (006), (015),
422 (113), (202), and (018), respectively (Gregg et al., 2015; Jiang et al., 2012). These results confirmed that
423 the ERN inhibition in synthetic brackish groundwater is mainly associated to the electrode scaling due to
424 the precipitation of inorganic salts of Mg²⁺ and Ca²⁺.

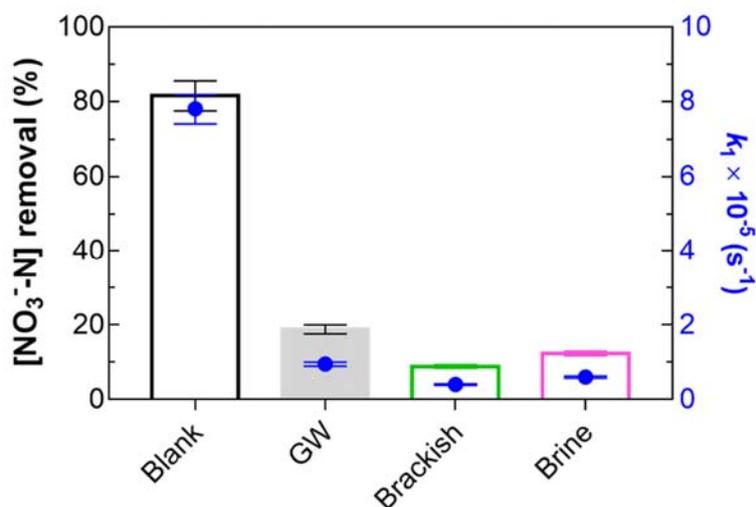
425



426
 427 **Figure 6.** (a) Elemental percentage composition of non-tin elements on the Sn cathode surface after
 428 ERN on different water matrices detected by XRF. XRD diffractogram of solid incrustation collected from
 429 the cathode surface after electrocatalytic treatment of (b) a water matrix containing Mg²⁺ (entry D in Table
 430 1) and the (c) synthetic brackish groundwater (entry B in Table 1).

431 432 3.3 Understanding boundaries limiting ERN feasibility on real water matrices

433 The selective reduction by physic-chemical means that transform nitrate to innocuous nitrogen gas
 434 can be a game changer for environmental protection. The treatment of nitrate contaminated real brackish
 435 groundwater (entry J in Table 1) and reverse osmosis brines collected from an inland desalination water
 436 treatment plant (entry L in Table 1) allowed identifying major barriers that coincide with those reported in
 437 the previous section for synthetic brackish groundwater treatment (entry B in Table 1). Figure 7 illustrates
 438 how the high fraction of nitrate removal achieved in a simple ternary brackish nitrate solution (entry A in
 439 Table 1) substantially decreased when the electrochemically-driven technology of advanced reduction was
 440 applied in a real water matrix scenario. Understanding barriers to technology adoption is an essential
 441 element for engineering research since this can provide guidelines for technology application and/or
 442 contribute to design preemptive strategies.

