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

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Abstract

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

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

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

1. Introduction

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

in noticeable concentrations in water that had been treated using wastewater treatment processes (143-4239 ng L^{-1}) as well as in 'natural' surface waters (1-2370 ng L^{-1}) [2]. Moreover, broader range of concentration of IBP can be found in medicinal effluents [12].

Pesticides are another class of recalcitrant micropollutants found in waters [4]. Their widespread use in agricultural activities (including urban gardening) results in pesticides entering waters. Diuron for example (Figure 1) is a herbicide used in gardening that can be harmful because it inhibits photosynthesis [13]. Diuron has recently been found at concentrations up to 408 ng L^{-1} in surface waters in Spain [14].

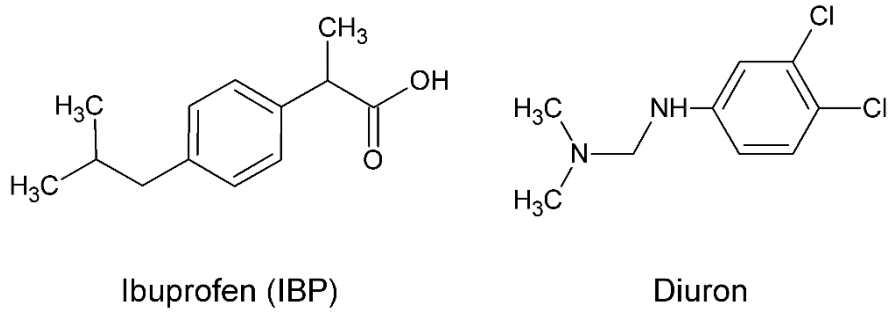

Figure 1. Chemical structures of Ibuprofen ((RS)-2-(4-(2-methylpropyl)phenyl)propanoic acid) and Diuron ((3-(3,4-dichlorophenyl)-1,1-dimethylurea)).

There is of course a booming industry in technologies to remove recalcitrant micropollutants from waters. Of these the advanced oxidation process (for example Fenton's chemistry (iron/peroxide), peroxonation (peroxide/O_3), photochemicals (chemical/light irradiation), catalysis, sonochemical (chemical/sound) and electrochemical [15–18]) is a promising class of technologies based on oxidation of compounds until mineralisation. Among the many process in advanced oxidation the only technique that does not require the addition of reagents in the oxidation stage is the electrochemical approach, since electrooxidation can be performed with the aim of two inert electrodes [16,19,20]. This has led to promising research into the development of materials as electrodes for use in the advanced oxidation process [16,18,21]. Research has typically focused on the catalytic effect of the material, or on its ability to locally

generate $OH^{\bullet}$ radicals through the oxidation of water, which in turn oxidise the pollutant [22]. For instance, boron-doped diamond has been studied for its chemical and electrochemical stability enabling high voltage water oxidation and direct oxidation of some compounds [20,23–25]. However, current high cost hampers large scale development [23,24,26]. The hunt is on to find cheaper electrode materials that can retain electrooxidize pollutants. The combination of electroactive materials with their ion exchange capabilities has also been used in wastewater treatment. These electroactive ion-exchange materials use their properties of ion doping during redox reactions to remove the target ion [27]. For instance, Prussian blue and analogues can be used to remove radioactive materials, such as ^{137}Cs [28]. Conducting polymers are other class of these materials, and are doped/dedoped during their redox reactions. Polypyrrole have been used for toxic anion removal [29] and also for Ca^{2+} removal from drinking water [30]. Hybrid inorganic/organic electroactive ion-exchange material can show the retention of multiple ions during operation, showing synergy between both materials [31]. Ion-exchange resins is another avenue of research into water treatment technologies. They have been used for desalinisation of water for many decades [32,33], and even the use for retention of organic compounds have been achieved [34]. Moreover, the selectivity of resins can be used to separate and recover molecules and ions [35–38]. There are of course limitations, as removal rates can depend on the presence of other ions, pH, and time of residence for example [39,40].Strong-base anion (SBA) exchange resin have been used to remove some pharmaceuticals molecules [41]. It was shown that van der Waals interactions between compound and the resin are responsible for the retention and that IBP was the least selectively retained among the molecules studied [41]. Clearly, producing a charge on the organic compound would facilitate compound retention due to favourable interaction between the charged molecule and the resin.

