Boron removal by electrocoagulation: Removal mechanism, adsorption models and factors influencing removal

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Graphical Abstract

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1 Boron removal by electrocoagulation: removal mechanism, adsorption models and

2 factors influencing removal

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10 Abstract: Boron (B), normally present in ground water and sea water, is a vital micronutrient for 11 plants, but is also toxic in excessive amounts. Under typical conditions, aqueous boron is present 12 as boric acid (H_3BO_3) , which is uncharged, making B particularly challenging to remove by mechanisms commonly applicable to removal of trace constituents. Adsorption of B onto 13 14 aluminum hydroxide solids $(Al(OH)_3(s))$ generated using aluminum-based electrocoagulation (EC) 15 is a promising strategy for B removal. Infrared spectroscopy analysis indicated complexation of 16 B(OH)₃ with aluminum hydroxide solids via surface hydroxyl groups, while X-ray and infrared 17 spectroscopy results indicated that the structure of the $AI(OH)_3(s)$ was influenced both by EC 18 operating conditions and by water quality. A linear adsorption model predicted B removal well 19 when initial concentrations were lower than 50 mg/L, but fit the experimental data poorly at 20 higher initial B concentrations. The Langmuir adsorption model provided a good fit for a broader 21 range of initial B concentrations (5 – 1000 mg/L). Factors affecting B adsorption during the EC 22 process, including current intensity, Al dissolution rate, boron concentration, pH, and total

23	dissolved solid (TDS), were investigated. Increasing current intensity initially led to a higher Al
24	dissolution rate, and therefore higher B adsorption, but there was a limit, as further increases in
25	current intensity caused rapid formation of $Al(OH)_3(s)$ having a large particle size and a low
26	capacity to complex B. Boron removal decreased as its concentration increased. The best
27	removal of B occurred at pH 8, corresponding to a slightly positive zeta potential for aluminum
28	hydroxide and a small but significant fraction of negatively charged B species. Higher TDS
29	concentrations facilitated the use of higher current intensities, i.e., the limit on the effective Al
30	dissolution rate increased with increasing TDS. Two real water samples (river water and oilfield
31	produced water) spiked with B were treated using EC, resulting in up to 50% B removal from
32	river water ($C_0 = 10 \text{ mg/L}$, current = 0.2 A) in 2 hours, and 80% B removal from produced water
33	(C_0 = 50 mg/L, current = 1.0 A) in 2 hours.

Keywords: Boron removal; electrocoagulation; adsorption model; aluminum hydroxide; surface
 complex.

36 1. Introduction

37 Boron (B) is a naturally occurring element, with freshwater concentrations typically less than 38 1 mg/L in most regions of the world (WHO, 2003; Hasenmueller and Criss, 2013). Seawater 39 infiltration, boron-rich soils and anthropogenic sources can all result in much higher aqueous 40 boron concentrations, in some cases > 100 mg/L (WHO, 2003; Hasenmueller and Criss, 2013; 41 Chen et al., 2017). Wastewater resulting from oil and gas production (produced waters) is often 42 particularly high in boron content (Sari and Chellam, 2015; Blondes et al., 2017; Chorghe et al., 43 2017). While boron is an essential plant nutrient at low concentrations (up to 0.3 mg/L), it is 44 toxic to some commercial crops at concentrations that are only marginally greater, from 0.5 - 2 45 mg/L (Hilal et al., 2011; Yıldırım and Kasım, 2018). Additionally, the World Health Organization

has determined a safe level of boron in drinking water to be 2.4 mg/L (WHO, 2011), although 46 47 some countries have established stricter standards down to 1.0 mg/L or less (Güler et al., 2015; Guan et al., 2016). 48

49 Boron removal is complicated by the properties of aqueous boron species. Boron is present in water as a mixture of boric acid $(H_3BO_3 \text{ or } B(OH)_3)$ and borate $(H_2BO_3^- \text{ or } B(OH)_4^-)$, with the 50 relative amounts of each species depending on pH, as described by the dissociation reaction and 51 52 equilibrium constant at 25 °C shown in eq 1 (Dolati et al., 2017). (A predominance area diagram 53 for boric acid is shown in **Figure 1S**.)

54
$$B(OH)_3 + H_2O \stackrel{K_a}{\Leftrightarrow} B(OH)_4^- + H^+$$
, $pK_a = 9.2$ (1)

55 At near-neutral pH values in dilute solutions (e.g., pH 6 to 8), aqueous B exists mainly as 56 neutrally charged boric acid, which is poorly removed by membrane processes such as reverse 57 osmosis (Xu and Jiang, 2008; Dolati et al., 2017). Increasing the pH above 9 increases boron 58 removal, but adds additional expense and process complexity (Jacob, 2007; Tu et al., 2010). 59 Chemical precipitation using calcium carbonate, hydroxyapatite, and aluminum and iron 60 coagulation have all been studied for boron removal, but again, these processes are more 61 effective when borate, rather than boric acid, is the predominant aqueous phase (Kitano et al., 62 1978; Sasaki et al., 2016; Chorghe et al., 2017; Dolati et al., 2017). Chorghe et al. (2017) found 63 that very high doses of aluminum or iron could remove up to 80% of boron from produced 64 water, but suggested that the amount of chemical required made this approach impractical. 65 While boron-selective ion-exchange resins have been developed, regeneration of these resins 66 requires high chemical dosages, resulting in correspondingly higher material and operational 67 costs (Hilal et al., 2011; Dolati et al., 2017).