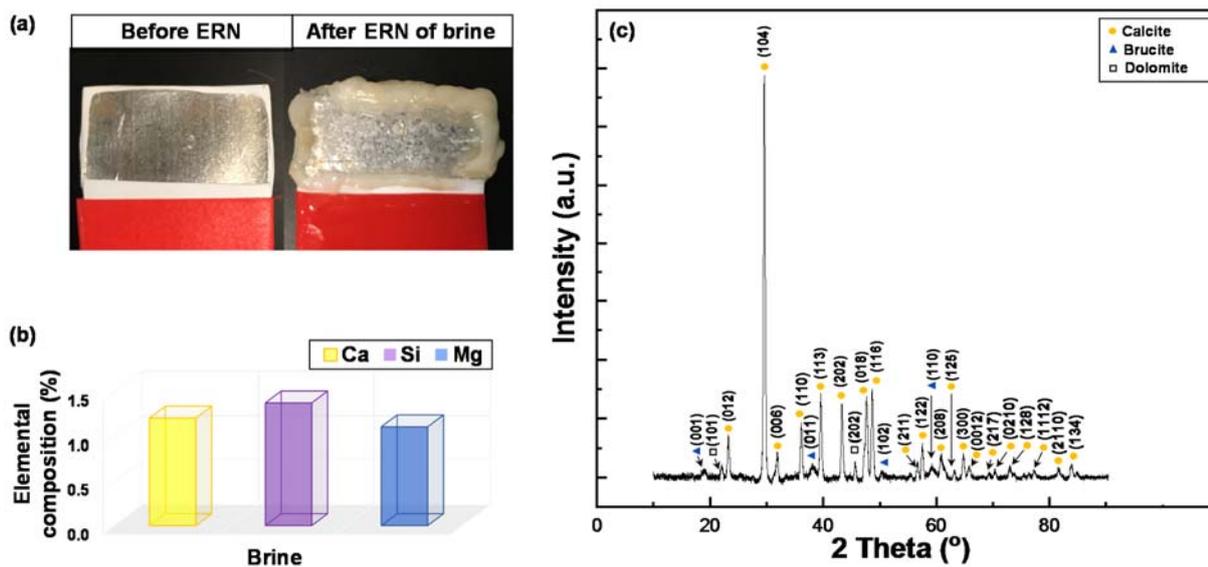


444 **Figure 7.** Electrochemical nitrate removal (bars) and kinetic constants (full blue circles) of 30 mg
 445 $\text{NO}_3^- \text{-N L}^{-1}$ in a ternary brackish water (blank, entry A), a complex synthetic brackish groundwater (entry
 446 B), a real brackish groundwater (entry J), and RO brine (entry L) after 360 min of treatment at 40 mA cm^{-2} .
 447 Compositions are listed in Table 1.

448

449 Similar to observations reported with the complex synthetic brackish groundwater, the Sn cathodes
 450 became scaled again with a white solid by treating real brackish groundwater and RO brine. The gel
 451 collected on the Sn cathode surface after the treatment using brine water (Figure 8a) was dried and analyzed
 452 by XRF, being identified mostly calcium, magnesium, and silicon as illustrated in Fig. 8b. The XRD
 453 diffractogram of the collected solid (see Figure 8c) had a predominant crystalline structure of calcite, which
 454 is the most stable polymorph insoluble CaCO_3 solid at alkaline pH (Guilheiro et al., 2021; Luo et al., 2020).
 455 Characteristic diffraction peaks at 2θ : 23.3, 29.6, 31.9, 36.1, 39.6, 43.3, 47.7, 48.7, 56.7, 57.5, 59.2, 60.8,
 456 64.8, 65.7, 69.3, 70.4, 73.0, 77.3, 81.7 and 83.9 correspond to Miller Index planes of (012), (104), (006),
 457 (110), (113), (202), (018), (116), (211), (122), (208), (125), (300), (0012), (217), (0210), (128), (1112),
 458 (2110) and (134) that are associated with the hexagonal crystal system of calcite. The diffraction peaks at
 459 18.6, 38.0, 50.9, and 58.7 related to the planes of (001), (011), (102), and (110) were characteristic signals

460 of brucite's hexagonal crystal system. The remaining peaks in the diffractogram corresponded to
 461 the hexagonal crystal system of dolomite observed at 22.1 and 45.0 with Miller Index planes of (101) and
 462 (202), respectively. These results highlight the relevant effect exerted by water hardness on scaling and the
 463 nature of the scalant formed.



464 **Figure 8.** Electrochemical reduction of nitrate treatment at 40 mA cm^{-2} in RO brine: (a) tin electrode before
 465 and after the electrolysis, (b) elemental composition of other elements different than tin on the Sn cathode
 466 surface after the electrolysis (tin corresponds to $>98\%$ of the XRF detected composition) and (c) XRD
 467 diffractogram of the solid incrustation collected from the cathode surface after treatment.

468 **Table 2.** Summary of water hardness and alkalinity nature of representative water matrices and their effect
 469 on nitrate removal after 360 min of treatment at 40 mA cm⁻² of 30 mg-N L⁻¹ of nitrate by electrocatalytic
 470 reduction on tin cathodes.

