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1 **Removal of boron, fluoride and nitrate by electrodialysis in the presence of organic matter**

2

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14 **Abstract**

15 *The removal of the trace inorganic contaminants boron ($B(OH)_4^-$), fluoride (F^-) and nitrate (NO_3^-)*
16 *from synthetic aqueous solutions containing organic matter using electrodialysis was investigated.*
17 *The transport of the contaminants through the ion-exchange membranes was evaluated in relation*
18 *to hydrated ionic radius, whereby a positive correlation was found in absence of organic matter.*
19 *NO_3^- , with the smaller hydrated ionic radius and weaker hydration shell, was removed more*
20 *effectively than F^- , which has a larger hydrated ionic radius and stronger hydration shell. The*
21 *removal of F^- and NO_3^- was not significantly influenced by solution pH due to their pH independent*

22 *speciation. However, the removal of boron was dependent on increasing solution pH and the degree*
23 *of demineralization. Dissolved organic matter (humic acid, tannic acid and alginic acid) resulted in*
24 *enhanced removal of boron and F⁻ as a result of the binding of F⁻ within the organic matter*
25 *structure and complexation of boric acid (B(OH)₃) with carboxylate groups in the organic matter.*
26 *Deposition of organic matter to the anion-exchange membranes was noted. Inorganic trace*
27 *contaminant and organic matter membrane deposition influenced system performance in regards to*
28 *an increase in stack resistance and decrease in removal and flux of total dissolved solids.*

29

30 *Keywords: Electrodialysis; Ion transport; Inorganic trace contaminant removal; Dissolved organic*
31 *matter; Fouling; Groundwater/Brackish water*

32

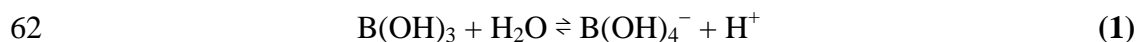
33 **1. Introduction**

34 Membrane processes such as electrodialysis (ED) are increasingly being utilised in water treatment
35 to remove dissolved contaminants. A wide range of inorganic trace contaminants, including fluoride
36 (F⁻) and nitrate (NO₃⁻), can be found in surface, brackish and groundwater. The occurrence and fate
37 of these contaminants is an environmental and public health concern. Concentrations of F⁻ in
38 surface water are relatively low (<0.1–0.5 mg/L) [1], while concentrations up to 20 mg/L have been
39 found in groundwater [2]. The harmful effects of excess F⁻ (dental and skeletal fluorosis) have been
40 widely studied [3, 4]. NO₃⁻ concentrations in surface and groundwater have increased worldwide
41 due to heavy utilization of artificial fertilizers [5]. Deleterious health effects due to NO₃⁻ include
42 infantile methemoglobinaemia (known as ‘blue-baby’ syndrome) and cancer risks for adults and
43 older children [5]. According to the World Health Organization (WHO) [1], the European Union
44 (EU) Drinking Water Directive [6] and the Australian Drinking Water Guidelines (ADWG) [7], the
45 maximum levels for F⁻ and NO₃⁻ in drinking water are 1.5 and 50 mg/L, respectively. However, for
46 NO₃⁻ a level of 25 mg/L has been recommended [1, 7]. Due to its high selectivity and low chemical
47 demand, ED has proved an efficient method for desalination and the removal of F⁻ and NO₃⁻ [8, 9].

48

49 Boron is another contaminant of interest due to its occurrence in seawater and difficulty of removal
50 in desalination. While natural concentrations in surface and groundwaters are usually low,
51 concentrations up to 100 mg/L have been found as a result of wastewater discharge [10]. Long-
52 term consumption of water and food products with increased boron content results in
53 malfunctioning of cardiac-vascular, nervous, and alimentary systems of humans [11]. The WHO
54 and EU Council have set limits of 0.5 mg/L and 1 mg/L for drinking water, respectively [1, 6].
55 Boron removal using ED has previously been studied [12, 13]; however its interaction with organic
56 matter (OM) and the subsequent impact on its removal has not been investigated. ED is capable of
57 removing 42 – 75 % of boron, with removal efficiency dependent on solution pH (97 % at pH 9 -
58 10) and the degree of desalination [10, 13]. In acidic and near neutral aqueous environments boron
59 is mainly present as B(OH)₃ and partially as borate ions according to the dissociation reaction ($K_a =$
60 6×10^{-10} , pK_a 9.24 at 25°C) [14]:

61



63

64 Organic matter (OM) occurs in aquatic ecosystems in concentrations of 0.5 to 100 mgC/L [15] and
65 have been a focal point in water treatment research as they are precursors to disinfection by-
66 products. Dissolved organic substances (e.g. humic substances) act as ligands for metal ions, oxides
67 hydroxides, minerals and organic micropollutants and form water-soluble and water-insoluble
68 complexes [16]. Organic matter comes with seasonal and location (origin) specific characteristics
69 and hence it is important to consider diverse groups such as humics, polyphenols, and
70 polysaccharides.

71

72 In ED, organic substances, such as humate, deposit on the ion-exchange membranes and can cause
73 increases in electrical resistance of the membranes [17]. HA in particular has been reported to be

74 responsible for fouling in ED which affects salt flux [18-20]. As most OM is negatively charged at
75 neutral pH, deposits form predominantly on the anion exchange membranes. The impact of such
76 deposits on removal of specific contaminants is not well understood. Further, solute-solute
77 interactions (such as complexation) of OM with inorganic compounds (B(OH)_4^- , F^- and NO_3^-) has to
78 date not been investigated. As such interactions are likely to affect removal, the main objective of
79 this study was to examine the influence of pH and three types of OM on the removal of B(OH)_4^- , F^-
80 and NO_3^- during ED systematically. In order to achieve this goal the project was conducted in five
81 stages, namely (1) mechanisms of inorganics removal (in absence of OM), (2) OM removal, (3)
82 impact of OM on inorganics removal, (4) inorganic membrane deposit formation, and (5) organic
83 deposit formation.

