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**Electrocoagulation of high salinity produced water: Lessons learned from its
early applications in unconventional reservoir plays**

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1 **Abstract**

2 Ample research has demonstrated that electrocoagulation is a versatile technology capable of
3 facilitating the removal of a wide range of physical, biological, organic, and inorganic constituents such as
4 suspended solids, turbidity, bacteria, viruses, oil and grease, organic carbon (including chemical and
5 biological oxygen demand), silica, fluoride, etc. Despite its purported advantages and extensive lab-scale
6 evaluations, it has not yet been widely adopted for water and wastewater treatment and reuse at
7 commercial scale. This is symptomatic of a chasm between its technological capabilities on one hand and
8 field performance and reputation on the other. Herein, we opine as to why this might be the case using
9 our collective experiences with the oil and gas industry as an exemplar. We highlight scientific,
10 technological, engineering, and business issues that need to be addressed to realize the full potential of
11 this promising technology.

12

13 **1. Background and motivation.** Conventional coagulation using salts such as alum and ferric sulfate is
14 chemically intensive [1]. Manufacturing necessary chemicals, transporting them to (waste)water
15 treatment and reuse facilities, storing them on site prior to dosing, and optimizing coagulation chemistry
16 generates substantial greenhouse gas emissions, is fraught with safety risks, requires a skilled workforce
17 for monitoring and maintenance, and increases costs especially when implemented at remote locations
18 associated with oil exploration and production.

19 A [potential](#) alternative is electrocoagulation wherein sacrificial aluminum or iron electrodes are
20 intentionally corroded to release precursors that hydrolyze and precipitate *in situ* to coagulate suspended
21 solids [2]. This technology shows promise for distributed (waste)water treatment by alleviating many of
22 the issues related to conventional coagulation because it (i) replaces hazardous chemicals with non-toxic
23 solid electrodes, (ii) inherently neutralizes acidic hydrolysis products of conventional coagulants by
24 cathodic production of hydroxide ions reducing the need to externally add strong base, (iii) can be
25 automated and responds quickly to changing feedwater chemistry, and (iv) may decrease sludge
26 production [3-5]. Additionally, electrifying a chemically intensive process enables decarbonization as
27 more renewable energy is adopted, enabling stakeholders to achieve their environmental, social and
28 governance ([ESG](#)) goals while avoiding high costs of managing hazardous chemicals onsite [6].
29 Consequently, electrochemical technologies are well-suited for small-scale installations to treat municipal
30 and industrial (waste)waters of widely varying composition even at remote locations [4, 7, 8].

31 Although electrolytically adding coagulants *in situ* by oxidizing sacrificial Fe(0) and Al(0) anodes
32 provides numerous advantages, electrocoagulation has not lived up to its promise due to a variety of
33 scientific, technological, and business reasons which we opine on herein. We focus our attention on saline
34 feedwaters typical of (waste)water streams associated with unconventional oil and gas production and
35 exploration primarily because (i) our team has extensive experiences in this arena from some of its early
36 suboptimal applications to generate “clean brine” for reuse in hydraulic fracturing, (ii) the low internal
37 electrical resistance reduces energy consumption making it very attractive, and (iii) there are significant
38 research and application opportunities in this realm. We categorize “high salinity” as waters with total
39 dissolved solids ([TDS](#)) concentrations > 70 g/L, typical of the Permian Basin [9].

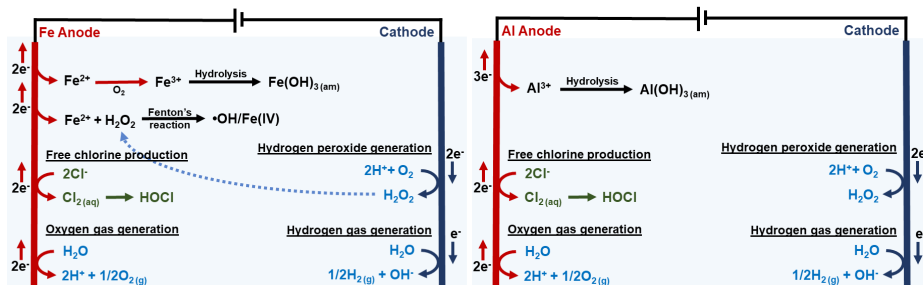
40 [Another consideration is that unconventional oil and gas extraction is highly water intensive](#) [10,
41 11], [which only increases further when coupled to drilling innovations such as using multiple well pads](#)
42 [and longer lateral lengths \(i.e., hydraulic fracturing stages\). Well completion water volumes in the](#)
43 [Permian Basin increased nearly 3-fold from ~128 thousand barrels to ~358 thousand barrels in the 4-year](#)