Entry	Water Sample	Initial pH	Water hardness (meq L ⁻¹)	Hardness	[Ca ²⁺] (mmol L ⁻¹)	[Mg ²⁺] (mmol L ⁻¹)	[HCO ₃ ⁻] (mmol L ⁻¹)	NO ₃ ⁻ removal (%)
A	Blank	5.95	0	Very soft	0	0	0	75
I	Synthetic Brackish Groundwater	6.22	3.0	Hard	1.02	0.50	3.00	19
J	Real Brackish Groundwater	7.90	9.0	Very hard	3.24	1.23	1.62	9
K	Softened real brackish	10.5	2.1	Hard	n.m.	n.m.	n.m.	37
L	Real RO Brine	8.10	41.2	Very hard	14.1	6.46	6.84	12

471
 472 Clearly, water hardness, and associated ions that adsorb to precipitated solids (e.g., silicates), are
 473 one of the major inhibitors of sustained ERN treatment. Table 2 suggests that the very hard characteristics
 474 of real brackish and RO brine waters may be indicative of high scaling risk and therefore the formation of
 475 a physical barrier on the electrode surface that will hamper the mass transport of nitrate from solution
 476 towards the electrocatalytic sites. Further consequences: 1) impermeable scale reduces electrode surface
 477 area, 2) semi-permeable scale causes an additional diffusion limited zone, and 3) scaling changes electrode
 478 interface and may induce electrostatic repulsion of nitrate ion. Understanding that the electrochemical
 479 reduction of water and nitrate induces a localized increase of pH on any electrocatalytic surface, water
 480 hardness can be identified as a major barrier for ERN treatment. Thereby, strategies that by-pass such
 481 shortcoming are considered herein.

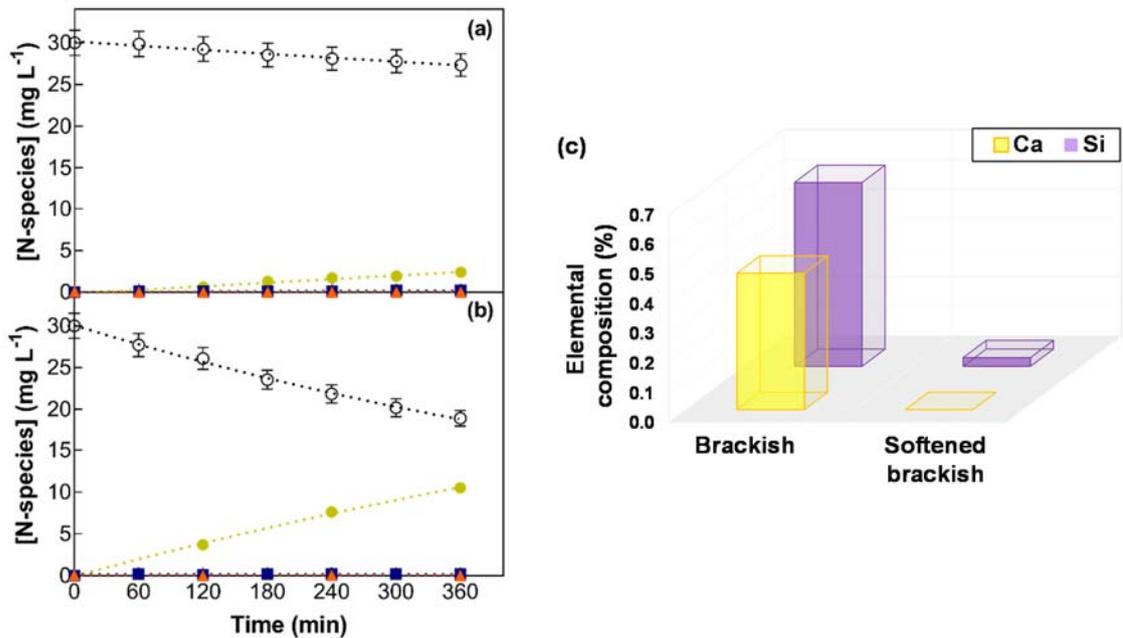
482 A widely considered approach to mitigate scaling on electrodes is reverse polarization, but it is a
 483 strategy limited to electrodes that can sustain both anodic and cathodic polarization conditions without
 484 surface degradation or electrodisolution (Chow et al., 2021). It should be pointed out that some earth-
 485 abundant catalysts such as tin and copper may dissolve under anodic potentials (Fajardo et al., 2014; Speck
 486 and Cherevko, 2020), while some metal oxides commonly used in electrochemical water treatment (e.g.,

487 dimensional stable anodes) may suffer from cathodic corrosion and degrade under cathodic potentials. In
488 this frame, other approaches must be designed. Implementing a chemical or electrochemical pre-treatment
489 of water softening may be a feasible alternative to be explored (Sanjuán et al., 2019).

