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1 **Opportunities for Coupled Electrochemical and Ion-Exchange Technologies to Remove**
2 **Recalcitrant Micropollutants in Water**

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12

13 **Abstract**

14 Micropollutants are found in many waters at concentrations that are concerning for living and
15 environmental systems. They are usually characterised as being persistent and are generally
16 difficult to remove from the water using traditional techniques. In this work, we investigate a
17 treatment technology that couples electrooxidation of micropollutants with subsequent
18 absorption of charged products and remaining compounds through a mixed strong acid and
19 strong base ion exchange resin. The results clearly show that carbon fibre is a promising

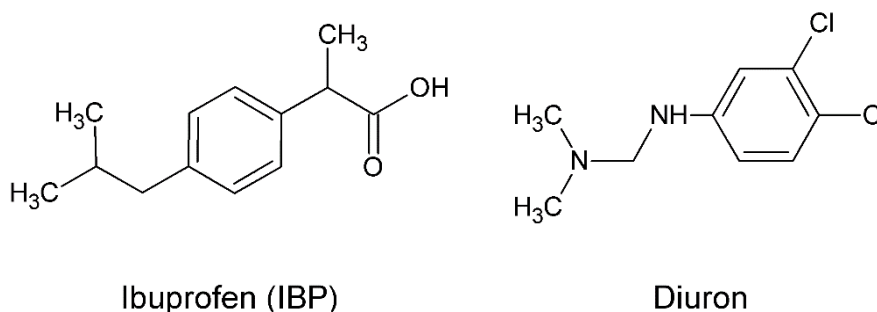
20 electrode material. Electrooxidation of the drug Ibuprofen using carbon fibre in a coulombic
21 efficiency of 13 mC/ppm removed 71% of the compound after two hours (down to 29 ppm).
22 The addition of sodium chloride led to a near doubling of the pseudo-first order reaction rate
23 from 1.7 to 3.0 10^{-4} s^{-1} . A mix of Ibuprofen and the pesticide Diuron showed similarly
24 promising results and while the overall oxidation decreased the positive effect of sodium
25 chloride was present. Strikingly, coupling electrooxidation with a mixed bed ion exchange
26 resin removed both compounds, decreasing levels of Diuron to below the limit of detection (18
27 ppb) and Ibuprofen down to 0.8 ppm. The approach shows potential as a treatment technology
28 for the removal of complex pollutants in water.

29 **Keywords:** electrooxidation, ion-exchange, micropollutants, wastewater treatment.

30 **1. Introduction**

31 Human activities have produced a wide range of pollutants which often find their way into
32 water (the universal solvent). Water is commonly treated at wastewater treatment plants that
33 rely mostly on biological treatment processes such as anaerobic and aerobic digestion, where
34 microorganisms degrade dissolved organic compounds to carbon dioxide, water and new
35 biomass. The latter is then removed using through simple settling techniques [1,2]. However,
36 water contains a number of compounds that are not readily degraded by microorganisms. A
37 common concern is the Persistent Organic Pollutants (POPs), which include pharmaceutical
38 compounds and pesticides [3]. Slow degradation rates not only make the standard treatment
39 processes ineffective but also leads to environmental accumulation [4,5]. POP's are usually
40 present in low concentrations but can still have important and major influences on aquatic and
41 terrestrial ecosystems, as well as on human health [6–10]. Recent research reported c.70
42 pharmaceutical compounds in environmental waters in Britain [2]. Ibuprofen (IBP, Figure 1),
43 which is a common daily use nonsteroidal anti-inflammatory drug (NSAID) [11], was found

44 in noticeable concentrations in water that had been treated using wastewater treatment
45 processes (143-4239 ng L⁻¹) as well as in 'natural' surface waters (1-2370 ng L⁻¹) [2].
46 Moreover, broader range of concentration of IBP can be found in medicinal effluents [12].
47 Pesticides are another class of recalcitrant micropollutants found in waters [4]. Their
48 widespread use in agricultural activities (including urban gardening) results in pesticides
49 entering waters. Diuron for example (Figure 1) is a herbicide used in gardening that can be
50 harmful because it inhibits photosynthesis [13]. Diuron has recently been found at
51 concentrations up to 408 ng L⁻¹ in surface waters in Spain [14].



52

53 Figure 1. Chemical structures of Ibuprofen ((RS)-2-(4-(2-methylpropyl)phenyl)propanoic
54 acid) and Diuron ((3-(3,4-dichlorophenyl)-1,1-dimethylurea)).

55 There is of course a booming industry in technologies to remove recalcitrant micropollutants
56 from waters. Of these the advanced oxidation process (for example Fenton's chemistry
57 (iron/peroxide), peroxonation (peroxide/O₃), photochemicals (chemical/light irradiation),
58 catalysis, sonochemical (chemical/sound) and electrochemical [15–18]) is a promising class of
59 technologies based on oxidation of compounds until mineralisation. Among the many process
60 in advanced oxidation the only technique that does not require the addition of reagents in the
61 oxidation stage is the electrochemical approach, since electrooxidation can be performed with
62 the aim of two inert electrodes [16,19,20]. This has led to promising research into the
63 development of materials as electrodes for use in the advanced oxidation process [16,18,21].
64 Research has typically focused on the catalytic effect of the material, or on its ability to locally