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45 [period 2015 – 2019 \[12\]](#). This implies that ~2 billion barrels of water will be required to complete the
46 [~5,500 Permian well permits \[13\]](#). On the other end, a well can produce 10-times as much wastewater as
47 [oil necessitating an estimated ~\\$18 billion for water management in the Permian \[12, 13\]](#). Consequently,
48 [much attention has been currently placed on \(beneficial\) reuse which also aligns with ESG objectives of](#)
49 [operators and addresses unpredictable and sometimes persistent droughts while taking advantage of the](#)
50 [favorable economics of water treatment. Electrocoagulation was initially implemented with the notion](#)
51 [of it being a “silver bullet” solution. However, it did not always work according to plans and valuable](#)
52 [lessons were learned regarding its proper application, enabling some of the authors to draw from their](#)
53 [experiences for this article.](#)

54 [Produced water quality varies considerably depending on the geographic location of the field, the](#)
55 [geologic formation, and the type of hydrocarbon product being produced. Because the water has been](#)
56 [in contact with hydrocarbon-bearing formations for millennia, it generally contains some of the chemical](#)
57 [characteristics of the formations and the hydrocarbons in those formations. About 600 different](#)
58 [chemicals have been detected in some produced water samples \[14, 15\], which ranges in TDS](#)
59 [concentrations between < 3,000 mg/L to > 300,000 mg/L \[16\].](#)

60 **Reactions involved.** Figure 1 schematically summarizes the major reactions associated with Fe(0) and
61 Al(0) electrocoagulation [2, 17-21] although several other reactions are also possible [4, 8, 22]. Al(0)
62 electrocoagulation generates Al(III) identical to alum addition [21], which can exceed Faraday’s law
63 predictions for brines [23]. In contrast, Fe(0) electrocoagulation generates highly soluble Fe(II) [24], which
64 needs to be oxidized to its insoluble Fe(III) form for effective coagulation, a process that is sensitive to pH
65 and redox conditions [25]. Anodic Fe(II) production can induce electro-Fenton reactions in conjunction
66 with cathodically generated peroxide [2, 20] adding to the technology’s capability while also making it
67 extremely sensitive to water chemistry and operating conditions. In saline waters, the chloride ion can
68 be oxidized to anodically generate chlorine [26]. Even though the rate and magnitude of the production
69 of these oxidants has not yet been quantified, the presence of highly reactive radicals derived from Fenton
70 chemistry and/or chlorine allow the possibility of intensifying coagulation to include *in situ* contaminant
71 oxidation and disinfection [27], another potential advantage.



72
73 **Figure 1. Schematic of iron (left panel) aluminum (right panel) electrocoagulation using elemental electrodes.**

74 Although recent research has uncovered many underlying mechanisms [28-30], more insights are
75 needed into homogeneous Fenton chemistry to identify and quantify associated short-lived intermediates
76 and elucidate their interactions with contaminants including reaction rates. This is critical to our ability
77 to design and operate electrocoagulation at its full potential. Further, the heterogenous chemistry of
78 electrode corrosion in the presence of high concentrations of pitting enhancers and inhibitors further
79 obfuscates electrocoagulation mechanisms [31-33]. Resolving issues related to electrode fouling and
80 passivation, critical considerations for long-term operation [34], typically require collaborations between
81 electrochemists, materials scientists, engineers, and field operators [35-37]. A hindrance to engineering
82 this technology and its widespread adoption (especially with iron, and to a lesser extent, with aluminum)
83 is our incomplete knowledge of its complex aqueous and interfacial chemistry in hypersaline matrices.