490

491 *3.4 Exploring benefits of water softening as pre-treatment to electrocatalysis*

492 Real brackish groundwater showed the highest inhibition of ERN (entry J in Table 2) with respect
493 to the idealistic conditions of ultrapure water solutions that are usually reported in research papers (entry A
494 in Table 2). Results suggest that the inhibiting effect is mostly associated with the scaling induced by water
495 hardness. Therefore, chemical softening was implemented as pre-treatment to evaluate if the decrease of
496 hardness cations and silica can reinstate ERN performance metrics. Figure 9 illustrates that decreasing
497 brackish water hardness from 9.0 meq L⁻¹ down to 2.1 meq L⁻¹ through lime soda ash softening positively
498 affects the electrocatalytic nitrate conversion (softened real brackish, entry K in Table 2). ERN attained 9%
499 nitrate conversion in real brackish groundwater after 360 min of electrocatalytic treatment with a 0.4×10^{-5}
500 s⁻¹ kinetic rate constant for nitrate reduction (Figure 9a). Meanwhile, after softening real brackish
501 groundwater ERN achieved 37% nitrate conversion after 360 min of treatment (Figure 9b) with 5-fold
502 kinetics (k_f of 2.1×10^{-5} s⁻¹). Visual inspection of the electrodes revealed a drastic difference since
503 appreciable scaling was not observed under softened water conditions. This effect was further verified
504 through XRF analyses that demonstrated a decrease in elemental composition of calcium and silicon on the
505 cathode (see Figure 9c); note that magnesium was not identified during XRF analyses of these samples.

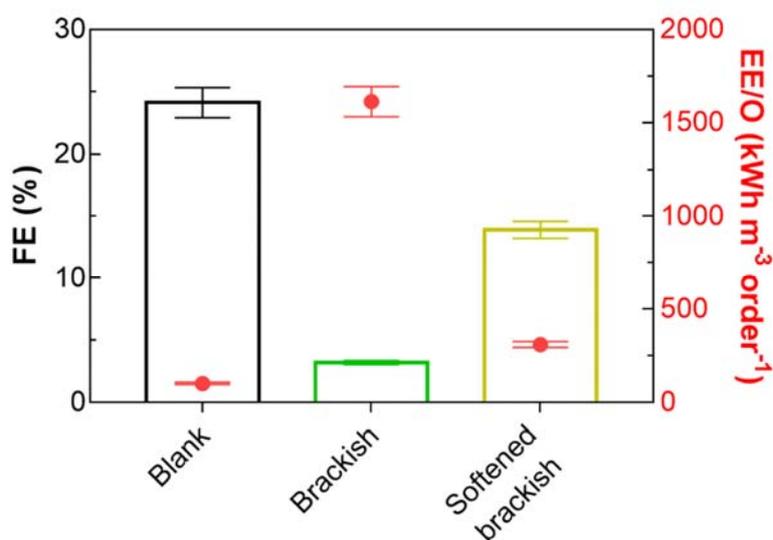


506 **Figure 9.** Time course of nitrogenated species ((○) NO₃⁻-N, (▲) NO₂⁻-N, (■) NH₃-N, (●) N₂-N) over time
 507 for the electrochemical reduction of 30 mg NO₃⁻-N L⁻¹ at 40 mA cm⁻² in (a) real brackish water with total
 508 hardness of 9.0 meq L⁻¹ and (b) softened real brackish water with total hardness of 2.1 meq L⁻¹ as CaCO₃.
 509 (c) Comparative elemental analysis by XRF of Sn electrode surface after ERN on real brackish and softened
 510 real brackish groundwaters.