65 generate OH• radicals through the oxidation of water, which in turn oxidise the pollutant [22].
66 For instance, boron-doped diamond has been studied for its chemical and electrochemical
67 stability enabling high voltage water oxidation and direct oxidation of some compounds
68 [20,23–25]. However, current high cost hampers large scale development [23,24,26]. The hunt
69 is on to find cheaper electrode materials that can retain electrooxidize pollutants. The
70 combination of electroactive materials with their ion exchange capabilities has also been used
71 in wastewater treatment. These electroactive ion-exchange materials use their properties of ion
72 doping during redox reactions to remove the target ion [27]. For instance, Prussian blue and
73 analogues can be used to remove radioactive materials, such as ¹³⁷Cs [28]. Conducting
74 polymers are other class of these materials, and are doped/dedoped during their redox reactions.
75 Polypyrrole have been used for toxic anion removal [29] and also for Ca²⁺ removal from
76 drinking water [30]. Hybrid inorganic/organic electroactive ion-exchange material can show
77 the retention of multiple ions during operation, showing synergy between both materials [31].
78 Ion-exchange resins is another avenue of research into water treatment technologies. They have
79 been used for desalinisation of water for many decades [32,33], and even the use for retention
80 of organic compounds have been achieved [34]. Moreover, the selectivity of resins can be used
81 to separate and recover molecules and ions [35–38]. There are of course limitations, as removal
82 rates can depend on the presence of other ions, pH, and time of residence for example
83 [39,40]. Strong-base anion (SBA) exchange resin have been used to remove some
84 pharmaceuticals molecules [41]. It was shown that van der Waals interactions between
85 compound and the resin are responsible for the retention and that IBP was the least selectively
86 retained among the molecules studied [41]. Clearly, producing a charge on the organic
87 compound would facilitate compound retention due to favourable interaction between the
88 charged molecule and the resin.

89 Building on the two processes described above, we decided to investigate the efficiency of a
90 somewhat novel coupled technology approach to the removal of micropollutants, since
91 combining AOP with other physical process has shown to be promising strategies [42,43]. The
92 approach makes use of an electrooxidation stage coupled with mixed bed ion exchange. The
93 electrooxidation of molecules IBP and Diuron was tested to either break them down into
94 smaller molecules or induce a charge. The idea of the coupled mixed bed (SBA/SAC) resin
95 was to remove charged molecules. Each step was assessed separately then an experimental
96 flow rig was assembled and tested with different parental solutions. The paper follows a simple
97 structure. After a detailed description of the methods to ensure replicability, the results are
98 presented, discussed and contextualised in the literature. The paper shows promising results
99 for the removal of micropollutants from water using electrooxidation, ion-exchange resins and,
100 importantly, the coupling of both technologies.

101 **2. Materials and Methods**

102 Dissolved IBP and Diuron were used to test a conventional electrochemical cell where the
103 electrochemical behaviour of IBP was assessed using different working electrode materials by
104 cyclic voltammetry and chronoamperometry. The NaCl concentration effect was studied by
105 both electrochemical techniques while measuring the remaining concentration of IBP by
106 HPLC-UV/Vis [44]. Diuron was then added to the solution to investigate the influence of a
107 more complex solution. Both electrooxidation and ion exchange coupled systems were
108 investigated using the mixed solution.

109 *2.1 Chemicals and Reagents*

110 Sodium Ibuprofen salt was supplied by Santa Cruz Biotechnology and Diuron by Scientific
111 Laboratory Supplies. NaCl and Dowex® Marathon™ MR-3 hydrogen and hydroxide form
112 (strong acid cation/strong base anion, SAC/SBA) were bought from Sigma-Aldrich. HPLC

113 grade water (Sigma-Aldrich) was used to prepare all solutions. Only HPLC grade organic
114 solvents were used for all experiments, since all solutions were analysed by HPLC-UV/Vis.
115 Electrodes were 0.7 cm² in size. Glassy Carbon and stainless steel (316) were purchased from
116 GoodFellow and were cut and then washed in both acetone and then water prior to use. Toray™
117 Carbon fibre (TGP-H-60, Alfa Aesar) was used without any purification. TiO₂ was obtained
118 from annealed Ti sputtered onto glass (200 nm thick) at 400 °C for one hour [45,46].

119 *2.2 Water treatment procedure: electrochemistry and ion-exchange column*

120 An electrochemical cell was built on a 25 mL glass cell with counter and reference electrodes
121 of gold mesh and Ag/AgCl/sat. KCl (IJ Cambria Scientific), respectively, and 0.7 cm² working
122 electrode, 10 mL solution was used as electrolyte. Cyclic voltammetry at 25 mV s⁻¹
123 (electrochemical window varied depending on working electrode) and chronoamperometry for
124 two hours (potential varied depending on working electrode) were carried out in an electrolyte
125 containing 2050 ppm of IBP (10 mmol L⁻¹ Na-IBP) and 0.1 mol L⁻¹ of NaCl. After determining
126 best working electrode material, concentration effects of Na-IBP and NaCl were similarly
127 investigated by cyclic voltammetry and chronoamperometry.

128 Electrochemical component and ion-exchange column were assessed in solution with lower
129 concentration of IBP (100 ppm). IBP removal was carried out by chronoamperometry for two
130 hours under stirring, taking 10 µL aliquots for HPLC analyses. Presence and absence of NaCl
131 were also investigated, as the addition of Diuron (40 ppm). All electrochemical experiments
132 were carried out using a Solartron Analytical 1470E Multi-channel Potentiostat/Galvanostat.
133 Ion-exchange batch extraction experiments were done in a single contact of 0.5 mL of wet
134 SA/SB resin bed and 10 mL of solution in 15 mL falcon tube shaken for 24 hours in an orbital
135 shaker at room temperature. Resin was washed with HPLC grade water five times with 200
136 bed volume before use [38]. Solutions containing 100 ppm of IBP, 40 ppm of Diuron and the
137 mixture of both were investigated, with and without NaCl.