84

85 **2. Materials and Methods**

86 *2.1. Chemicals and solution preparation*

87 The feed solution (diluate and concentrate, 4L each) was prepared by dissolving ACS reagent grade
88 NaCl (5 g/L) and NaHCO_3 (84 mg/L) (Fisher Scientific UK), NaF (5 mg/L; total mass 2.1 mmol),
89 NaNO_3 (100 mg/L; total mass 57 mmol) and H_3BO_3 (10 mg/L; total mass 7.4 mmol) (Sigma
90 Aldrich UK) in ultrapure water. The concentrations of H_3BO_3 , F^- and NO_3^- were selected within the
91 range found in brackish waters [12, 21]. Experiments with an identical concentration of 10 mg/L for
92 H_3BO_3 , F^- and NO_3^- as well as detailed investigation of the pH range 8.5 to 9.5 for the initial NaCl
93 concentrations of 5 g/L and 20 g/L (results not shown). Data on hydrated ionic radii and hydration
94 energy are outlined in Table 1.

95

96

[Table 1]

97

98 Na₂SO₄ (99 % purity) was used in the electrode rinse solution (Fisher Scientific UK) and analytical
99 grade reagents NaOH and HCl (Fisher Scientific UK) were used for pH adjustments and membrane
100 cleaning.

101

102 Three different types of OM were selected for use in this study: humic acid sodium salt (HA),
103 tannic acid (TA) and alginic acid sodium salt (AA) (all Sigma Aldrich UK). The concentration of
104 OM in different waters is highly variable [15] and hence an average OM concentration of 12.5
105 mgC/L was used in all experiments. The respective OM solutions were prepared by dissolving HA,
106 TA and AA in ultrapure water and adding them to the feed solution. Physical and chemical
107 properties of the OM compounds are outlined in Table 2.

108

109 [Table 2]

110

111 Major functional groups of HA include carboxylic, phenolic, alcohol/aldehyde acids, and methoxyl
112 and HA is negatively charged at neutral pH [22]. As a polyphenol, TA can form inter- and
113 intramolecular hydrogen bonds and often exists in solution as loosely bound complexes of
114 molecules [23]. At acidic pH TA is neutrally charged, however as pH increases the charge becomes
115 negative [24]. AA is a naturally occurring hydrophilic colloidal polysaccharide, is obtained from
116 brown seaweed and exhibits negatively charged carboxylate and neutral hydroxyl groups at pH 7
117 [25]. Below pH 4, the charge density decreases causing increased aggregation, whereas above pH 8
118 dissociation has been observed [26].

119

120 2.2. Electrodialysis System

121 The ED stack used was a BEL-500 unit (Berghof, Germany) with seven Neosepta CMX-SB cation-
122 exchange membranes (CEMs) and six Neosepta AMX-SB anion-exchange membranes (AEMs)
123 (supplied by Eurodia, Germany; manufactured by Astom Corporation, Tokyo, Japan) with an

124 available membrane area of 58 cm² each. The ED cell was connected to a DC electric potential
125 (GW Instek DC Power supply Model GPR-1810HD, Taiwan) through TiO₂-coated titanium
126 electrodes. A schematic of the ED system is shown in Figure 1.

127

128 [Figure 1]

129

130 The limiting current density (LCD, 7.8 mA/cm²) was derived from a set of current-voltage curves
131 measured in the ED cell and in consequence the applied voltage fixed to 10V to operate below the
132 LCD. Diluate and concentrate were recirculated through the ED cell at a flow rate of 1.5 L/min until
133 the desired product concentration (0.5 g/L NaCl) was achieved in the diluate. 0.5 mol/L Na₂SO₄
134 was used as an electrode rinse solution at a flow rate of 1.5 L/min, in order to prevent the generation
135 of chlorine or hypochlorite, which could be hazardous for the electrodes, had NaCl been used
136 instead.

137

138 The resistance across the ED stack was calculated using Ohms law:

139
$$R = \frac{E}{I} \quad (2)$$

140 Where, R is the resistance (Ohm), E the electrical potential (Volt) and I the electrical current
141 (Ampere).

142

143 2.3. Analytical Methods

144 The pH, electrical conductivity (EC) and temperature of samples taken from the diluate and
145 concentrate during each experiment was measured using a pH/Conductivity meter (Multiline P4
146 combination pH electrode, WTW Germany).

147

148 F⁻ and NO₃⁻ concentrations were determined using ion-selective electrodes (ISE) in conjunction
149 with a standard reference electrode connected to a Metrohm 781 Ion Meter (UK). The ISEs were

150 regularly calibrated, with and without OM, and cleaned using standard methods. Standards and
151 samples were mixed with a total ionic strength adjustment buffer (TISAB) to avoid possible
152 interferences resulting from changes in solution pH and conductivity. NO_3^- sample analysis was
153 checked using a Quickchem 8500 FIA Nutrient Analyser (Lachat Instruments, Colorado, USA) and
154 F^- analysis was verified using a DX-500 ion chromatograph (DIONEX, Sunnyvale, CA, USA).
155 Sample concentrations were in agreement with ISE results. Total concentrations of H_3BO_3 were
156 determined by ICP-OES using a Perkin Elmer Optima 5300DV instrument (Perkin Elmer, UK).

157

158 UV-Visible Spectrometry (Varian Cary 100 Scan, UK) was utilized to determine the absorbance of
159 OM in experimental samples. HA was analyzed at a wavelength of 254 nm, whereas TA and AA
160 were analyzed at wavelengths of 275 nm and 198 nm, respectively. Specific UV absorbance
161 (SUVA, $\text{L}/\text{mg}\cdot\text{m}$) values were calculated for HA as in equation (2):

$$162 \quad \text{SUVA} = \frac{\text{UV Abs}(/m)}{\text{DOC (mgC/L)}} \times 100 \quad (2)$$

163

164 Non-purgeable organic carbon (NPOC) concentrations were determined using a total organic
165 carbon analyser (Shimadzu TOC-VCPH, UK).

166

167 The mass of contaminants deposited on the membranes was calculating using a mass balance:

$$168 \quad M_{\text{Dep}} = M_{\text{F}} - M_{\text{D}} - M_{\text{C}} \quad (3)$$

169 where M_{Dep} is deposit, M_{F} feed, M_{D} diluate and M_{C} concentrate mass (mmol for H_3BO_3 , F^- , NO_3^-),
170 respectively.