68	Electrocoagulation (EC) is an electrochemical water treatment method that utilizes a
69	sacrificial anode, typically made of aluminum or iron, to generate coagulants in-situ. For EC
70	using aluminum anodes (Al-EC), aluminum ions generated at the anode react with hydroxide
71	ions generated at the cathode, forming a variety of dissolved aluminum hydrolysis products
72	(complexes) and aluminum hydroxide solids, $Al(OH)_3(s)$ (Sari and Chellam, 2015; Chorghe <i>et al.</i> ,
73	2017). The distribution of aluminum species formed depends on pH; operating conditions,
74	including current intensity and operating time; and the chemical characteristics of the solution
75	(Ghosh et al., 2008). Electrocoagulation has already seen extensive study for its efficacy in
76	removing a variety of contaminants including total suspended solids (TSS), turbidity, organic
77	matter (as measured by chemical oxygen demand, COD), phosphate and arsenic (Emamjomeh
78	and Sivakumar, 2009; Zhao et al., 2014; Tian et al., 2016). EC also has several reported
79	operational advantages over chemical coagulation, including compact size, simple operation,
80	low capital costs and less waste sludge (Zhang et al., 2016; Shamaei et al., 2018). Several recent
81	studies have examined electrocoagulation for boron removal, with positive results (Ezechi et al.,
82	2014; Isa et al., 2014; Dolati et al., 2017). Sari and Chellam (2015) showed that boron removal
83	from produced waters using EC is achieved primarily through sorption to amorphous $AI(OH)_3$
84	precipitates, rather than co-precipitation. Electrocoagulation produces hydroxide ions at the
85	cathode that can react with boric acid to form borate ions, which facilitates increased boron
86	sorption compared to chemical coagulation processes using aluminum or iron sulfate (Dolati et
87	<i>al.</i> , 2017).

Electrocoagulation may be particularly suited to boron removal from high-salinity waste
streams, including oil produced water. While high background salt concentrations typically
hinder other treatment processes, high conductivity decreases the energy requirements for EC
operations compared to freshwater conditions. Research to date on B removal by aluminum EC

has given little attention to the removal mechanisms involved, to the adsorptive capacity of Al
solids generated under a range of conditions that might alter their characteristics (e.g., structure,
morphology and settling rate), and to quantitative models for B adsorption. In particular, the
characteristics of Al(OH)₃ solids formed during EC depends both on operating conditions and
water composition (e.g., salt concentration) (Wellner *et al.*, 2018) which may have a marked
influence on boron adsorption.

98 The current study uses a two-electrode EC cell to examine the impact of operating 99 parameters and water quality on boron removal through electrochemical generation of 100 dissolved aluminum species. Aluminum hydroxide solids generated during EC were analyzed 101 using X-ray, infrared spectroscopy and dynamic light scattering (DLS) to reveal the relationship 102 between the morphology and structure of EC generated $AI(OH)_3(s)$ and B removal. Quantitative 103 models for B removal were developed based on boron adsorption isotherms and mass balance equations to predict B removal using EC. The specific objectives were: (1) to examine the 104 105 mechanism(s) of B removal; (2) to develop quantitative models describing B removal by 106 aluminum EC; (3) to optimize B removal by determining the effects of significant operating 107 parameters (especially time and current intensity) and water quality (initial B concentration, pH 108 and TDS); and (4) to experimentally investigate B removal from real waters (e.g., a river water 109 and an oilfield produced water) using aluminum EC.

110 **2. Materials and Methods**

111 2.1 Materials

All reagents were of analytical grade, and were used as received without further

113 purification. Boric acid (99.8%), purchased from Fisher Scientific (Fair Lawn, NJ, US), was used as

the boron source. Ultrapure water (18.2 MΩ/cm, Milli-Q Direct 8 system) was used in all

115	experiments. NaCl was used to adjust the TDS concentration of experimental water samples,
116	while the pH of experimental solutions was adjusted using sodium hydroxide (0.5 M) or nitric
117	acid (2%). The electrodes used for generating aluminum and hydroxide ions in situ consisted of a
118	99+% aluminum rod anode and 99.999% graphite carbon rod cathode, both purchased from
119	Strem Chemicals (Newburyport, MA, US).

120 The natural water sample used in this study was collected from the Kansas River, and an

121 oilfield produced water sample was collected from an oil well in Douglas County, KS. The

122 chemical compositions of the water samples are provided in Tables 1S and 2S in the Supporting

123 Information. The Kansas River water sample was spiked with 10 mg/L boron and the oilfield

124 produced water was spiked with 50 mg/L boron.

125 **2.2 Electrocoagulation setup and sample collection**

126 The scheme and a photo of the EC cell are shown in Figure 2S in the Supporting Information. 127 The electrocoagulation reactor consisted of a 150 mL Nalgene plastic beaker with two rods 128 immersed in the aqueous solution, and a Metrohm 804 Ti Stand stirrer. The electrode rods were 129 1.2 cm in diameter, 5 cm long, and were placed 2.5 cm apart in the solution. Before each 130 experiment, Al electrodes were abraded with sand paper to remove scales and cleaned with 2% HNO₃ and then ultrapure water. An Extech DC regulated power supply (0-30 V) was used as the 131 132 power source and the electric current was monitored and held constant during each experiment 133 by continuously adjusting the cell voltage. During each experiment, the pH of the solution in the 134 beaker was periodically measured with a pH electrode (Metrohm, 6.0262.100) and adjusted to the target value by the titrator (Metrohm 905 Titrando with 800 Dosino). Because the current 135 136 interfered with the pH measurement, the current was turned off when pH was measured (Wan 137 et al., 2011).