138 The flow rig was composed of two components, the electrochemical cell coupled with the ion-
139 exchange column. The electrochemical component received stock solution from the bottom of
140 the cell with aid of one peristaltic pump, then solution exited by the top, moving to the bottom
141 of the ion-exchange column component, with the aid of a second peristaltic pump and then
142 collected on the top. Both peristaltic pumps were calibrated and worked at 0.7 mL min^{-1} . The
143 electrochemical component was composed of a glass cell of 100 mL, a carbon fibre electrode
144 (0.7 cm^2) used as positive electrode and a stainless-steel mesh used as negative electrode.
145 Ag/AgCl/sat. KCl was used as reference electrode. The Ion-exchange column component with
146 6 mL wet bed in reverse flow was used at the end of the flow rig. Solutions for flow experiments
147 were composed of 100 ppm Na-IBP, 40 ppm of Diuron, mixtures of both, with and without
148 NaCl, *ie.* 0 and 0.5 mol L^{-1} .

149 *2.3 Analytical methods*

150 IBP and Diuron concentration were determined by high performance liquid chromatography
151 (HPLC, Thermo Scientific UltiMate3000) using a C-18 column (Supelcosil LC-PAH C18 15
152 cm x 4.6 mm x $5 \mu\text{m}$) and a four channels UV-Vis detector (IBP at 220 nm and Diuron at 254
153 nm). The oven was set to $30 \text{ }^\circ\text{C}$, and the mobile phase used was 1% of acetic acid and a mixture
154 of ultrapure water ($> 18 \text{ M}\Omega$) and methanol (HPLC grade, Fisher) 25/75 at a flow rate of 1.0
155 mL min^{-1} [44]. Fractions of $10 \mu\text{L}$ were collected at different times and injected into the HPLC.
156 Diuron and IBP were observed at 5.0 and 9.1 minutes, respectively. IBP and Diuron calibration
157 curves were carried out using water and methanol for sample preparation, respectively. Total
158 organic carbon (TOC) was quantified using a Hach Lange DR3900 with an LCK380 kit.

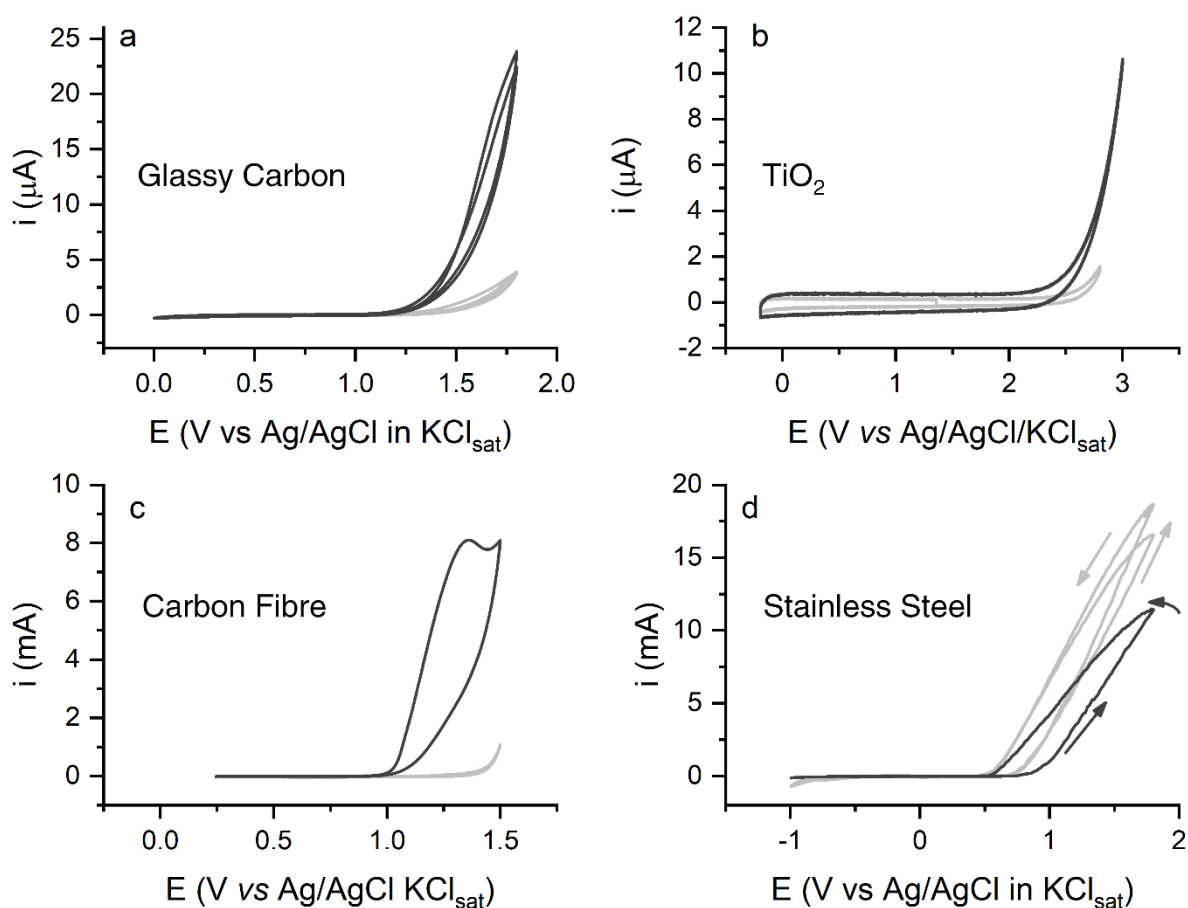
159 **3. Results and discussion**

160 *3.1 The electrochemical component*

161 3.1.1 Electrooxidation of Ibuprofen

162 We initially investigated four different materials: glassy carbon, TiO₂, carbon fibre and
163 stainless steel (316) to find an appropriate positive electrode for the electrochemical component
164 of the flow rig. Figure 2 shows cyclic voltammetry curves of the four materials in 0.1 mol L⁻¹
165 of NaCl and 2050 ppm of IBP (10 mmol L⁻¹) and clearly shows a higher oxidation current when
166 IBP is in solution. There are two probable reasons for the higher current observed. It could be
167 due to the depletion of radical hydroxyl generated at such potentials by the reaction with IBP,
168 following the advanced oxidation process path. Alternatively, it could be due to the direct
169 electrooxidation of IBP [22].