171

172 *2.4. Experimental Protocol*

173 Concentrate and diluate pH was maintained constant during the experiments and adjusted by the
174 addition of 1 mol/L HCl and/or NaOH in the range of pH 3-12. EC of both solutions was
175 continuously monitored and samples were collected at the beginning and at 20 minute intervals for

176 analyses of H₃BO₃, F⁻, NO₃⁻, UV-Vis absorbance and non-purgeable organic carbon (NPOC). After
177 the completion of each experiment, cleaning solutions of 0.1 mol/L HCl, 0.1 mol/L NaOH and
178 ultrapure water were circulated through the ED cell for 20 minutes each in order to remove any
179 deposits. Samples taken from the cleaning solutions were analysed for UV-Vis absorbance and
180 NPOC. After each set of OM experiments, the ED cell was dismantled and photographs were taken
181 of the anion- and cation-exchange membranes.

182

183 Ion and EC removal (R_D , %) from the diluate was calculated using eqn (4):

$$184 \quad R_D = \frac{(C_{Di}^0 - C_{Di}^T)}{C_{Di}^0} \times 100\% \quad (4)$$

185 where, C_{Di}^0 is the initial diluate ion concentration or EC and C_{Di}^T is the diluate ion concentration or
186 EC in the time period T (hours). Average ion and EC removal (%) was calculated along with
187 standard deviation (\pm %). Note that ion removal includes deposit formation, while the flux of ions
188 and EC (J_i , mmol/m².h for ions and mS/cm/m².h for EC) across the membranes was calculated
189 using eqn (5):

$$190 \quad J_i = \frac{(C_{Ci}^T - C_{Ci}^0)}{A_m T} \quad (5)$$

191 where, C_{Ci}^T (mmol for B(OH)₄⁻, F⁻ and NO₃⁻, mS/cm for EC) is concentrate mass (ions) in the
192 concentrate in the time period T , C_{Ci}^0 is the initial mass within the concentrate and A_m is the
193 membrane area (m²) used in the transport of the respective ion.

194

195 **3. Results and Discussion**

196 *3.1. Inorganic trace contaminant removal*

197 As a first stage the removal of ions in the absence of OM was determined to establish a baseline.

198 The removal of F⁻ from the diluate is shown in Figure 2A. The removal of F⁻ was independent of

199 pH, which is due to the pH independence of F^- speciation [27]. F^- ions removal was $65.6 \pm 12.0 \%$,
200 while F^- flux was approximately $10 \text{ mmol/m}^2\cdot\text{h}$ (see Figure 3A).

201

202 [Figure 2]

203

204 [Figure 3]

205

206 Removal of NO_3^- is higher than that of F^- but equally pH independent (Figure 2B), again because
207 NO_3^- speciation does not vary over the pH range studied [28]. The average removal of NO_3^- was
208 $94.1 \pm 1.3 \%$ while NO_3^- flux was significantly higher than for F^- and decreased gradually from
209 830 to $408 \text{ mmol/m}^2\cdot\text{h}$ (Figure 3B).

210

211 B(OH)_3 does not dissociate at pH 3-8 and in consequence is not transported effectively through the
212 AEM (see Figure 2C). Above pH 9 removal increases to 61.2% at pH 12 due to B(OH)_3
213 dissociation and speciation hence plays an important role. While Yazicigil *et al.* [13] determined
214 that pH 9 was the optimal point for B(OH)_4^- removal, in this study it was only 13.7% at pH 9.
215 B(OH)_4^- flux is in the same order of magnitude as F^- but increased during experiments (see Figure
216 3C) which confirms the findings of Yazicigil *et al.* who attributed this to the increase in
217 electrochemical potentials gradient between the diluate and concentrate (i.e. larger difference in salt
218 concentration) [13]. The dissociation constant of B(OH)_3 decreases with increasing NaCl
219 concentration [29]. Further ED experiments were undertaken to examine this effect with a solution
220 pH range between 8.5 and 9.5 (insert Figure 2D) at two feed NaCl concentrations of 5 and 20 g/L
221 NaCl. In the 5 g/L experiment B(OH)_4^- removal ranged from 6.1% at pH 8.5 to 29.4% at pH 9.5.
222 B(OH)_4^- was not removed over this pH range in the 20 g/L experiment presumably due to the
223 higher concentration of competitive ions within the diluate. In consequence, no discernable shift in

224 the dissociation constant of $B(OH)_3$ was observed. The results demonstrate however that NaCl
225 concentration affects removal of other ions.

226

227 The ionic characteristics (Table 1) can be used to explain differences in the transport (removal and
228 flux) of F^- and NO_3^- through the ion-exchange membranes. As no data was available on the
229 hydrated radius of $B(OH)_4^-$, comparison of $B(OH)_4^-$ removal and ionic characteristics is not
230 discussed. Ions with smaller intrinsic crystal radii have higher hydration numbers, larger hydrated
231 radii and hold their hydration shells more strongly [30], as illustrated in Figure 4. The crystal ionic
232 radius of F^- is 0.116 nm compared with 0.179 nm for NO_3^- . The larger the crystal ionic radius the
233 more diffuse the electric charge and the fewer water molecules surround the ion [31]. Therefore,
234 NO_3^- ions are less hydrated than F^- ions may separate from its hydration layer [30] and transport
235 through the ion-exchange membranes more easily.

236

237 The strength of hydration of F^- and NO_3^- is quantified by the Gibbs energy of hydration and the
238 number of water molecules within their hydration shells. NO_3^- has a lower Gibbs free energy (-275
239 kJ/mol compared to -345 kJ/mol for F^-). While it is to date not understood if water molecules
240 separate from their ions during transport through ion-exchange membranes, it is hypothesised that
241 separation is possible if the 'transport energy' is greater than the Gibbs free energy that bonds the
242 hydrated shell to the ion.