138	The total concentrations of B and NaCl (as TDS) in the 150-mL experimental solutions were
139	50 mg/L and 2000 mg/L, respectively, except when explicitly described otherwise. Every 15 or 30
140	min during each experiment, 2-4 mL of solution were collected from the beaker, and a 1 mL
141	aliquot was diluted by 2% ${\sf HNO}_3$ to 10 mL and analyzed to determine the total concentrations of
142	B and Al in the solution. The rest of the sample was filtered using a 0.45 μm Nylon filter
143	(Fisherbrand), and 1 mL of the filtrate was acidified and diluted with 2% HNO_3 to 10 mL, then
144	used to determine the dissolved concentrations of selected elements. The concentrations of B
145	and Al were determined using an inductively coupled plasma-optical emission spectrometer
146	(ICP-OES, PerkinElmer, Optima 2000 DV). Triplicate ICP analyses were performed for each
147	sample, and measurements accepted if all results were within 10% of the averaged value. The
148	difference between the total and dissolved concentrations represented B removed from
149	solution and the amount of AI precipitate formed. Aluminum hydroxide solids concentrations
150	are reported herein in mg/L as Al.

To compare the EC process with conventional alum coagulation, boron removal experiments were conducted using solid aluminum sulfate (16-hydrate) as a coagulant. Solid aluminum sulfate was added directly to the solution at varying dosages. After alum addition, the pH was adjusted back up to the desired value, the beaker sealed and stirred for one and a half hours, and the suspension was left to settle for 24 hours. A sample of the supernatant was then collected, acidified, and analyzed for boron using ICP as described above.

157 2.3 Precipitate analysis

After selected experiments, aluminum solid samples were collected after standing for 24 h (without stirring) in the beaker to measure their size distribution. The mean particle size of the Al solids was determined by dynamic light scattering (DLS) using a NanoBrook Omni particle

161	sizer (Brookhaven Instruments Corp.). Three consecutive 1-min measurements were obtained
162	while detecting light scattering at a 90° angle. The mean effective diameter was determined by
163	the method of cumulants (Cordova et al., 2008).
164	Samples of Al coagulant solids were collected, dried, and prepared for FTIR and XRD analysis
165	after selected EC experiments. Al coagulant solids were collected by filtering each treated
166	sample through a 10 kDa ultrafiltration membrane (shown in Figure 3S in the supporting
167	information). The resulting filter cakes were frozen at less than -20°C. The frozen samples were
168	then freeze-dried in a Labconco Freezone 4.5 and ground to obtain powder with <5% moisture.
169	Complexation between B and Al coagulants was characterized using attenuated total reflectance
170	Fourier-transform infrared spectroscopy (ATR-FTIR, Agilent Technologies Cary 630). The
171	structure of AI coagulant samples was examined using X-ray diffraction (XRD, Bruker D2 PHASER)
172	with a Co K α radiation source (λ = 1.79026 Å) operated at 30 kV and 10 mA, and the 20 scanning
173	angle ranged from 25° to 100° with a speed of 11°/min.

174 **2.4 Predictive model of boron removal**

175 The B removal fraction during electrocoagulation, η , can be calculated by **eq 2**,

176
$$\eta = 1 - \frac{[B]_{aq}}{[B]_{total}}$$
 (2)

where [B]_{total} and [B]_{aq} refer to the total and aqueous concentrations, respectively, of B in
solution in mg/L.

Boron removal was modeled as an adsorptive process with B adsorbing on Al solids (eq 3).

180 Al solids production was a function of time and current intensity (eq 4), while the total

181 concentration of B in the beaker remained constant (**eq 5**).

182
$$[B]_{Al} = f([B]_{aq})$$
 (3)

$$183 mtextbf{m} = f(t, I) (4)$$

184
$$[B]_{total} = \frac{m}{V} [B]_{Al} + [B]_{aq}$$
 (5)

185 In these equations, $[B]_{A}$ refers to the concentration of B on Al coagulant solids, mg/g; m is the

186 mass of Al dissolved from anode and precipitated as Al coagulant solids, g; t and I represent EC

187 operating time and current, with units of s and amperes (A), respectively; and V is the volume of

the EC reactor, in L. Once the adsorption model (eq 3) and mass of Al solids (eq 4) are

determined, B removal can be predicted under a range of different conditions (Chen and Jafvert,

190 2017, 2018a).

191 3 Results and Discussion

3.1 Aluminum dissolution as a function of current intensity

Aluminum dissolution rates as a function of EC reaction time at varying current intensities are shown in **Figure 1** for a solution at pH 8 with 2000 mg/L NaCl. The current intensities ranged from 0.1 to 1.4 A and were kept constant by continuously adjusting the cell voltage during each experiment (0-2 h). The relationship between the current (*I*) and the amount (*m*) of aluminum dissolved in the EC reactor over time (*t*) can be theoretically predicted using Faraday's law (Moussa *et al.*, 2017) (**eq 6**), which was used to plot the lines shown in **Figure 1a**.

$$199 mtextbf{m} = \frac{IMt}{zF} (6)$$

where *I* refers to current flow, A, and *M* is the atomic weight of Al, 27 g/mol; t represents

201 operating time, s; z is the number of electrons transferred in the reaction at the electrode (z=3

electrons per mole of Al, based on the reaction $Al(s) \rightarrow Al^{3+}(aq) + 3e^{-}$ occurring at the anode); and *F* is Faraday's constant, 96,486 C/mol.