170



171

172 Figure 2. Cyclic voltammetry curves in 0.1 M NaCl (light grey) and 2050 ppm IBP in 0.1 M

173 NaCl (black) using glassy carbon (a), TiO₂ (b), carbon fibres (c) and stainless steel (d) as

174 working electrode. Au mesh as counter-electrode, scan rate of 25 mV s⁻¹. Stationary
175 experiment. Note 2050 ppm is 10 mmol L⁻¹ of Na-IBP.

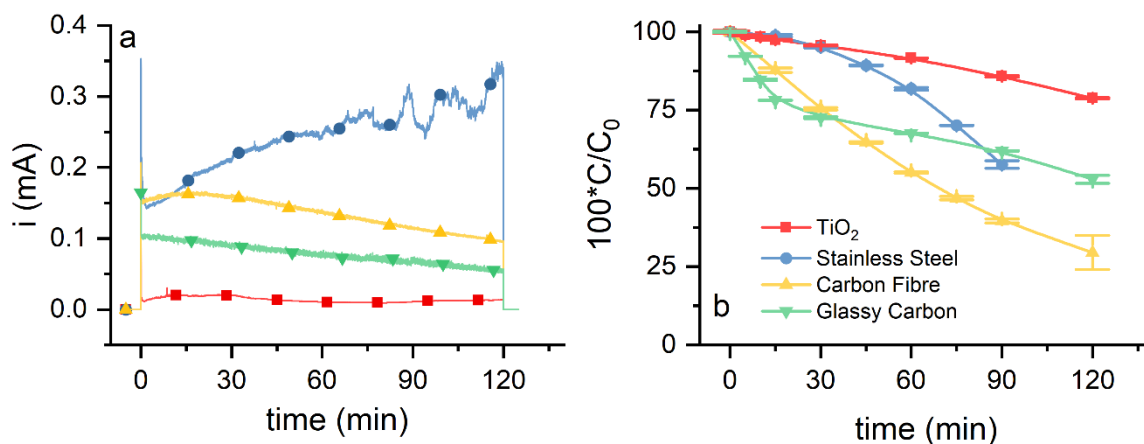
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177 Glassy carbon, TiO₂ and Carbon fibre showed different electrochemical window (range of
178 potential where no reactions is observed) in 0.1 mol L⁻¹ NaCl, and it is possible to see that the
179 oxidation current increases at different potentials when Na-IBP is present. Moreover, when
180 Carbon fibre was used, there was an oxidation peak at 1.35 V *vs* Ag/AgCl indicating that the
181 IBP oxidation directly or indirectly occurs at different potential depending on the electrode
182 material.

183 On the other hand, Figure 2d shows the cyclic voltammetry curves of stainless steel in both
184 absence and presence of Na-IBP. Stainless steel shows low electrochemical stability and
185 suffers from corrosion, clearly indicated by the *i vs E* profile. Oddly, IBP presence seems to
186 improve the electrode stability against corrosion, since the current starts to increase at higher
187 potential and the current observed is smaller when the drug is present.

188 To better quantify the efficiency of the four electrodes in IBP oxidation, constant voltage
189 experiments were performed in a start solution of 100 ppm Na-IBP with no addition of NaCl.
190 (Potentiostatic regime was used instead of galvanostatic in order to better control the
191 electrooxidation of IBP and avoid the oxidation of water or chloride). Figure 3a shows the
192 measured current for each electrode. Stainless Steel, Carbon fibre and glassy carbon, all held
193 at 1.5 V *vs* Ag/AgCl, showed higher current than TiO₂, that was held at 2.5 V *vs* Ag/AgCl.
194 When stainless steel was used, the current increased over time due to the corrosion expected
195 from the cyclic voltammetry and showed a coulombic efficiency (Coulombs/removed IBP) of
196 40 mC/ppm of IBP. Carbon fibre, glassy carbon and TiO₂ showed a relatively constant current
197 over time and coulombic efficiency of 13, 11 and 4.4 mC/ppm of IBP, respectively.

198 Figure 3b shows the decay of IBP concentration over time. Although TiO₂ showed the highest
 199 coulombic efficiency in removing IBP, it is also the electrode that showed the lowest total
 200 removal after two hours of treatment. Stainless steel started with a removal as low as TiO₂ in
 201 the first 30 minutes, but the removal rate increased and almost reached 50% of removal after
 202 90 minutes. However, due to corrosion the coulombic efficiency was the lowest observed. It is
 203 worth noting that coagulation was observed when stainless steel was used, since its corrosion
 204 introduce iron ions into solution promoting the coagulation of IBP and its higher removal from
 205 solution [20]. Glassy Carbon showed a fast removal in the first 15 minutes, but then a slow
 206 constant rate of IBP removal was observed. Carbon fibre showed an almost linear rate in the
 207 first hour of treatment and then slowed down, but it showed the best performance to remove
 208 IBP after two hours, achieving a removal of 71% of the 100 ppm of IBP (down to 29 ppm).
 209



210
 211 Figure 3. (a) Chronoamperometry in a solution of 100 ppm of Na-IBP using four different
 212 working electrodes: stainless steel (blue circle), carbon fibre (yellow up triangle), glassy
 213 carbon (green down triangle), all operating at 1.5 V vs Ag/AgCl, and TiO₂ (red square),
 214 operating at 2.5 V vs Ag/AgCl. (b) %IBP remaining during the above chronoamperometry,
 215 determined by HPLC/UV-Vis. Error bars indicate standard deviation of three measurements.
 216 Solution under stirring during all time.