243

244

[Figure 4]

245

246 Ion mobility ionic permeabilities [32] further influence transport through ion-exchange membranes.
247 The ionic mobility of NO_3^- in solution ($7.4 \times 10^{-8} \text{ m}^2/\text{sV}$) solution is greater than the ionic mobility
248 of F^- ($5.7 \times 10^{-8} \text{ m}^2/\text{sV}$) [33]. The current passing through an ionic solution in ED and the resultant
249 transport of ions is related to the conductivity of the ionic solutions. The ion equivalent conductivity

250 of NO_3^- ($71.5 \text{ cm}^2/\Omega.\text{equiv}$) is also greater than that of F^- ($55.4 \text{ cm}^2/\Omega.\text{equiv}$), all factors
251 contributing to higher flux of NO_3^- than F^- . To confirm those results independent of their
252 concentration, an experiment with the same initial mass concentration for boron, F^- and NO_3^- (10
253 mg/L at pH 10) was carried out. The removal of NO_3^- was 95.3 % compared with 76.2 % for F^- ,
254 further indicating that NO_3^- with the smaller hydrated radius is removed more efficiently than F^-
255 with the larger hydrated radius.

256

257 *3.2. Organic matter removal*

258 Figure 5 shows the removal of OM as a function of solution pH in diluate and concentrate. The fact
259 that OM is removed from both compartments indicates that this removal is a deposition on the
260 membrane rather than transport through the membrane. However, staining of the membranes
261 indicates that membrane penetration also occurs. Removal of AA from the diluate is low with an
262 average of $9.2 \pm 1.6 \%$ and independent of pH given its negative charge at pH 3-12. The removal of
263 HA and TA from the diluate is higher with an average removal of $19.1 \pm 3.7 \%$ and $19.8 \pm 9.5 \%$,
264 respectively. While HA removal is pH independent, the removal of TA increased with pH to 44.3 %
265 at pH 12 due to its increasing negative charge. Removal of OM from the concentrate was less than
266 from the diluate due to electrostatic repulsion with the negatively charged functional groups in the
267 CEMs adjacent to the concentrate compartment. This confirms the results of Park et al. who found
268 that deposits occur mostly on the diluate side of AEM membranes.

269

270 [Figure 5]

271

272 *3.3. Effect of organic matter on inorganic trace contaminant removal*

273 Organic matter (OM) deposits on the membranes and interacts with inorganic contaminants. The
274 removal of F^- was greater in the presence of OM (Figure 2A), which can be attributed to the binding
275 of F^- to the OM [16]. The average percentage of F^- ions removed with TA was $74.8 \pm 6.0 \%$,

276 followed by AA and HA with 72.9 ± 5.8 % and 72.5 ± 4.5 % respectively. The flux of F^- was
277 reduced in the presence of OM. The final flux (after 140 minutes) was $10.0 \text{ mmol/m}^2\cdot\text{h}$, 8.6
278 $\text{mmol/m}^2\cdot\text{h}$ and $9.4 \text{ mmol/m}^2\cdot\text{h}$ with HA, TA and AA, respectively compared to $10.7 \text{ mmol/m}^2\cdot\text{h}$ in
279 the absence of OM. Combined increase in removal and reduced flux indicates F^- membrane
280 deposition.

281

282 No significant difference in NO_3^- due to OM; HA (91.9 ± 3.5 %), TA (91.4 ± 4.9 %) and AA (92.6
283 ± 0.8 %) removal was observed. For experiments with TA, NO_3^- removal was highest under acidic-
284 neutral pH conditions ($95.2 - 93.2$ % at pH 3 - 7). In HA experiments, NO_3^- removal was pH
285 independent while the flux of NO_3^- (Figure 3B) was reduced in the presence of OM. This again
286 demonstrated some degree of membrane deposition.

287

288 The presence of OM also enhanced boron removal between pH 3 and 8 (Figure 2C) while above pH
289 9, the removal of B(OH)_4^- in the presence of OM was lower. B(OH)_4^- flux at high pH was lower in
290 the presence of OM (Figure 3C), and again results indicate B(OH)_4^- -OM complexation and
291 B(OH)_4^- membrane deposition.

292

293 *3.4. Inorganic trace contaminant membrane deposition*

294 The deposit formation can be quantified using mass balance. The mass of F^- deposited on the
295 membranes is shown in Figure 6A, with negligible deposition in experiments without OM. In the
296 presence of OM the mass of F^- deposited was between 0.1 and 0.6 mmol (4.7 and 28.8 % initial
297 mass); with a greater amount deposited with HA and TA. HA contains voids which can trap
298 inorganic compounds [34] and binding of F^- has been shown to be pH dependent [16]. Hayes [16]
299 studied the binding of F^- to HA as a function of solution pH (5.0 - 6.6) and in this narrow pH range
300 F^- was being trapped within the large structure of HA rather than bound to a particular functional
301 group. As solution pH increases HA deprotonates and the negative charge on the carboxylates

302 repels the F^- ion. This phenomenon was not observed in this current study due to the fact that the
303 adsorption of F^- in ED would be governed by several other factors (e.g. presence of other
304 contaminants).

305

306 The mass of NO_3^- deposited on the membranes was greater in experiments with OM (Figure 6B)
307 with values of between 4.6 and 13.8 mmol (8.1 and 24.2 % initial mass). Contrary to the negative
308 charge of HA above pH 5 (Table 2) the mass of NO_3^- adsorbed to the membranes in the presence of
309 HA increased above pH5. Adsorption of NO_3^- in experiments with TA was independent of pH. In
310 the presence of AA, the mass of NO_3^- adsorbed was lower at pH 6 - 8 because repulsion between
311 the negatively charged AA and NO_3^- would be expected.

312

313 The mass of $B(OH)_4^-$ deposited on the membranes is greater in experiments with OM (Figure 6C)
314 with values of between 0.3 and 1.4 mmol (4.0 and 19.0 % initial mass). Removal of $B(OH)_3$
315 between pH 3 and 8 (Figure 2C) may be the result of $B(OH)_3$ complexation with polar organic
316 compounds [35], such as HA. Schmitt-Kopplin *et al.* [36] postulated that $B(OH)_3$ binds to
317 carboxylate groups (COO^-) within HA where it forms a transient hydrogen bonded structure with
318 the HA. A schematic of this complexation mechanism is shown in Figure 7. Due to the transport
319 direction of the negatively charged HA, $B(OH)_4^-$ is deposited on the AEMs.