84 **2. Technological considerations for field-scale applications.**

85 **Lack of standardization.** The absence of well-accepted guidelines and operating protocols makes it
86 challenging to consistently implement on a commercial scale necessitating the establishment of
87 standardized practices and design criteria [38].

88 **Complex system design and scalability.** Electrode spacing, reactor configuration, and process
89 optimization need to be carefully considered and standardized to ensure efficient and repeatable
90 performance at larger scale [39]. Also, scale-up equations and procedures are not yet widely available
91 posing challenges for the design and implementation of larger systems necessitating trial and error
92 considerations and engineering expertise [40].

93 **Difficulties in predicting electrode behavior.** Systems consist of electrolytic cells, electrodes, and other
94 components that need regular maintenance to ensure optimal performance. Electrodes foul, scale, and
95 degrade over time, necessitating periodic cleaning or replacement [33]. Proper maintenance is essential
96 to ensure sustained performance and equipment longevity and avoid electrode overheating and failure.

97 Electrode replacement requires continual operating expenses in terms of manual labor. Additionally, non-
98 uniform corrosion (e.g., due to formation of impermeable scale) can lead to incomplete dissolution of
99 electrodes and their out-of-phase replacement needs.

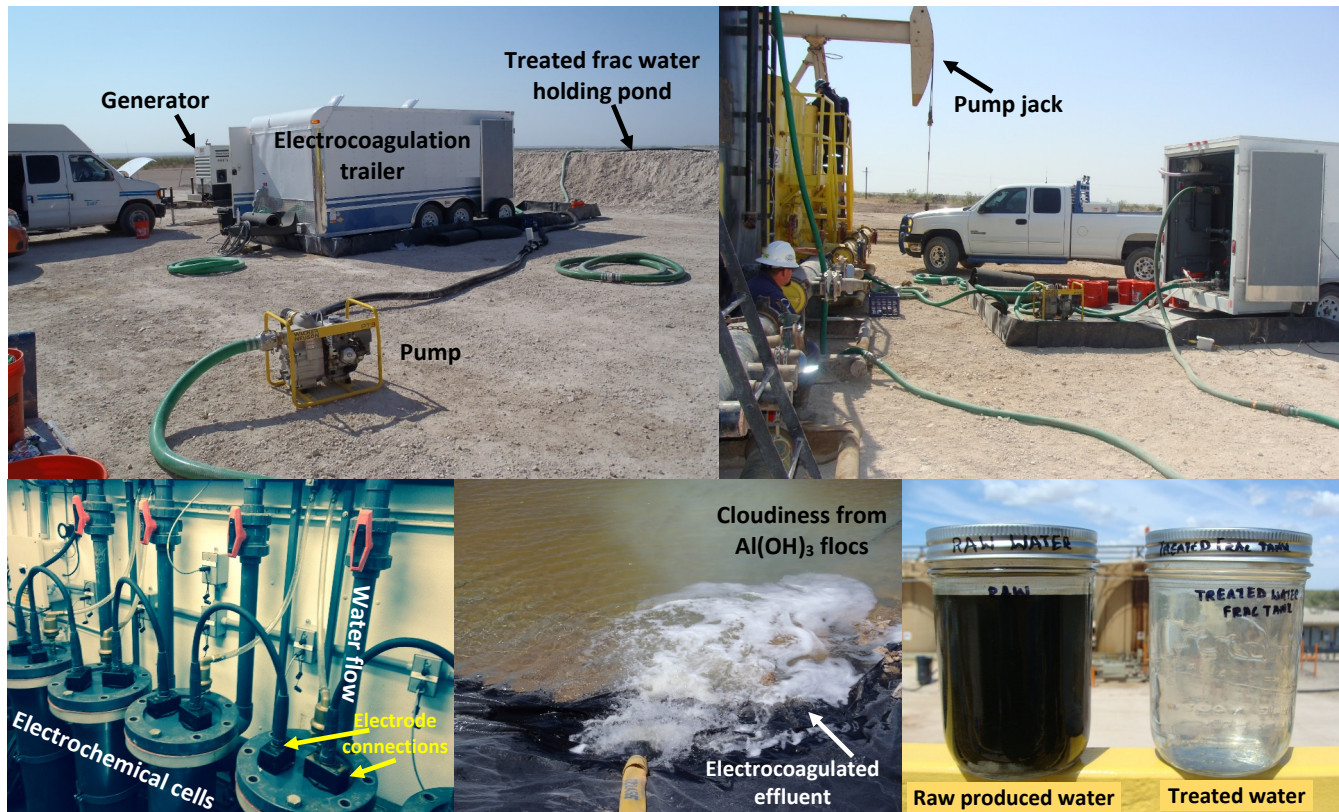
100 **Limited demonstration and validation.** Although electrocoagulation has shown promising results in
101 laboratory studies (and, to a limited extent, at pilot-scale) [34, 41], there is a need for more comprehensive
102 demonstration and validation of its performance and reliability under real-world, commercial-scale
103 applications in shale plays. The limited availability of case studies and proven track records can thwart its
104 adoption, particularly when it is competing with well-established conventional technologies, which have
105 a long history of full-scale applications and operator comfort levels.