511

512 The benefits of pre-softening brackish water were analyzed in function of engineering figures of
 513 merit related to FE and EE/O. Figure 10 shows the detrimental effect of scaling formation on the cathode.
 514 Scaling decreases charge transfer efficiency from a FE of 24 % in the blank (entry A in Table 2) down to a
 515 discrete FE of 3 % for real brackish groundwater (entry J in Table 2). Meanwhile, negligible effect was
 516 observed in terms of N₂ gas selectivity that maintained a similar value of ~95 ± 2 % for brackish and softened
 517 brackish water. However, the notorious decrease in FE showed an impact on the treatment economics.
 518 Noteworthy is that EE/O drastically increases by 16-fold from 102 kWh m⁻³ order⁻¹ for the blank up to 1612
 519 kWh m⁻³ order⁻¹ for the Brackish water. The increase in EE/O which can be explained by the decrease in
 520 mass transfer of nitrate form solution towards the electrode surface because of the electrode scaling, but

521 also by the increased resistance induced by the physical barrier of the crystalized insoluble salts on the
522 cathode. Softening treatment can improve performance of ERN under real water matrix conditions and
523 effectively increase FE up to 13 % and diminish the EE/O down to 310 kWh m⁻³ order⁻¹ (entry K in Table
524 2). These results allow inferring the driving role of water hardness as a barrier for effective reduction of
525 nitrate in real water matrices. Implementing pre-treatments that decrease water hardness can enable
526 successful translation of ERN technologies to decrease nitrate levels below MCL under real water matrix
527 conditions.
528

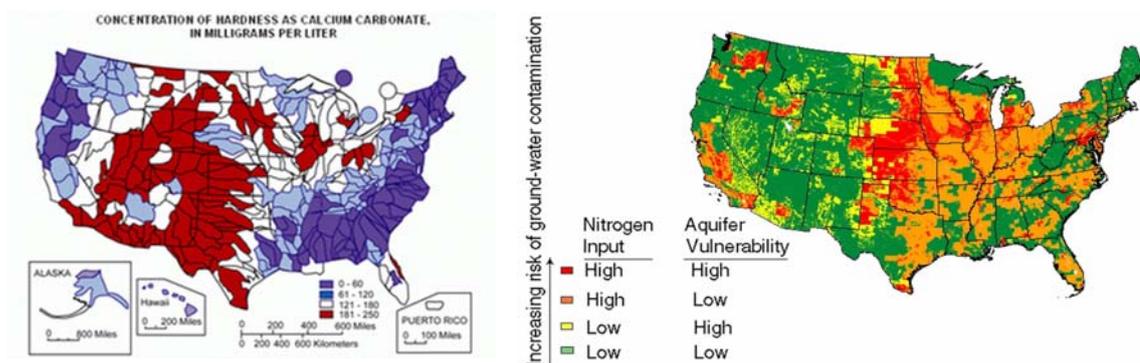


529 **Figure 10.** Faradaic efficiency (bars) and electric energy per order (full red circles) after 360 min
530 of the ERN for the treatment of 30 mg NO₃⁻-N L⁻¹ at 40 mA cm⁻² in simple ternary brackish, real brackish,
531 and softened real brackish waters (entries A, J and K in Table 2, respectively).
532

533 In the United States, groundwaters commonly contain high nitrate concentrations, which impacts
534 both municipal and private groundwater wells. Private wells receive little attention and have no mandatory
535 treatments. In the USA alone there are ~45 million people that may be impacted by high nitrate
536 concentrations in water sources (EPA, 2017; Pennino et al., 2017). Human activities such as fertilizer use,
537 manure application, and sewage treatment can contaminate sources of drinking water with nitrate, which

538 can easily leach through soil into groundwater and surface water. The maps illustrated in Figure 11 show
 539 the comparative distribution of high nitrate concentration and the water hardness distribution around the
 540 US. It is important to remark that not all the areas experience simultaneously hard waters with high
 541 concentrations of nitrate. However, the South-West illustrates several overlapping water quality conditions
 542 that lead to high nitrate concentrations and high-water hardness, which may represent a barrier for
 543 electrochemical reduction of nitrate without conducting a preliminary softening. Thus, opportunities for
 544 commercialization lay ahead for these regions that require development of hybrid softening/nitrate removal
 545 systems. However, most regions that face high nitrate concentration in soft waters (see Figure 11) can still
 546 benefit from direct deployment of electrochemical point of use (POU) treatment units. Our research results
 547 demonstrate that strategies that minimize scaling will benefit implementation and adoption of emerging
 548 ERN technologies. Beyond chemical softening, other emerging research opportunities arise to design
 549 strategies to prevent scaling formation such as the use of current pulses, implementation of anion-exchange
 550 films to prevent water hardness ions transport close to the electrode surface, or surface modifications that
 551 may decrease scaling extent (e.g., hydrophobic vs hydrophilic surfaces, nanostructures, crystallographic
 552 interface engineering, etc.) (Garcia-Segura et al., 2020b; Hanssen et al., 2016).