320

321 [Figure 7]

322

323 3.5. Organic matter membrane deposition

324 UV-Vis and NPOC measurements showed a decrease in OM within the ED system over the
325 duration of each experiment. The reduction of OM in both diluate and concentrate indicates that the
326 OM is deposited. Figure 8 shows that the mass of OM (mgC) deposited on the AEMs was greater
327 than the mass deposited on the CEMs, which confirms results Lee *et al.* [20]. The negatively

328 charged HA deposits more readily on the positively charged AEMs in experiments with a higher
329 solution pH. However, Park *et al.* [37] showed that HA has a negative zeta potential in a wide pH
330 range, so that it can foul AEMs in almost the entire pH range. In this study the amount of HA
331 deposited on the AEMs showed a slight decrease with increasing solution pH (from pH 6) (Figure
332 8A) which cannot be explained by repulsive forces. The macromolecular structures of humic
333 substances influences the properties and affinities of these materials [38]. According to Chen and
334 Schnitzer [39], humic substances behave like uncharged (spherical) polymers at very low pH
335 whereas at high pH, they exhibit polyelectrolytic character of linear shape. Lee *et al.* [17] postulated
336 that the fouling of an AEM is related more to the properties of the foulant (humate) than the
337 electrostatic force between the foulant and the membrane.

338

339

[Figure 8]

340

341 Unlike HA, the mass of TA deposited on the AEM was pH independent (Figure 8B), with an
342 exception (decrease) at neutral pH. As large molecular weight organics have more difficulty in
343 permeating the AEMs [37], TA, with its lower molecular weight, has increased potential for
344 transportation through the AEM compared to HA.

345

346 The mass of AA deposited on the AEMs was lower than HA and TA over the studied pH range
347 (Figure 8C). Avaltroni *et al.* [26] found that the structure of AA follows three pH dependent trends
348 (1) increased aggregation below pH 4 due to a decrease in charge density, (2) molecular expansion
349 between pH 4 and 8 and (3) dissociation above pH 8. The variability seen in the mass above pH 8
350 could be attributed to AA dissociation.

351

352 The AEM surface in contact with the diluate showed visible fouling with HA and TA. This fouling
353 was not reversed by chemical cleaning indicative of strong binding of the OM to the AEM

354 functional groups and penetration into the membrane. The observed colour change was more
355 pronounced on the area of membranes in contact with ED cell inlets. The fouling of the AEMs was
356 also accompanied by visible swelling. The hydrophobic and hydrophilic acids contained in OM
357 cannot pass through the membranes due to their high molecular weight and it is thought that a
358 fraction of the OM is transported through the membranes as a result of their negative charge density
359 and molecular structure [17, 18]. The surface of the CEMs in contact with both the concentrate and
360 diluate presented little visible evidence of fouling, due to electrostatic repulsion of the negatively
361 charged functional groups within the CEM.

362

363 SUVA (L/mg.m) values for HA experiments are shown in Figure 8D. SUVA is used as an indicator
364 for the aromatic content of carbon within a water sample [40]. SUVA values in the diluate and
365 concentrate for the HA experiments were pH and time independent with a values between 2.6 and
366 5.6 L/mg.m. Shin *et al.* [41] stated that the non-aromatic (aliphatic nature) fractions of HA have a
367 larger molecular size in comparison to the aromatic and carboxylate groups of smaller size
368 fractions. Results from this study, therefore, indicate that ED does not separate the aromatic and
369 non-aromatic fractions of HA.

370

371 *3.6. ED parameters and performance*

372 An increase in ED stack resistance (see Eqn (2)) was observed at the beginning of the ED process in
373 all experiments as a result of ion depletion within the diluate and membrane boundary layer. An
374 increase in resistance observed at the end of the ED experiments without OM is attributed to the
375 higher demineralization rate in the diluate solution. ED stack resistance as a function of solution pH
376 is shown in Figure 9.

377

378

[Figure 9]

379

380 The deposition of inorganic trace contaminants and OM on the membranes has implications for ED
381 performance. OM deposition as a foulant layer on and/or inside the membranes increases the
382 resistance at the membrane surface [19, 42]. Between pH 3 and 8 the average stack resistances were
383 indeed greater in the presence of OM; HA ($46.3 \pm 2.2 \Omega$), TA ($51.3 \pm 5.0 \Omega$) and AA (44.5 ± 1.6
384 Ω), due to enhanced OM deposition within this pH range (Figure 8). Above pH 8, resistance
385 decreased due to decreased OM membrane deposition.

386

387 The performance of the ED process can also be evaluated by the removal of EC (Figure 2D). The
388 average percentage of EC removed without OM was $93.0 \pm 2.1 \%$ compared with $91.7 \pm 2.5 \%$,
389 $92.6 \pm 3.0 \%$ and $89.4 \pm 4.8 \%$ with HA, TA and AA respectively. The presence of OM on the
390 membranes did not significantly lower EC removal. It is possible the OM was loosely packed on the
391 AEM still allowing for the migration of salt ions through the membrane; though at a slightly
392 decreased initial flux (Figure 4D).

393

394 **4. Conclusions**

395 The purpose of this study was to understand the impact of OM on inorganic contaminant removal.
396 The removal of the contaminants followed the order $\text{NO}_3^- > \text{F}^- > \text{B}(\text{OH})_4^-$. The hydrated radius and
397 subsequent strength of hydration shells is a parameter that plays a significant role in the transport of
398 the ions during ED; as NO_3^- with a smaller hydrated ionic radii and subsequent weaker hydration
399 shell was removed more effectively than F^- with a larger hydrated ionic radii and stronger hydration
400 shell. The transport of $\text{B}(\text{OH})_4^-$ in ED was solution pH and hence speciation dependent with
401 increased removal at high pH.

402

403 The removal of the inorganic contaminants was enhanced by the presence of OM while the flux
404 decreased indicating mutual dependence of inorganic and organic contaminants in ED. The
405 mechanism for this involves the possible territorial binding and/or complexation of the inorganic

406 contaminants to the negatively charged OM and the subsequent OM deposition on the positively
407 charged AEMs. This membrane deposition led to an increase in stack resistance and a slight
408 reduction in initial EC flux. It is important to study the behaviour of these trace contaminants with
409 OM to better understand the feasibility and applicability of ED for the treatment of real waters.