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

2. Materials and Methods

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

2.1 Chemicals and Reagents

Sodium Ibuprofen salt was supplied by Santa Cruz Biotechnology and Diuron by Scientific Laboratory Supplies. NaCl and Dowex® Marathon™ MR-3 hydrogen and hydroxide form (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 cm^2 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. TiO_2 was obtained
118 from annealed Ti sputtered onto glass (200 nm thick) at 400 ºC 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 cm^2 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 μm) and a four channels UV-Vis detector (IBP at 220 nm and Diuron at 254
153 nm). The oven was set to 30 ºC, and the mobile phase used was 1% of acetic acid and a mixture
154 of ultrapure water (> 18 MΩ) and methanol (HPLC grade, Fisher) 25/75 at a flow rate of 1.0
155 mL min^{-1} [44]. Fractions of 10 μL 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, TiO_2, 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].

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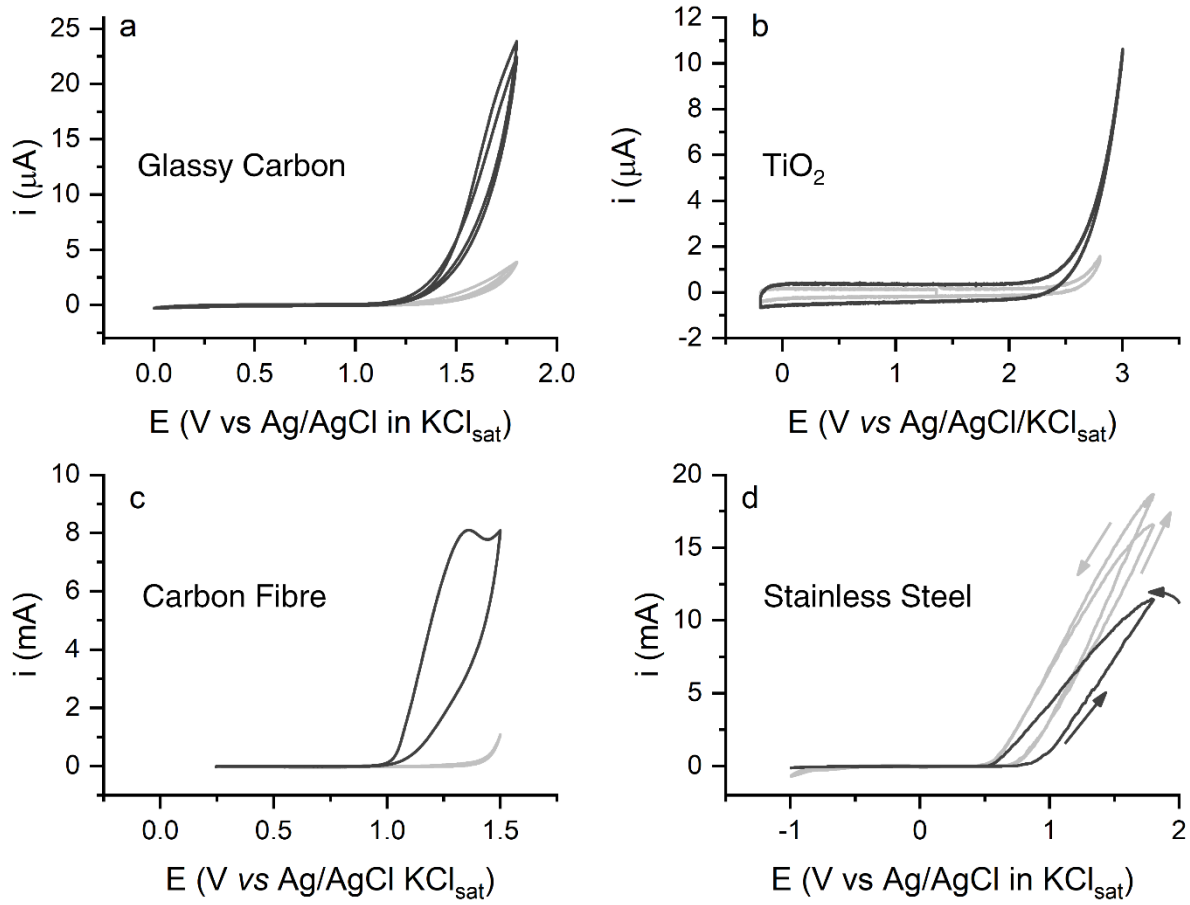