The faradaic efficiency (FE) of Al generated during EC, or the percentage of actual to theoretical Al production, can be calculated based on **eq 7** (Lv *et al.*, 2014), to describe the charge transfer efficiency in a system facilitating an electrochemical reaction.

$$207 FE = \frac{zNF}{lt} \times 100\% (7)$$

where *N* is the amount of the generated products in the EC process, in mole Al; and the
remaining parameters are the same as in eq 6. Figure 1b shows the faradaic efficiency of the EC
cell at different current intensities and reaction times.

211 From Figure 1a, experimental Al dissolution rates were slightly elevated compared to 212 theoretical predictions using Faraday's law (eq 6) for currents ranging from 0.10 A to 0.50 A. 213 Previous studies (Yilmaz et al., 2007; Sari and Chellam, 2015) have also observed a similar trend. 214 The observed super-faradaic dissolution may be caused by the presence of chloride ions, which 215 can adsorb onto the oxide passivation film on the Al anode surface, and react with Al species in 216 the oxide film, reducing the thickness of the oxide film as a result of chemical dissolution 217 (Mouedhen et al., 2008; Sari and Chellam, 2015). Additionally, the chloride ions also cause 218 pitting corrosion which produces small pits or holes on the Al electrode surface, leading to 219 elevated metallic aluminum loss (Mameri et al., 1998; Jiménez-Come et al., 2012; Wellner et al., 220 2018). From Figure 1b, currents from 0.10 to 0.50 A all produced FE values above 100% during 221 the 2 h EC process, consistent with observed super-faradaic dissolution. Based on a regression of 222 the experimental data (0.10- 0.50 A), the mean ratio of the actual dissolution of the Al anode to

Faraday's law model lines (i.e., the mean FE values) was 1.16. (This is similar to the average
value of all single FE values, 1.17).

225 The faradaic efficiency at the two highest currents was much lower than at 0.5 A or lower. 226 The FE at 0.70 A started to decrease at 60 min, where FE was ~ 1, then decreased markedly to 227 around 0.6 at 120 min. At 1.40 A, FE decreased dramatically after only 30 min (to 0.6) and 228 remained below 0.8 at 60 min. The low faradaic efficiencies were likely caused by passivation of the Al anode. The high dissolution rates of Al at these currents caused rapid formation of a 229 stable oxidized film that covers and passivates the Al anode, inhibiting the further dissolution of 230 231 Al to the solution, which increases resistance and reduces efficiency (Badawy et al., 1999). The 232 "pitting corrosion" effect of the high chloride ion concentration is slower than this passivating 233 process. The passivation behavior of electrodes is a serious concern for the longevity of the EC 234 process (Kabdaşlı et al., 2012), particularly given the increasingly early passivation effects as 235 current increased.

To better predict the amount of AI released under the conditions of this study, including the effects of super-faradaic dissolution, the average FE value (1.16) was applied as a modification factor to current intensities ≤ 0.50 A, and the value of *m* in the AI mass balance model (**eq 4**) was determined using a modified Faraday's law (**eq 8**),

$$240 mtextbf{m} = FE \frac{IMt}{zF} (8)$$

Based on the experimental data, *FE* = 1.16 was used for all experiments in this study when the
current intensity was 0.50 A or less.



Figure 1. Aluminum dissolution during EC: (a) Al concentration as a function of time and current
intensity (Lines are predictions based on Faraday's law.); (b) Faradaic efficiency of Al generation.

246 **3.2 Boron complexation with aluminum hydroxide solids**

243

Figure 2 shows the ATR-FTIR results for dried Al(OH)₃(s) precipitated using the 247 248 electrocoagulation process at pH 8 both with and without boron present in solution. The boron 249 solution initially contained 50 mg/L B, of which approximately 65% was removed to the solid phase. Two new peaks associated with B removal appeared at around 1433 cm⁻¹ and 1280 cm⁻¹ 250 251 for Al(OH)₃(s). These peaks are also distinct from those for boric acid in a saturated B(OH)₃ solution, which were observed at 1403 cm⁻¹ and 1144 cm⁻¹, in agreement with previously 252 253 reported spectra (Su and Suarez, 1995). These results indicate complexation of boron on the Al(OH)₃(s) surface, leading to formation of a strong Al-O-B bond. The peak close to 1430 cm⁻¹ 254 appears due to B-O asymmetric stretching, and the peak near 1280 cm⁻¹ arises because of in-255 256 plane bending of trigonal boron (Su and Suarez, 1995). Chorghe et al. (2017) also reported broad peaks at similar wavelengths (1426 cm⁻¹ and 1312 cm⁻¹) in an alum coagulated NaCl solution 257 258 containing 130 mg/L B, which were interpreted as depicting boron trigonally coordinated with

- Al(OH)₃(s). Lefèvre (2004) reported peaks at 1420 and 1280 cm⁻¹ for Al(OH)₃(s) paste with
- adsorbed B at pH 7, indicating strengthening of O-B and B-OH bonds in the surface complex =Al-
- 261 O-B(OH)₂. Sari and Chellam (2015) reported that the adsorption of B on Al(OH)₃(s) was based on
- 262 outer-sphere and inner-sphere complexation of B(OH)₃ with Al(OH)₃, confirmed by the B-O bond
- 263 shifting toward lower binding energies in XPS.