410

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422

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- 540
- 541

542 **List of Tables**

543

544 Table 1: Characteristics of the ions.

545

546 Table 2: Physical and chemical properties of organic matter (OM).

547 Table 1

Parameter	Unit	Na ⁺	Cl ⁻	F ⁻	NO ₃ ⁻	B(OH) ₄ ⁻	References
Crystal ionic radii, r	nm	-	-	0.116 - 0.119	0.179 - 0.189	0.244-0.261	[30, 31, 43-46]
		0.117	0.164	0.133 - 0.135	0.206		[45, 47]
Hydrated ionic radii, Δr	nm	0.358	0.332	0.352	0.340	^a	[31]
Number of water molecules in hydration shell, n	-	3.5	2.0	2.7	2.0	^a	[47]
Molar Gibbs energy of hydration, $\Delta_{\text{hyd}} G_{\text{calc}}^*$	kJ/mol	-385	-270	-345	-275	^a	[47]
Ion mobility at 25°C, u	m ² /sV	5.19	7.91	5.70	7.40	^a	[33]
Ion equivalent conductivity, λ° equiv	cm ² /Ωequiv	50.1	76.4	55.4	71.5	^a	[48]

548 ^aData not available.

549 Table 2

Organic Type	Category	Origin	Molecular Formulae	MW (g/mol)	Carbon (%)	pKa	Acidic pH	Charge			References
								Neutral pH	Basic pH		
Humic Acid (HA)	OM surrogate	Soil	$C_{342}H_{388}O_{124}N_5$ ^a	4100	56	3.5-5.04	Neutral	Negative	Negative	[22, 34, 41, 49-52]	
Tannic Acid (TA)	Polyphenol	Plants	$C_{76}H_{52}O_{46}$	1701	54	2.5-10	Neutral	Negative	Negative	[23]	
Alginic Acid (AA)	Polysaccharide	Brown seaweed and algae	$[C_6H_8O_6]_n$	21000	36	2.0-3.5	Negative	Negative	Negative	[26]	

550 ^a Based on model by [53]. ^b Sigma Aldrich Humic Acid.

551 **List of Figures**

552

553 **Figure 1.** Schematic of the ED system used in this study

554

555 **Figure 2.** The removal of (A) F^- , (B) NO_3^- , (C) H_3BO_3 and (D) EC (%) from the diluate as a
556 function of solution pH (Initial concentrations 5 mg/L (F^-), 100 mg/L (NO_3^-), 10 mg/L (H_3BO_3), 5
557 g/L NaCl; experiment duration 140min for each pH value).

558

559 **Figure 3.** Flux of (A) F^- (B) NO_3^- , (C) $B(OH)_4^-$ and (D) EC (Initial mass 2.1 mmol (F^-), 57 mmol
560 (NO_3^-), 7.4 mmol (H_3BO_3) (diluate and concentrate combined)).

561

562 **Figure 4.** Schematic representation of hydration shells around F^- and NO_3^- ions (adapted from
563 [35]).

564

565 **Figure 5.** Organic matter (OM) removal as a function of solution pH (Initial OM concentration 12.5
566 mgC/L).

567

568 **Figure 6.** Membrane deposit of (A) F^- (B) NO_3^- and (C) $B(OH)_4^-$ as a function of pH. (Initial mass
569 2.1 mmol (F^-), 57 mmol (NO_3^-), 7.4 mmol (H_3BO_3) (diluate and concentrate combined)).

570

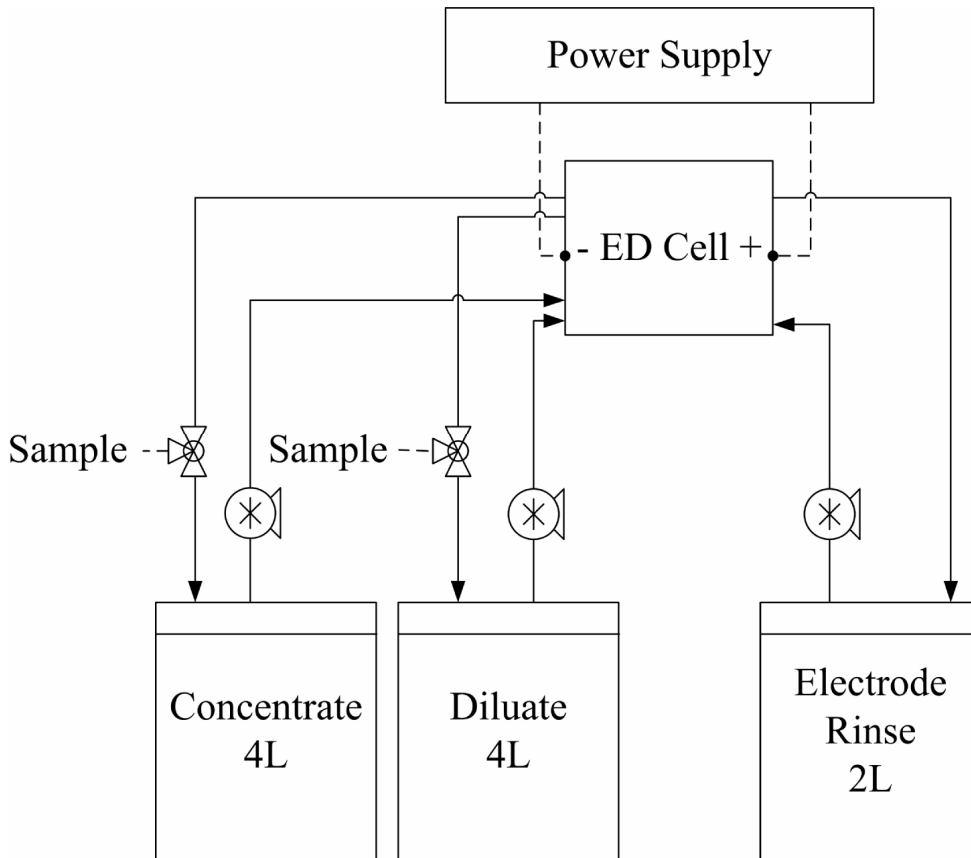
571 **Figure 7.** Schematic of $B(OH)_3$ complexation with humic substances.