553



554

555 **Figure 11.** Geographic information system mapping of (a) water hardness and (b) nitrogen input
 556 in USA (USGS, 2018, 2005) .

557

558

559 **4. Conclusions**

560 This work explores in what extent the most common anions/cations present in natural water sources
561 (synthetic brackish groundwater, real brackish groundwater, and RO brine) affect the electrochemical
562 reduction of nitrate. The effect of controlling pH over time was analyzed showing that the maintenance of
563 circumneutral pH during the ERN of synthetic solution did not result in either an acceleration of kinetics
564 nor an increase in nitrogen gas selectivity. Therefore, the solution pH was not controlled in the following
565 electrochemical treatment experiments.

566 Electrochemical reduction of nitrate in a brackish groundwater matrix that contains a complex
567 mixture of coexisting ionic species showed a 4-fold decrease when compared against a conventional
568 synthetic solution (containing only sodium nitrate and sodium sulfate as electrolyte). The drastic loss in
569 performance was attributed to inorganic scaling formation on the cathode surface. Brucite ($\text{Mg}(\text{OH})_2$),
570 calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) compounds precipitated on the cathode surface during the
571 electrolysis. Silicon was also detected at the cathode, and likely adsorbed or co-precipitated with this water
572 hardness related minerals. Collectively, formation of these precipitates decreased the ERN efficiency by
573 creating a physical barrier, which makes difficult the electron transfer at the electrode surface.

574 The treatment of real brackish and brine waters (maximum nitrate conversion ~ 9 and 12% ,
575 respectively) allowed to recognize key obstacles that match with those verified for the treatment of the
576 synthetic brackish groundwater. The perception of these barriers and their effect on the technology
577 translation are fundamental aspects to offer ideas for technology application and/or promote the outline of
578 new action plans. The Sn cathodes became scaled with a white solid for both real waters. The gel collected
579 on the surface of the cathode after treatment using brine water was analyzed by XRF that identified Ca^{2+} ,
580 Mg^{2+} , and SiO_2 . These results emphasized the importance of the water hardness on scaling and the nature
581 of the scalant formed. Chemical water softening was used as a pre-treatment to assess if decreasing the
582 amount of Mg^{2+} and Ca^{2+} could improve the ERN performance. Softening pre-treatment enabled an increase
583 of 4-fold in the ERN, together with an acceleration in the reduction kinetics of 5-fold and a decrease of 5-
584 fold in the electric energy per order (EE/O). During this treatment no visual scaling was observed on the

585 surface of the Sn electrode. Understanding that in the US most of the regions with high risk of groundwater
586 contamination by nitrate overlap with areas with high water hardness, makes it clear that there is a need for
587 water softening pre-treatment prior ERN implementation. The results presented in this manuscript outline
588 research opportunities to enhance sustained performance of ERN treatments by developing compatible
589 preemptive anti-scaling strategies (e.g., current pulses, implementation of anion-exchange, or cathode
590 engineering).

591

592 **Acknowledgments**

593 This material is based upon research supported by the Transatlantic Research Partnership of the
594 Embassy of France in the United States and the FACE Foundation. This project has received funding from
595 the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie
596 grant agreement No 843870. This work was partially funded by the National Science Foundation (NSF)
597 through the Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment
598 under project EEC-1449500. The authors acknowledge the support of the Centre National de la Recherche
599 Scientifique (CNRS). We thank De Nora Tech, LLC for kindly providing the DSA® electrodes used as
600 anode in our electrochemical system. The use of facilities within the Eyring Materials Center at Arizona
601 State University supported in part by NNCI-ECCS-1542160 is acknowledged.

602

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