264

265

Figure 2. FTIR of boron complexation with aluminum hydroxide solids

266 **3.3 Boron removal using AI-EC at varying current intensities**

Figure 3 shows boron removal by EC, using an Al anode at pH 8, as a function of time and the applied current. As shown in Figure 3a, increasing B removal was observed with increasing time and with increasing current for currents ranging from 0.10 A to 0.50 A. As the total applied electric charge is the product of current and time, increasing operation time or current both result in a greater total applied charges. From 0.10-0.50 A current intensity, boron removal increased with increasing applied charge (Figure 4S in the Supporting Information). The highest

273 removal of B, 70%, was observed in 2 h at 0.50 A. Dolati et al. (2017) also reported 70% B 274 removal, from a solution with an initial B concentration of 100 mg/L, using aluminum EC at pH 8. 275 For a current of 0.70 A, B removal was higher than that obtained using 0.50 A during the 276 first 30 min, but then increased only 10% from 30 min to 2 h, resulting in much lower overall removal. At 1.40 A, boron removal was below that at 0.35 A at 30 minutes. These results 277 278 indicate that using too high a current adversely affects B removal by AI-EC. One of the possible 279 reasons for this is that Al ion generation is inhibited (as shown in Figure 1) by the formation of a 280 passive layer on the Al anode at high currents. Other possible reasons involve changes in the 281 morphology and structure of the $Al(OH)_3(s)$ formed in the reaction, which will be discussed in 282 the following section.

283 Figure 3b shows the relationship between B removal and Al dose (i.e., total Al generated by 284 Al-EC or added in the form of aluminum sulfate) for both Al-EC (using currents of 0.10 to 0.50 A) and coagulation using aluminum sulfate. The model line is based on the model described in 285 286 Section 3.4. Boron removal increased as more Al ions were generated, with 70% removal of B achieved by EC at an Al dose of around 2.5 g/L. Yilmaz et al. (2007) observed even higher B 287 288 removal, up to 94% when generating at Al dose of 7.45 g/L during the Al-EC process. It can be 289 seen that B removal by Al-EC was much higher than that achieved using coagulation with 290 aluminum sulfate when comparing the two processes based on total Al added, e.g., ~60% 291 removal for AI-EC at 1500 mg/L AI, versus only ~40% removal by coagulation with aluminum 292 sulfate. There are several possible explanations for the higher B removal during EC. The 293 continuous generation of $Al(OH)_3(s)$ due to Al dissolution over time in the EC system may allow 294 more B to incorporate into the Al solid structure as it forms and aggregates, while the rapidly 295 formed $AI(OH)_3(s)$ produced by chemical coagulation may result in less surface contact area or

- time for B incorporation. Additionally, hydroxide generated at the electrode results in locally
- high pH values that could induce formation of negatively charged B(OH)₄, which would adsorb
- 298 better to the Al solids.



Figure 3. Boron removal at pH 8 at varying current intensities: (a) *versus* operating time; (b)
 versus Al dose for current intensities of 0.10 A to 0.50 A, with the results compared to model
 results (solid line) and to chemical coagulation with aluminum sulfate. (Initial B concentration =
 50 mg/L; NaCl = 2000 mg/L)

To investigate the effect of Al dissolution rate (i.e., current) on B removal, samples were compared based on the B removal observed after the same concentration of Al (~900 mg/L) was generated (with longer operating times being required for samples treated with lower currents). **Figure 4a** shows B removal by Al-EC with currents of 0.20, 0.35, 0.70, and 1.40 A, which required operating times of 105, 60, 30, and 15 min, respectively, to generate about 900 mg/L of Al ions. Currents of 0.20 A and 0.35 A produced similar B removal (~52%), higher B removal than observed using 0.70 A (~43%) and 1.40 A (~27%). Particles generated using the 1.40 A current

settled rapidly (< 30 minutes), while those generated at lower currents required several hours to
settle and formed a less compact floc layer (photo, Figure 4b). Mean effective size
measurements collected after allowing the particles to stand for 24 hours (Figure 4b) show that
the solids generated with a current of 1.40 A were much larger than those in the other samples,
with the largest mean effective size of ~120 µm. The Al solids generated by currents of 0.20 A
and 0.35 A had essentially identical mean particles sizes, while the particles at 0.7 A were larger,
but still much smaller than those at 1.40 A.





Figure 4a also shows that boron was released from the Al(OH)₃ solids between initial
 collection and 24 hours, except for those of larger particle size produced by the 1.40 A current.
 B release from these samples ranged from 6 to 15% and can be explained by structural changes