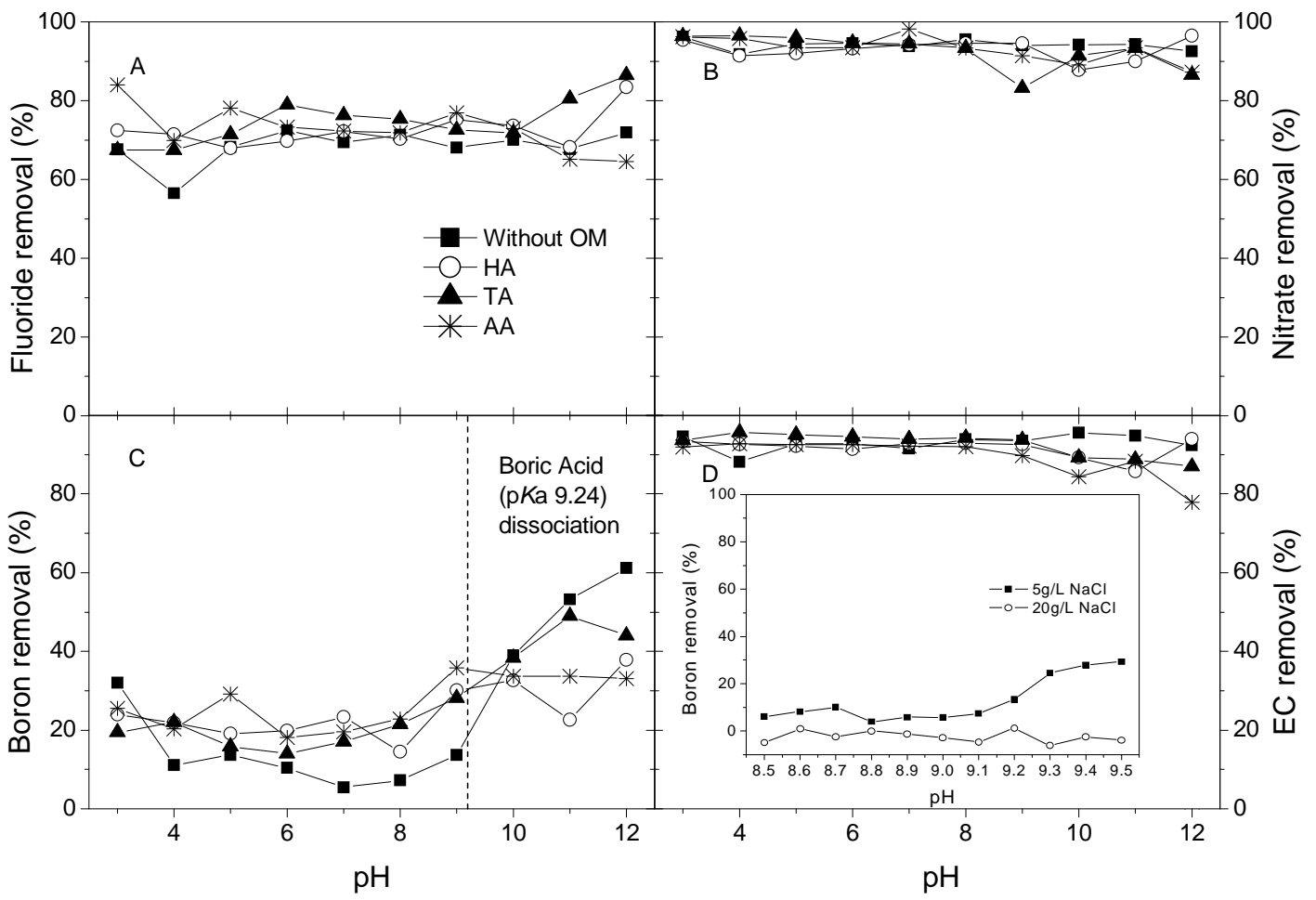
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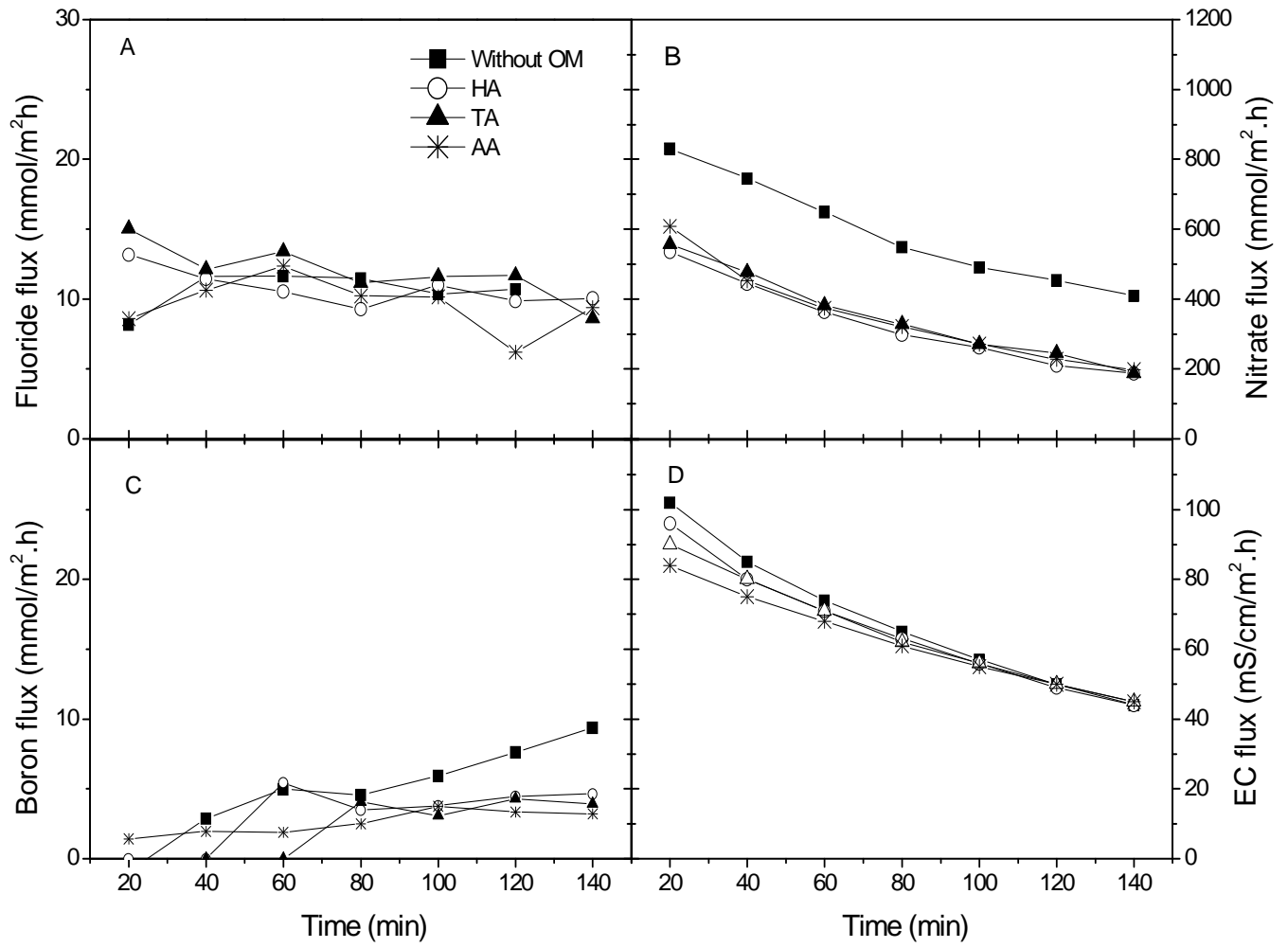
573 **Figure 8:** Membrane deposit of (A) Humic, (B) Tannic and (C) Alginic acids and (D) SUVA
574 (L/mg.m) for HA as a function of pH (Initial mass of OM 100 mgC).