106 **Safety.** Electrocoagulation units for saline waters may be operated at high current (hundreds of amps
107 and tens of volts), which due to its proximity to water, makes electrical insulation of paramount
108 importance. Another consideration is hydrogen gas evolution that requires adequate ventilation to avoid
109 explosion hazards.

110 **Regulatory acceptance.** Primacy agencies often require comprehensive long-term data on performance,
111 reliability, and safety of new water treatment technologies before granting regulatory approval [42]. The
112 limited number of commercial full-scale applications and lack of standardized guidelines may contribute
113 to the hesitation of regulatory bodies in endorsing and permitting electrocoagulation systems.

114 Some pictures of electrocoagulation in the Permian Basin are shown in Figure 2 to orient the
115 reader on its scale under field conditions.

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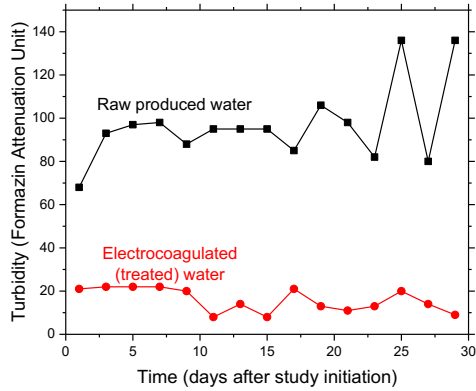
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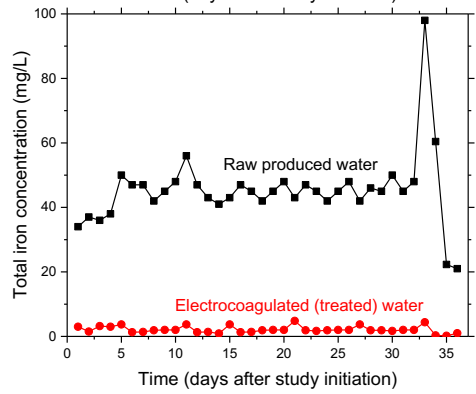
Figure 2. Representative photographs from the Permian Basin to visualize the scale of electrocoagulation under field conditions. Top left: typical set up showing a portable electrocoagulation unit, electrical generator, and a treated water holding tank. Top right: different view showing the pump jack extracting oil and generating the produced water. Bottom left: Close up view of the electrocoagulation unit and associated plumbing. Bottom middle: Treated water after electrocoagulation pumped into the holding pond for sedimentation. The cloudiness and white color of aluminum flocs is apparent on the top right of this image. Bottom right: Dramatic visual differences in the color and opacity of the produced water before and after treatment.