326	in the Al(OH) ₃ (s), as shown in Figure 5 . XRD analysis (Figure 5a) shows no obvious peaks for the
327	Al(OH) $_3$ (s) generated using a 0.35 A current and collected immediately after Al-EC, but distinct
328	peaks in the solids generated with 1.40 A. After contact with the solution for 24 h, the 0.35 A
329	solids also show the same peaks as initially observed in the higher current sample. FTIR
330	spectroscopy (Figure 5b) of these samples shows a similar pattern. The initial solids generated at
331	0.35 A have only one peak, at 1634 cm $^{-1}$, while the 24 h aged sample shows two new peaks at
332	1063 and 879 cm ⁻¹ , which are similar to the peaks at 1065 and 880 cm ⁻¹ for the initial sample
333	generated by high current (1.40 A). Liu <i>et al.</i> (2012) reported similar peaks (1072 and 884 cm ⁻¹)
334	for boehmite (γ -AlOOH). The color of Al(OH) ₃ (s) generated at 0.35 A also changed visibly from
335	gray to white during the 24 h period, as shown in Figure 3S in the Supporting Information.
336	The XRD and FTIR results indicate that Al(OH) ₃ (s) solids generated by Al-EC using a lower
337	current intensity are initially more amorphous and better able to complex with B to form Al-O-B
338	bonds. As the solids gradually crystallize, a portion of the B is released as some of the Al-O-B
339	bonds are slowly transformed to Al-O-Al bonds. Wu et al. (2019) also reported observing
340	structural changes in Al(OH) $_3$ (s), evidenced by similar XRD and FTIR analyses, indicating a shift
341	from amorphous to more crystalline structure after 24 h. Based on their study, given enough
342	time (which can be affected by stirring or other processes), Al solid would form boehmite
343	structure. The small-intensity peaks in the XRD pattern for Al solids obtained immediately after
344	production at 1.40 A indicate some crystal structure is already present in these precipitates,
345	with characteristics similar to boehmite, which is consistent with the FTIR results (Liu et al.,
346	2012). Al solids analyzed immediately after reaction at 0.35 A show no evidence of crystal
347	structure in their XRD pattern. However, ageing for 24 hours produces the same peaks as those
348	found in the 1.40 A sample at shorter times. These results, particularly in comparison to Wu et

- al.'s results, indicate that Al solids produced from EC form similar phases under both conditions,
- 350 but that crystallization is much faster at higher currents.



351

352 Figure 5. (a) XRD and (b) FTIR analysis of Al(OH)₃(s) samples generated at 0.35 or 1.40 A

353 3.4 Boron adsorption models

To obtain a better view of boron removal over a wider concentration range, EC experiments were conducted at pH 8 using initial B concentrations ranging from 5 to 1000 mg/L and current of 0.5 A. The results are shown in **Figure 6a**, and the classic Langmuir adsorption isotherm (**eq 9**) (Chen and Jafvert, 2018b) was used to express B concentrations on the Al(OH)₃(s) as a function of the aqueous B concentration.

359
$$[B]_{Al} = \frac{K[B]_{aq}[B]_{max}}{1+K[B]_{aq}}$$
(9)

360 where $[B]_{Al}$ and $[B]_{aq}$ refer to the B concentrations in the solid phase (Al(OH)₃(s)) (mg/g) and

361 aqueous phase (mg/L), respectively; K represents the Langmuir adsorption constant, calculated

based on data shown in Figure 6a as 0.0021 L/mg, and [B]_{max} is the calculated maximum B
concentration adsorbed on Al coagulant, 538 mg/g.

As can be seen from **Figure 6a**, when the aqueous B concentration is < 100 mg/L the relationship is approximately linear, so a linear model (**eq 10**) can be used to predict B removal at low initial concentrations. Using the data shown in **Figure 3** and the same background aqueous conditions (total B concentration of 50 mg/L at pH 8) and currents ranging from 0.10 A to 0.50 A, a boron adsorption isotherm for Al(OH)₃(s) was simply regressed using a linear adsorption model (**eq 10**),

370
$$[B]_{Al} = a[B]_{aq}$$
 (10)

where *a* is the linear adsorption constant, and was found from linear regression to be 1.14 L/g
for our experimental data (Figure 6b, R²=0.96). (Using a similar approach to model B removal by
coagulation with aluminum sulfate, as shown in Figure 3b, the "a" value was only 0.392,
showing the lower affinity of boron for Al(OH)3 produced through chemical coagulation.)

375 Figure 6c shows B removal using EC with varying initial concentrations at pH 8. B removals 376 were similar for B initial concentrations of 5 mg/L and 50 mg/L, which were higher than for an 377 initial B concentration of 250 mg/L, and the data show a clear trend of decreasing B removal as 378 the initial B concentration increased. Yilmaz et al. (2007) showed that B removal decreased as 379 initial concentration increased from 100 mg/L to 1000 mg/L for both EC and chemical 380 coagulation. On the contrary, Dolati et al. (2017) reported that removal of B declined when the 381 initial B conentration was reduced from 100 mg/L to 10 mg/L. A predictive model (Section 2.4) 382 describing B removal by AI-EC was developed by coupling the linear adsorption model (eq 10) for an initial B concentration of 50 mg/L with mass balances on B (eq 5) and Al (eq 8). As can be 383 384 seen in Figure 6c, the predictive model was in reasonably good agreement with experimental

values for initial B concentrations of 5 and 50 mg/L, but the model did not predict the observed
decrease in boron removal at 250 mg/L.

Figure 6d shows B removal versus initial B concentration after 15 and 30 min of Al-EC 387 treatment at 0.50 A, which produced about 320 and 640 mg/L of Al(OH)₃(s), respectively. The 388 results clearly show that B removal decreased with increasing initial B concentration, confirming 389 390 the earlier results (Figure 6c). Combining a Langmuir adsorption isotherm with the mass balance 391 equation yields predictions in good agreement with experimental data for a broad range of 392 initial B concentrations and for varying Al concentrations, and much better predictions for high 393 initial B concentrations than those when using the linear adsorption model. As boron 394 concentrations increase, the deviation between the two models also increases, as shown in 395 Figure 6d. Indeed, the values predicted using the Langmuir adsorption model were also in good 396 agreement with the experimental data for an initial B concentration of 250 mg/L shown in 397 Figure 6c (model lines shown in Figure 5S). In summary, the Langmuir model can be used to 398 describe B removal by EC from various water environmental conditions over a broad range of 399 initial B concentrations (e.g., freshwater, seawater, wastewater or produced waters), while the 400 linear model is reasonably accurate only for initial B concentrations of 100 mg/L or less.