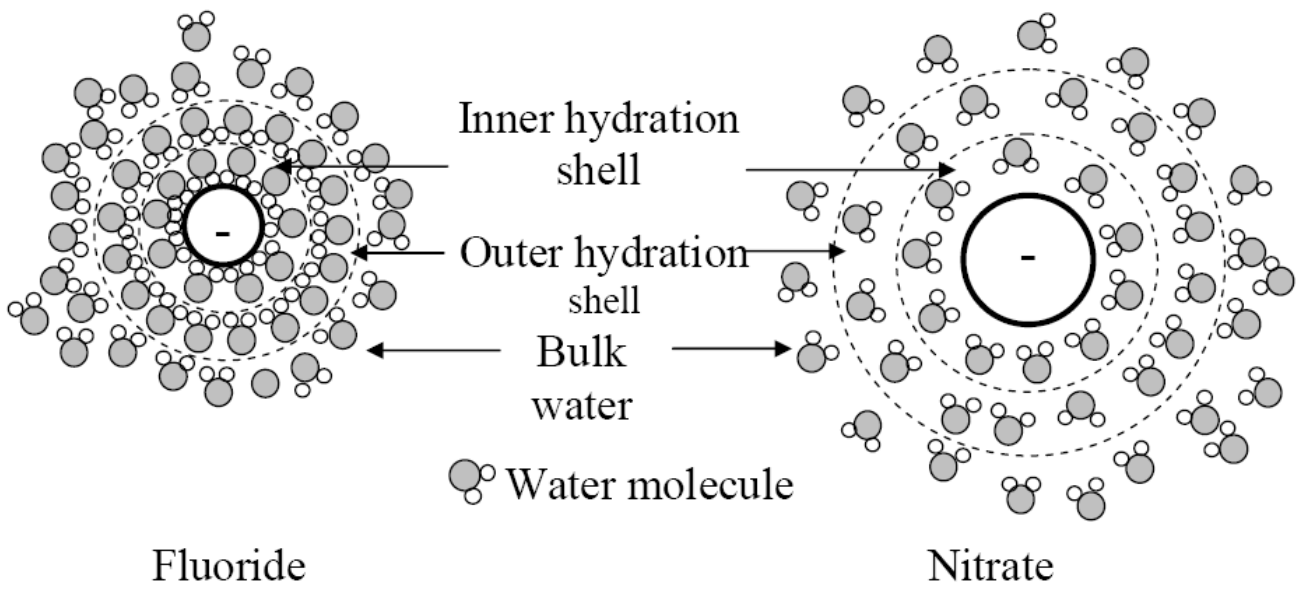
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576 **Figure 9.** ED stack resistance as a function of solution pH.

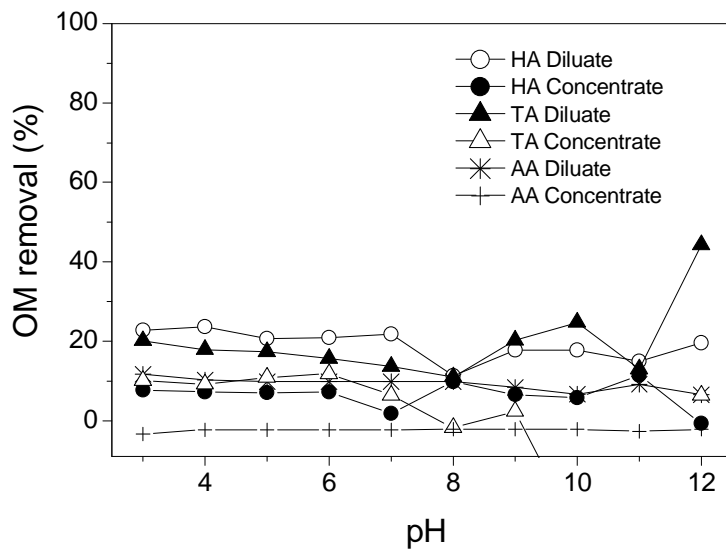








585 Figure 5



586