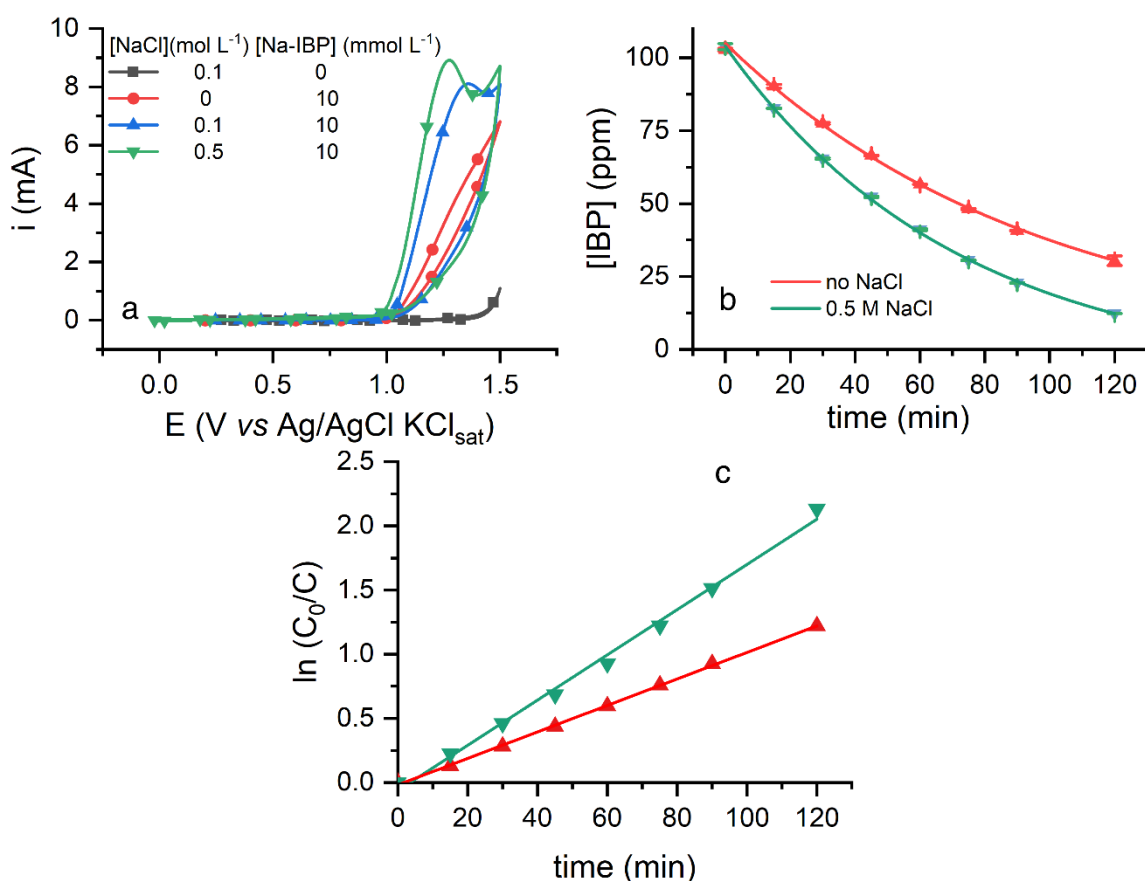
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218 IBP removal using carbon fibre was slightly higher than published elsewhere using mesopore
219 carbon and platinum as electrodes [44]. It is worth noting the different techniques employed,
220 while the present work uses a potentiostatic regime, previous work used galvanostatic regimes.
221 Therefore, their electrooxidation showed a coulombic efficiency 225 C/ppm, which is much
222 higher than the charge consumed when the potentiostatic regime was used, as showed above.
223 Based on the results, it was logical to select carbon fibre as the electrode material to further
224 investigate. It clearly showed a good coulombic efficiency per ppm of IBP removed and the
225 best performance after two hours of experiments. The cyclic voltammetry curves were
226 performed with addition of 0.1 mol L⁻¹ of NaCl, and at first the treatment experiment was
227 performed with an absence of salt. Figure 4a shows the cyclic voltammogram of 10 mM of Na-
228 IBP with no salt (red line). It shows a lower current at higher potential when compared with a
229 cyclic voltammogram with 0.1 mol L⁻¹ of NaCl (blue line). The latter also showed the oxidation
230 peak at *ca.* 1.35 V *vs* Ag/AgCl. Further increasing of salt, *i.e.* addition of 0.5 mol L⁻¹ of NaCl
231 (green line), shifted the oxidation peak to lower potential, *ca.* 1.28 V *vs* Ag/AgCl and a higher
232 current was observed.

233 Figure 4b compares the %IBP remaining over time during a treatment without NaCl (red) and
234 with addition of 0.5 mol L⁻¹ NaCl (green). As suggested by the cyclic voltammograms, the
235 system containing NaCl removed a greater amount of IBP, indicating that wastewater
236 contaminated with salt or even the addition of salt to the wastewater to be treated is beneficial
237 to the treatment process, as was reported earlier [17].