Figure 6. Modeling boron removal by AI-EC: (a) Langmuir adsorption isotherm for initial B
 concentrations ranging from 5 mg/L to 1000 mg/L; (b) Linear adsorption isotherm for an initial B
 concentration of 50 mg/L; (c) Boron adsorption with varying initial B concentrations compared
 to linear model for an initial B concentration of 50 mg/L; (d) Comparison of Langmuir model
 (solid lines) and linear B removal model (dashed lines) to removal data at 0.5 A for higher initial
 boron concentrations.

409 **3.5 Effect of pH on boron adsorption**

410 Solution pH has a notable impact on boron removal using Al-EC. Figure 7a shows fractional B 411 removal as a function of time for various initial pH values when the pH was not controlled during 412 the EC process (In these experiments, the current was 0.50 A, the initial B and NaCl 413 concentrations were 50 mg/L, and 2000 mg/l, respectively, and initial pH was adjusted by adding HNO₃ or NaOH before EC process.). For starting pH values between 6 and 8, pH increased over 414 415 time to a final pH of about 8.5 after one hour. For a starting pH of 10, the pH decreased quickly to 9.4 during the first 5 min, then remained constant for the rest of the experiment. For a 416 starting pH of 9, the pH stayed relatively constant throughout the experiment. The final B 417 418 removals (after 1 h) were similar for starting pH values between 6 and 8, and higher than those 419 obtaining with an initial pH of 9 or 10. The stabilization of pH over time is attributed to the 420 buffering effect of boric acid. Sayiner et al. (2008) reported that the pH values of B solutions in 421 iron and aluminum EC systems changed sharply until a maximum value was reached, then 422 remained relatively stationary, in similar fashion to what was observed for the aluminum EC 423 system in this study.

424 Boron removal at constant pH values ranging from 6 to 10 is shown in Figure 7b. Boron 425 removal increased with increasing pH from 6 to 8, and then decreased at higher pH values of 9 426 and 10. The best removal of B occurred at pH 8 with approximately 40% removal at 30 min, and 427 60% at 60 min. These results were virtually the same as those of Yilmaz et al. (2005), who also 428 reported that a pH of 8 was optimal for B removal by EC with aluminum. EC produced similar 429 amounts of solids at initial pH values of 7, 8 and 9, but slightly less at pH 6 (presumably due to 430 formation of more positively charged soluble Al hydroxo complexes) and much less at pH 10, 431 which is attributable to the formation of substantial amounts of tetrahydroxoaluminate ions,

432	$Al(OH)_4$. A pH of 8 was also found to be optimal for boron removal by alum coagulation (Figure
433	6S). The zeta potential of the Al solids produced by Al-EC at varying pH values is shown in Figure
434	7c. Zeta potential decreased with increasing pH, as expected, switching from positive to
435	negative at pH slightly below 9. Based on the dissociation of boric acid ($pK_a = 9.2$, eq 1), at pH 9
436	less than half of the B would be present in the form of negatively charged borate ions. At higher
437	pH values, the concentration of borate ions increases, but so does the negative charge on the Al
438	solids according to Al(OH) $_3$ stability diagram (Kartikaningsih <i>et al.</i> , 2016). At a pH of 8, less than
439	10% of the B is present as borate ions, but as borate ions are bound to the positively charged
440	$Al(OH)_3(s)$ solids, additional borate ions form and then are removed. Although the zeta potential
441	of Al solids is higher at pH 6 and 7, the fraction of negatively charged B species is negligible, and
442	neutrally charged boric acid is not attracted to the positively charged Al solids.





Figure 7. pH effect on boron removal by AI-EC using a current of 0.50 A: (a) Boron removal and
pH changes during AI-EC treatment with an initial B concentration of 50 mg/L; (b) Boron removal
after 30 and 60 min. for selected constant pH values; (c) Zeta potential of AI solids after 60 min
at selected constant pH values.

3.6 Effect of TDS on boron adsorption

450	Figure 8 shows the effect of varying the NaCl (TDS) concentration on B removal using Al-EC
451	at pH 8. Boron removal using a current of 0.50 A was around 40% for solutions with 600, 2,000,
452	and 10,000 mg/L NaCl (Figure 8a). In high TDS solutions (2,000 and 10,000 mg/L NaCl), B
453	removal increased as time and Al generation increased, with up to 70% removal at 2 h.
454	However, B removal did not increase after 60 min for the 600 mg/L NaCl solution, and
455	decreased at 90 min. Figure 8b shows the mean effective sizes of Al solids at 30 min and 60 min
456	for each solution. At 30 min, when the concentration of Al solids was around 640 mg/L, the
457	effectives size of the AI solids in varying TDS solutions were similar; all were around 5 μ m. But at
458	60 min, the effective size of the Al solids in the 600 mg/L NaCl solution increased dramatically to

120 μ m, much larger than those of the solids in the other two solutions, although all of the 459 460 solutions had similar total Al solids concentrations. As can be seen in the picture in Figure 8b, 461 the sedimentation performance of the Al solids in the 600 mg/L NaCl solution was also better 462 than those of the solids in the other two solutions. Lee and Gagnon (2016) also reported that EC 463 formed larger, more compact flocs in low salt solutions. These results indicate that higher TDS 464 (or ionic strength) leads to Al solids with a more amorphous structure and worse sedimentation 465 performance, but better adsorption of B than the more crystalline solids formed at low TDS. In 466 addition, TDS was increased by adding NaCl. With increased chloride ion concentration the 467 removal of passivating layers on Al anode surface accelerates, allowing the reaction to act in a super-faradaic capacity. Electrode passivation in high chloride solutions is therefore reduced at 468 equivalent operating conditions. For these reasons, higher TDS (NaCl) concentrations facilitate 469 470 use of higher current intensities, i.e., the limit on the Al generation rate for achieving optimal B removal increases with increasing TDS. Figure 8c confirms this conclusion by demonstrating that 471 472 a lower current intensity (0.35 A) led to similar B removal in the 600 and 2000 mg/L NaCl 473 solutions in 2 h.