123 **3. Early user's perspective.** Initially, electrocoagulation was touted as a “silver bullet” in the oil industry
124 and its capabilities were often exaggerated. It was marketed as an emulsion breaker, replacement for
125 conventional coagulation to remove solids and iron, and both as a standalone technology and
126 pretreatment process. Although low technology readiness level research (i.e., TRL 2-4) had demonstrated
127 its potential, there was a lack of extensive mid-TRL testing at pilot-scale under real-world conditions. This
128 resulted in a critical knowledge gap required to successfully transition from controlled laboratory
129 experiments to larger-scale commercial applications. Field engineers within the energy industry carried
130 the burden of necessary, onsite technical evaluation in order to identify its operational envelope under
131 real world conditions and separating it from the hype. One early lesson learnt was that electrocoagulation
132 performed well within a treatment train that included flocculation, sedimentation, and filtration but was
133 insufficient as a standalone technology. While it was a workhorse for facilitating turbidity removal, its
134 capabilities with respect to boron, metals, and hydrogen sulfide were markedly lower than what was
135 promoted and were not cost-effective. It successfully floated oil and grease only when skimming
136 equipment was installed. Often, the need for auxiliary equipment to realize electrocoagulation's
137 capabilities was not fully appreciated resulting in suboptimal installation, a poor user experience, high
138 retrofitting costs, and consequently hurting its credibility with end users.

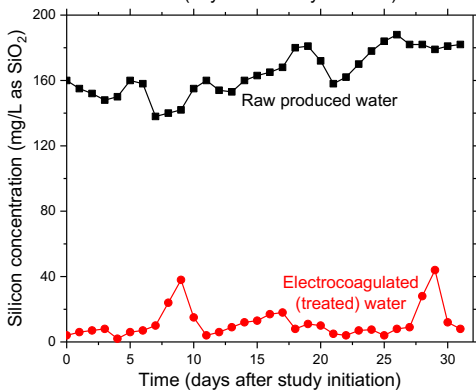
139 Example results from a successful electrocoagulation installation are provided in Figure 3,
140 validating its capabilities. The effluent turbidity was consistently below 20 FAU, iron concentrations were
141 always < 4 mg/L (achieved via NaOH addition), and silica removal was excellent (>90%). However,
142 implementation required careful and extensive attention by competent technical staff, not unlike
143 chemical coagulation, which unfortunately was not always available, resulting in several failed
144 applications.



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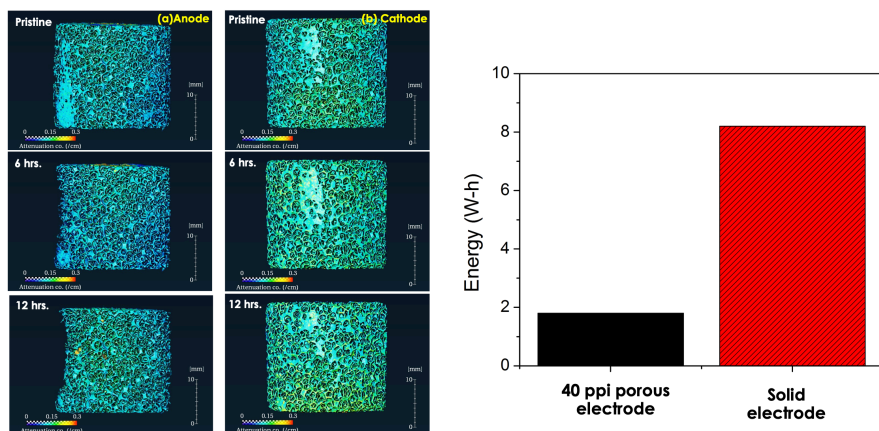
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Figure 3. Facile removal of turbidity (top panel), iron (middle panel $7.5 \leq \text{pH} \leq 8.5$), and silica (bottom panel, $\text{pH} = 9.0$) from a month-long field test (250-300 gallons per minute) of aluminum electrocoagulation in the Permian Basin. Effluent turbidity was relatively high because no attempt was made to further minimize turbidity since it met process requirements.