238 The results suggest that the increase in ionic conductivity of the electrolyte – or treated water
239 – improves the overall cell performance. This is evidenced by the oxidation peak shift to lower
240 potential and the increase in current. The presence of chloride ions of course was known to

241 improve the oxidation of organic compounds through the production of chlorine species that
 242 reacts with organic compounds [20,47].
 243 The decay of Ibuprofen was well fitted with a pseudo-first-order rate reaction equation for both
 244 with and without NaCl (Figure 4c) [11,48]. The apparent rate constants were $1.7 \cdot 10^{-4} \text{ s}^{-1}$ ($R^2 =$
 245 0.9993) and $3.0 \cdot 10^{-4} \text{ s}^{-1}$ ($R^2 = 0.9944$) when NaCl is absent and present, respectively, showing
 246 that the salt addition improves the reaction rate by 1.7 times. The kinetic parameters observed
 247 in Figure 4c agree with the order reactions found by Li and collaborators³², but the reaction
 248 order apparent constant is an order of magnitude lower, which can be directly correlated to the
 249 potentiostatic regime.



250
 251 Figure 4. (a) Cyclic voltammetry curves of Carbon fibre in 0.1 mol L⁻¹ NaCl (black square),
 252 2050 ppm of IBP without NaCl (red circle), with 0.1 mol L⁻¹ NaCl (blue up triangle), with 0.5
 253 mol L⁻¹ NaCl (green down triangle), at 25 mV s⁻¹, Au mesh as counter electrode and
 254 stationary experiment. (b) IBP remaining during chronoamperometry of Carbon fibre in 100

255 ppm of Na-IBP without NaCl (red up triangle) and with 0.5 mol L⁻¹ NaCl (green down
256 triangle), with stirring of solution. (c) Pseudo-first-order kinetics analysis of IBP
257 concentration decay. Note 2050 ppm is 10 mmol L⁻¹ of Na-IBP.

258

259 3.1.2 Electrooxidation of mixture of Ibuprofen and Diuron

260 Micropollutants are generally small concentration constituents in complex water streams,
261 hence for any treatment method it is important to test how the method performs when the water
262 composition increases in complexity [9,49]. To assess the impact of increased complexity on
263 the electrochemical oxidation process performance, electrooxidation performance was tested
264 with the addition of the pesticide Diuron.

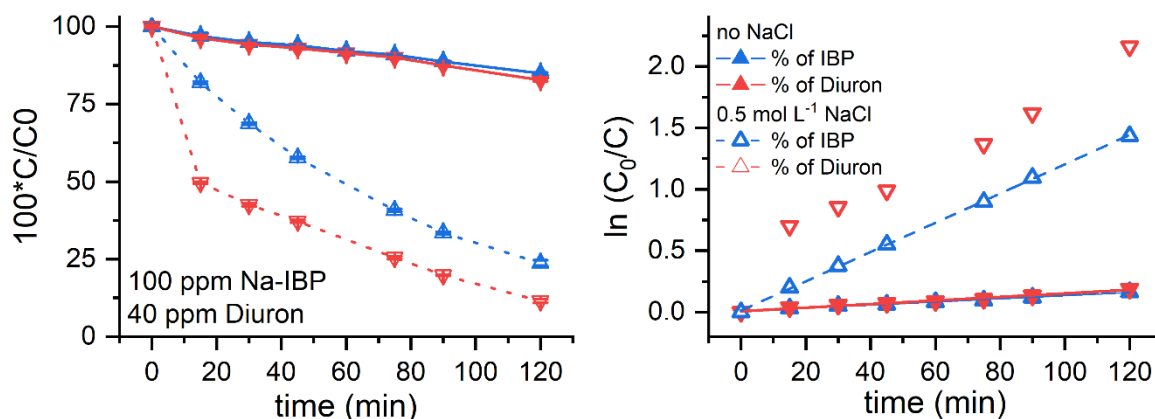
265 Figure 5 shows both compounds, IBP and Diuron, concentrations decay during treatment.
266 When no salt was added, the removal was very low for both compounds, removing only 16%
267 of the 100ppm IBP and 18% of the 39 ppm Diuron, respectively. The removal of IBP in the
268 mixture was lower when compared to the removal of IBP alone, in the presence or absence of
269 salt. The addition of 0.5 mol L⁻¹ NaCl in the mixture greatly improved the removal of both
270 micropollutants with only 23% (to 23 ppm) IBP and 11% (to 4.4 ppm) Diuron remaining.

271 Comparing the removal of IBP in mixture with Diuron with salt with the solution of IBP with
272 salt, it was observed that the removal is higher in the latter. The results suggest a competition
273 for the oxidation of both compounds that specifically diminished IBP oxidation. Overall, the
274 removal of both compounds can be achieved using the addition of salt to the mixture. Figure
275 5b shows the best fits for pseudo-order reactions of IBP and Diuron decay in mixtures without
276 and with NaCl. The rate constants for IBP alone in solution and in the mixture (both containing
277 salt) were 3.0 10⁻⁴ (R² = 0.9944) and 2.0 10⁻⁴ s⁻¹ (R² = 0.9997). In other words, it decreased
278 33% when Diuron was present. Moreover, the addition of salt to the mixture increased the IBP

279 removal apparent rate constant almost 10 times. Diuron electrooxidation kinetics do not seem
280 to fit with a pseudo-order equation.

281

282



283

284 Figure 5. (a) Remaining percentage of IBP (up blue triangle) and Diuron (down red triangle)

285 during chronoamperometry of carbon fibre in solution containing both 100 ppm Na-

286 Ibuprofen and 39 ppm Diuron without (solid lines) and with 0.5 mol L⁻¹ NaCl (dashed lines),

287 stirring of solution during all time. (b) pseudo-first-order reaction analysis.