476 Figure 8. Boron removal by Al-EC from solutions with varying NaCl concentrations: (a) Boron
477 removal *versus* time at 0.50 A; (b) Mean effective size of Al solids and total Al generated after 30
478 and 60 min at 0.50 A; (c) Boron removal over time at 0.35 A with 600 and 2,000 mg/L as NaCl
479 added.

3.7 Boron removal from natural and produced waters by Al-EC

481	Figure 9 shows boron removal at pH 8 from a Kansas River water sample and an oilfield
482	produced water sample, both collected in Douglas County, KS. For the Kansas River water
483	sample spiked with 10 mg/L B (Figure 9a), B removal increased with increasing time. Up to 50%
484	B removal was achieved in 2 h using 0.20 A, and the removals predicted (using the Langmuir
485	adsorption model) were close to the experimental values. Using 0.35 A, B removal increased
486	during the first hour, and exceeded the removal achieved using 0.20 A, but decreased after that.
487	The model predicted removals were much greater than the experimental values and the
488	difference increased after 1 h. A likely reason for these results is that given the low TDS of the

Kansas River water, the 0.35 A current began generating more crystalline solids after 1 h, which
reduced the solids' capacity to adsorb B.

491 Figure 9b shows B removal from an oilfield produced water sample spiked with 50 mg/L B. Because the TDS of the water sample was much higher than that of Kansas River water (31,000 492 493 mg/L; see Table 2S), higher currents were applied. B removal increased over time at both 0.5 A 494 and 1.0 A, and up to 80% B was removed in 2 h with a 1.0 A current. The gaps between model 495 predictions and experimental data were large during the first hour, but became smaller at 90 496 min and 120 min. Possible reasons why B removal was less than predicted include: 1) the high 497 conductivity caused by high TDS (31,000 mg/L) may adversely affect contaminant removal 498 during the EC process because the corresponding high ionic strength clearly affects the kinetics 499 and equilibria of reactions between charged species (Lin and Peng, 1994; Can et al., 2003); and 2) removal of divalent cations (or hardness, e.g., Ca²⁺, Mg²⁺, Ba²⁺, and Sr²⁺), which occurred 500 501 primarily during the first hour (as shown in Figure 7S), may have altered the composition and characteristics of the Al solids and affected their ability to adsorb B (Brahmi et al., 2016; 502 503 Hakizimana et al., 2016).



- Figure 9. Boron removal by AI-EC from real water samples spiked with B: (a) Kansas River water
 spiked with 10 mg/L B; (b) Oilfield produced water from Douglas County, KS, spiked with 50
- 507 mg/L B. (Lines show Langmuir model predicted values.)

508 Conclusions

509 Under typical water quality conditions, aqueous boron (B) is present primarily as boric acid 510 (H₃BO₃), which is neutrally charged, making B particularly challenging to remove. This research 511 investigated B removal using electrocoagulation (EC), with aluminum and carbon electrodes 512 electrolytically dissolving aluminum ions into the water to act as a coagulant. FTIR analysis 513 showed the formation of surface complexes of B with Al solids $(Al(OH)_3(s))$, providing a pathway 514 for B removal from solution. B removal increased with Al dissolution (and Al solids formation), 515 and electrocoagulation was found to achieve better B removal than coagulation with aluminum 516 sulfate when the same amount of AI was added. More amorphous AI solids with a higher B 517 adsorption capacity are formed using low currents, while more crystalline solids with a lower 518 adsorptive capacity for B, but better sedimentation properties, are formed using higher currents. 519 The optimal pH for AI-EC was found to be 8. A linear adsorption model was found to be suitable 520 for predicting B removal for initial B concentrations up to 50 mg/L. At higher initial B 521 concentrations of B, the linear model over-predicted B removal, but the Langmuir adsorption 522 model predicted B removal by AI-EC reasonably well for initial B concentrations ranging from 5 523 to 1,000 mg/L, provided that the current was low enough to avoid formation of less amorphous 524 Al solids. The limiting current depends strongly on the TDS concentration; samples having a 525 higher TDS concentration, such as produced water, can tolerate a higher current without 526 forming solids having a lower adsorptive capacity for B. Two real water samples (a river water 527 and an oilfield produced water), both spiked with B, were treated using the AI-EC process. Up to

528
50% of the B was removed from the river water (spiked with 10 mg/L of B) in 2 hours with a 0.2
529
A current; and 80% of the B was removed from produced water (spiked with 50 mg/L B) in 2
530
hours with a 1.0 A current.

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- 657

- FTIR analysis indicated B(OH)₃ complexation with Al(OH)₃(s) via surface hydroxyl groups;
- X-ray analysis showed B removal influenced by morphology of Al solid generated by EC;
- Quantitative models were developed to describe B removal using AI-EC;
- Effects of significant AI-EC operating parameters were determined for B removal.

Journal Prevention

Declaration of interests

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

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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