152 **4. Porous electrodes and long-term performance.** Increasing specific surface area of electrodes can
 153 enhance energy efficiency, which has been pursued by implementing porous electrodes [43-45]. Neutron
 154 computed tomography of porous aluminum electrodes has demonstrated that electrolysis occurs over its
 155 entire outer and inner surfaces [46] leading to more uniform electrodisolution (Figure 4, left panel). This
 156 enabled a four-fold reduction in energy requirements [for dissolving the same mass of aluminum compared](#)
 157 [to the energy needed by](#) solid electrodes (Figure 4, right panel). The current cost of fabricating porous
 158 electrodes is probably higher than what could be offset by such energy savings, necessitating alternative
 159 manufacturing techniques (e.g., using recycled metals).

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 161 **Figure 4.** Neutron computed tomography of porous aluminum foam electrodes before and after 6-hours and 12-
 162 hours of electrocoagulation (left panel). Energy comparison between solid aluminum electrodes and 40-pores per
 163 inch (ppi) porous aluminum electrodes (right panel) [for the same mass of dissolved aluminum](#). Figures adopted
 164 from reference [46].

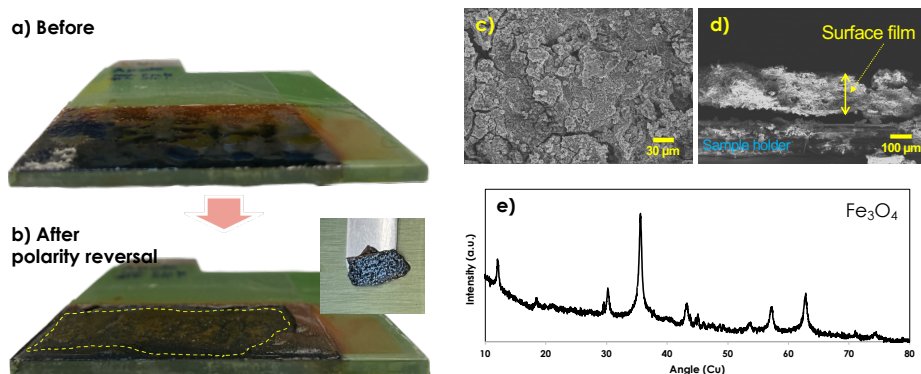
165 Challenges associated with maintaining stable electrocoagulation performance over extended
 166 time periods include:

- 167 • **Fouling** caused by the precipitation of solids or growth of oxide layers on electrode surfaces
 168 that forms a passivating layer that reduces energy and performance efficiency [33, 47].
- 169 • **Storage and startup issues** that lead to fouling and corrosion of electrodes between
 170 treatment cycles necessitating the removal of passivating layers during startup [48].
- 171 • **Non-uniform electrode depletion** arising from their differential dissolution rates, which can
 172 compromise their structural integrity and require premature replacement [34].

173 In iron electrocoagulation, a dense passivating oxide layer forms on solid anode surfaces over
 174 many operating cycles, which can reduce Faradaic efficiency, overall energy efficiency, and contaminant

176 removal. A porous and thin oxide layer is formed on the anode, which traps Fe(II) allowing it to grow in
 177 thickness, thus decreasing the mass transfer of Fe(II) to the bulk solution necessary for its oxidation,
 178 precipitation, and uptake of contaminants. Over time, the porous oxide layer is transformed into a dense
 179 passivation layer consisting of less-conductive iron oxide minerals that increases charge transfer
 180 resistance and energy consumption. Eventually, the increasing potential favors oxidation of H₂O to O₂
 181 instead of coagulant electrodisolution [33, 34]. Techniques to mitigate passivation-layer growth and
 182 stabilize performance have been proposed: (i) reversing electrode polarity (not labor intensive), (ii) storing
 183 electrodes in a dry environment (not labor intensive), and (iii) mechanical abrasion (highly labor intensive).

184 Figure 5 shows a black iron oxide anodic layer, which was removed after polarity reversal
 185 attributed to H₂(g) evolution (Figure 5b inset). It was >150 μm thick (Figures 5c and 5d) and significantly
 186 worsened electrical energy efficiency and identified to be Fe₃O₄ (Figure 5e).