288

289 3.2 The ion-exchange column component

290 Although the removal of compounds was observed organic carbon did not decay at the same

291 rate as the parental compound. For instance, 108 ppm IBP as starting solution without NaCl

292 shows 81 ppm of TOC, and after electrochemical treatment, the TOC decayed to only 74 ppm,

293 while IBP decayed to 29 ppm. It is clear that the electrooxidation of IBP does not lead to

294 complete mineralisation of the organic carbon, and products of the oxidation were still present

295 in solution. To help the removal of the remaining parental compound (IBP or Diuron) and also

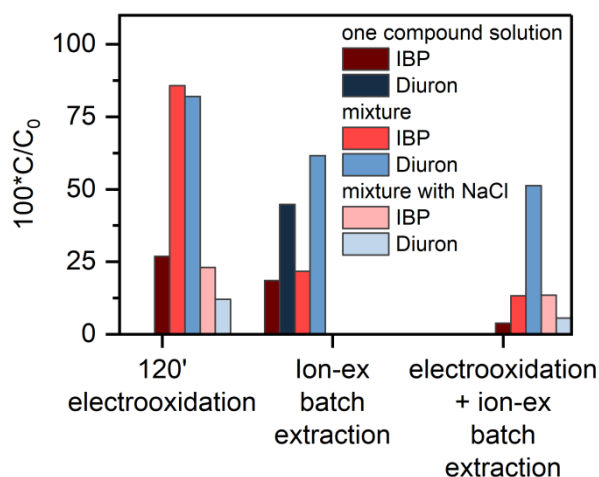
296 of any generated product, which are likely charged species, a mixed bed strong acid/strong

297 base (SA/SB) ion exchange resin was investigated.

298 Batch extraction of some starting solutions and after electrochemical treatment were performed
299 and the results are presented in Figure 6. IBP starting solution containing 108 ppm decreased
300 to 20 ppm (removal of 81%) after 24 hours in contact with resin. A Diuron starting solution
301 containing 29 ppm decreased to 13 ppm (removal of 55%) after the batch extraction. When
302 both micropollutants are present, initially with 105 and 39 ppm of IBP and Diuron,
303 respectively, the batch extraction was able to remove 78% and 38% of IBP and Diuron,
304 respectively. The higher retention of IBP over Diuron was expected to be due to the charge
305 present in IBP (sodium salt was used and the micropollutant presents negative charge).
306 Although Diuron presents no charge, its retention by the resin must be facilitated by the amine
307 groups in its structure, especially the secondary amine. What is interesting is that the removal
308 of IBP was very similar in both the presence and absence of Diuron. This indicates that each
309 compound is retained by a different portion of the mixed bed resin.

310 Figure 6 shows that coupling the electrooxidation stage with the batch extraction with mixed
311 bed ion exchange resin produced promising removal rates. The starting solution with 100 ppm
312 of IBP showed electrochemical treatment removal of 73%, and the batch extraction carried out
313 after electrochemical treatment removed a further 85% of the remaining IBP. In other words,
314 the coupled approach removed 96% of IBP from the starting solution (4 ppm of IBP
315 remaining). Importantly TOC analysis showed that the electrochemical treatment marginally
316 decreases the % of TOC, despite the drastic removal of IBP. This is probably because of
317 oxidation products; however, the batch extraction retained 90% of the TOC, revealing that the
318 coupled technology was not only more efficient removing the micropollutants but also removed
319 undesired oxidation products.

320



321

322 Figure 6. Remaining % of IBP (red) and Diuron (blue) using electrooxidation for 120
 323 minutes, ion-ex batch extraction and ion-ex batch extraction after the electrooxidation, of
 324 solutions containing only one compound (darker colours), mixture of both compound (middle
 325 shade colours) and mixture of both compound with NaCl (lighter colours).

326

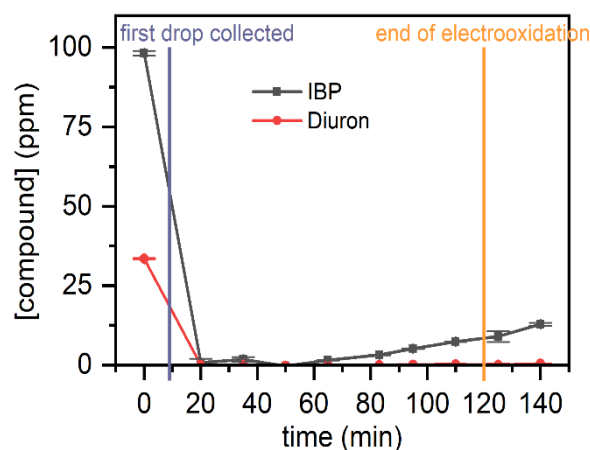
327 The removal of micropollutants was comparatively low when the starting solution contained
 328 both IBP and Diuron and salt was absent. But the batch extraction was able to improve the
 329 overall performance to remove 86% (final concentration of 14 ppm) and 48% (final
 330 concentration of 20.8 ppm) of IBP and Diuron, respectively. When salt was added to the
 331 starting solution containing both micropollutants, the amount of IBP removed after
 332 electrochemical treatment was much higher compared with when salt is absent but the
 333 remaining IBP is the same after batch extraction, 14 ppm. On the other hand, Diuron
 334 concentration decreases considerably after electrochemical treatment and batch extraction
 335 when salt is added, showing a final concentration of 2.2 ppm when salt is added against 20
 336 ppm when salt was absent. It is clear that coupling both electrooxidation and ion-ex resin had
 337 a complementary effect. It is believed that part of the compound is broken down to smaller
 338 molecules by electrooxidation which is more efficiently absorbed by the ion-exchange resin.

339 3.3 The flow rig

340 To observe how both steps would perform in series, a proof-of-concept flow system coupling
341 an electrochemical cell and ion-exchange column was assembled. The parental solution was
342 fed to the electrochemical cell at a constant flow rate of 0.7 mL min^{-1} and also collected from
343 electrochemical cell and fed to the ion-exchange column at the same rate. Samples were
344 collected after the column for quantification by HPLC/UV-Vis, as in previous experiments.
345 Figure 7 shows the concentration of both micropollutants over time. The electrochemical cell
346 operated for five minutes before flow started, and the first sample was collected after nine
347 minutes, (four minutes after the initiation of flow).

348 The concentration of both micropollutants dropped to below the detection limit in the first
349 measurement. Concentrations were kept constant until 60 minutes, and then IBP concentration
350 slightly increased over time. The electrooxidation was turned off at 120 minutes, and the flow
351 of parental solution was kept constant. IBP concentration reached 8 ppm just after the end of
352 electrooxidation, and 13 ppm 20 minutes after electrooxidation. Diuron concentration was kept
353 below detection limit during the whole experiment. For comparison, others AOPs can show
354 different time response for IBP removal [12], for instance, thermally activated persulfate can
355 take from minutes to hours for a removal of around 80% (initial concentration of *ca.* 4 ppm)
356 [50], while oxone process using Fe^{2+} and UV light took 97% of IBP in 10 minutes (initial
357 concentration of 10 ppm) [51], in another process using Fe^{2+} and superoxide, 20 days were
358 necessary for a nearly complete removal of IBP (initial concentration of 1 ppm). On the other
359 hand, adsorption of IBP using activated carbon or graphene oxide took 120 and 60 minutes, to
360 remove 99.16% and 98.17%, respectively (initial concentrations of 20 and 6 ppm, respectively)
361 [52,53].

362



363
 364 Figure 7. IBP and Diuron concentration over time after flow through proof-of-concept
 365 device. Electrochemical cell using carbon fibre as positive electrode at 1.5 V vs Ag/AgCl
 366 coupled with SA/SB ion-exchange column. Electrooxidation for 5 minutes before flow of 0.7
 367 mL min⁻¹, first drop was collected at 9 minutes and 16 seconds after experiment started.

368
 369 However, the wastewaters vary greatly in composition, and the solution tested herein is far
 370 from that found in any wastewater treatment plants. Concentrations of pollutants will vary
 371 within the treatment plant, depending on the stage considered. For instance, the first stage can
 372 accumulate chemical wastes and increase the concentration of pollutants [54]. Therefore, the
 373 performance of the tested system will depend on the solution composition [44], since the
 374 products of the oxidation process will be different when other organic materials are present,
 375 which in turn, will also affect the adsorption of the species into the ion-exchange resin.
 376 Nonetheless, the flow rig was able to remove Diuron to below detection limits (18 ppb) and
 377 IBP to 0.8 ppm. Based on these positive results, the next step is to optimise the electrochemical
 378 cell volume and electrode size ratio and investigate the ion-exchange column size. The
 379 assessment of solutions using concentration closer to that found in wastewater and increase on
 380 complexity must also be considered. We expect that playing with the arrangement of both
 381 operations (series and parallels) will present opportunities for a more adaptive and
 382 customisable treatment capability to meet different water treatment needs.

383 **4. Conclusions**

384 The removal of micropollutants was evaluated by electrooxidation, ion-exchange resin and the
385 coupling of both technologies. Carbon fibre showed the best performance with comparatively
386 good coulombic efficiency and high Ibuprofen removal among the four electrode materials
387 evaluated (stainless steel, carbon fibre, glassy carbon and TiO₂). The addition of NaCl
388 improved the overall performance which was related to the increase in ionic conductivity and
389 generation of chlorine species.

390

391 Diuron was added to the solution to investigate the effects of complexity. The amount of
392 micropollutant removed by electrooxidation decreased in the mixture, but salt helped in the
393 breakdown of the pollutant. Batch experiments and flow through strong acid/strong base ion
394 exchange resins were shown to remove micropollutants without prior electrooxidation and after
395 electrooxidation. When the technologies were coupled in a flow rig, Diuron was removed down
396 to concentrations below the detection limit (18 ppb) and Ibuprofen down to 0.8 ppm.

397 The proof-of-concept research now underpins investigation of the configuration of the flow
398 system, using carbon fibre and ion exchange resins to allow for coulombic efficiency (*ie.*
399 decrease energy consumption). The idea next step is to investigate space and time (bigger
400 electrodes and better and longer contact between electrodes and solution) to adapt the
401 functionality on the surface of the ion exchange resin to target specific pollutants.

402 **Conflicts of interest**

403 “Authors declare no conflicts of interest”.

404 **Contributors**

405 All authors have contributed to the final version of the article.

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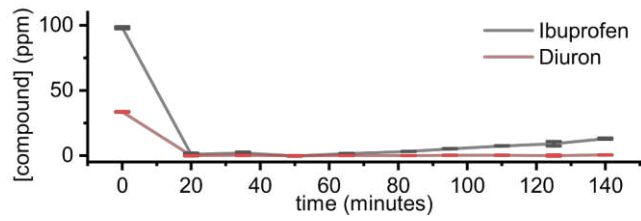
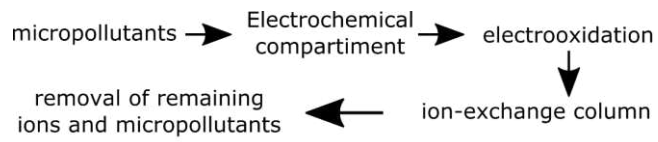
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590 Graphical abstract



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