187
 188 **Figure 5.** (a) Black rust layer formation on the anode after operation over 15 days while treating a simulated
 189 secondary municipal wastewater effluent. (b) Surface cleaning after polarity reversal. Shown in the inset is a
 190 broken piece of the passivating oxide film formed on the anode after polarity reversal. The yellow dashed line
 191 indicates the area of film removal by polarity reversal. (c) Scanning electron microscopy image of the broken film.
 192 (d) Corresponding cross-sectional electron micrograph of the film. (e) X-ray diffraction pattern of the broken oxide
 193 film showing Fe₃O₄ presence.

194 **5. Estimating performance and costs for full scale electrocoagulation.** Cost analyses of
 195 electrocoagulation should account for initial investment costs, operational expenses, maintenance
 196 requirements, and residuals disposal and evaluate payback periods. Most available models of system cost
 197 and energy consumption neglect crucial scale-up issues. For example, the energy associated with the
 198 electrode dissolution processes can be estimated based on Faraday's law but empirical models have
 199 not been validated at high current densities (>10 mA/cm²) [49]. Simply optimizing Faradaic efficiency
 200 does not translate to optimized target contaminant removal efficiency at pilot-scale due to confounding

201 factors such as long residence times required for electrode cleaning [50]. While energy use associated
202 with electrode dissolution, mixing within reactors, and producing a metal ingot and metal sheet are
203 typically estimated [47], energy inputs for pumps, instrumentation, controls, and downstream treatment
204 processes along with indoor temperature control (if any) are not. Cost models sometimes neglect key
205 factors such as maintenance [51], electrode manufacturing, sludge management and disposal, labor,
206 chemical reagents, ancillary equipment and installation costs, and conveyance, e.g., [52, 53]. These costs
207 are required for accurate economic analysis at full-scale.

208 Published costs and energy demands span a wide range and, understandably, depend on the
209 application, location, and estimation methodology. Comparing results is difficult when they are reported
210 in inconsistent units and using different cost categories. For example, energy consumption for oil
211 elimination has been reported as 0.43 kWh/g of oil and gas for biodiesel wastewater and 0.74 kWh/m³
212 and 32 kWh/g of phenol for two different studies of petroleum refinery wastewater [54].

213 **6. Path forward.** Finding the right fit for electrocoagulation within the oil and gas market requires an
214 improved scientific understanding of (i) associated homogeneous, heterogeneous, and interfacial
215 chemistry including formation of reactive intermediates, (ii) the extent of and mechanisms underlying
216 contaminant removal (including microorganisms), and (iii) kinetics of electrode corrosion and
217 fouling/passivation. An essential consideration is the variability and high concentrations of myriad
218 electrolytes, organic matter, and proprietary chemicals in oilfield brines [14], which necessitates advanced
219 geochemical and electrochemical modeling coupled with high energy characterization techniques to
220 interpret experimental data [55, 56]. Follow-up process engineering work should target (i) establishing
221 technology operating envelope and lower/upper bounds of its capability, (ii) making electrode corrosion
222 more uniform and predictable, (iii) experimentation with flow-through reactors based on batch tests, and
223 (iv) upscale laboratory tests to mid-TRLs via long-term pilot-scale evaluations with close collaboration
224 between equipment manufacturers, energy companies, and end users. Identifying operational
225 parameters where electrocoagulation has the greatest advantage(s) over conventional coagulation
226 techniques (e.g., flow rates, water chemistry, turbidity influent/effluent limits, etc.) is also essential.
227 Technical work to integrate electrocoagulation within a complete treatment train needs to be augmented
228 with building trust and familiarity by training end users and carefully documenting its competences and
229 limitations to realize its full potential and streamline commercial-scale installation. Similarly, better
230 documentation of cost and energy demands of full-scale systems evaluated with consistent units would
231 provide helpful information to end users considering adopting electrocoagulation. This could be
232 facilitated via academic-industrial collaborative technoeconomic analyses using extensive datasets

233 generated by the practicing engineers that are not often shared in the peer-reviewed literature. These
234 lessons can be extrapolated to other brines including seawater [57], brackish (ground)water [58], reverse
235 osmosis and nanofiltration concentrates [59], and other industrial process water and wastewater [60].

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