171

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), TiO_2 (b), carbon fibres (c) and stainless steel (d) as

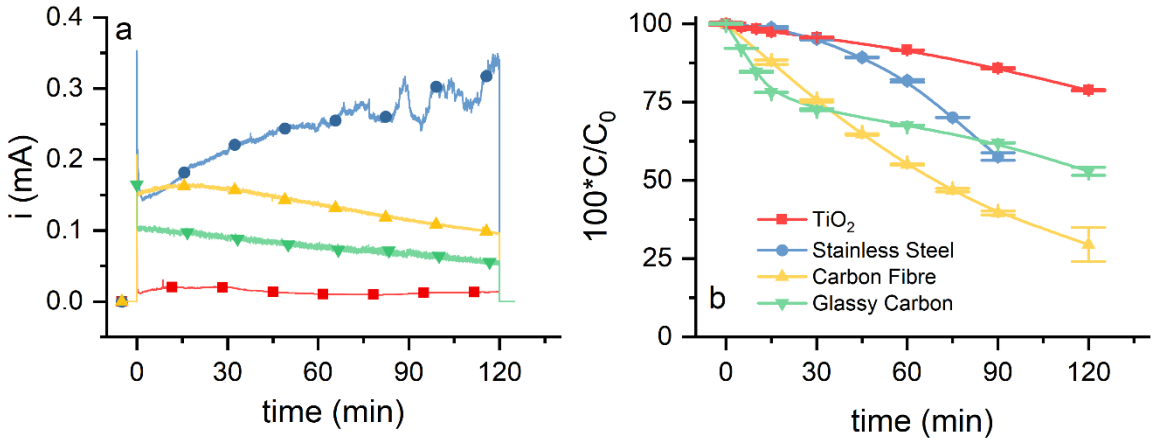
working electrode. Au mesh as counter-electrode, scan rate of 25 mV s^{-1}. Stationary experiment. Note 2050 ppm is 10 mmol L^{-1} of Na-IBP.

Glassy carbon, TiO_2 and Carbon fibre showed different electrochemical window (range of potential where no reactions is observed) in 0.1 mol L^{-1} NaCl, and it is possible to see that the oxidation current increases at different potentials when Na-IBP is present. Moreover, when Carbon fibre was used, there was an oxidation peak at 1.35 V *vs* Ag/AgCl indicating that the IBP oxidation directly or indirectly occurs at different potential depending on the electrode material.

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

To better quantify the efficiency of the four electrodes in IBP oxidation, constant voltage experiments were performed in a start solution of 100 ppm Na-IBP with no addition of NaCl. (Potentiostatic regime was used instead of galvanostatic in order to better control the electrooxidation of IBP and avoid the oxidation of water or chloride). Figure 3a shows the measured current for each electrode. Stainless Steel, Carbon fibre and glassy carbon, all held at 1.5 V *vs* Ag/AgCl, showed higher current than TiO_2, that was held at 2.5 V *vs* Ag/AgCl. When stainless steel was used, the current increased over time due to the corrosion expected from the cyclic voltammetry and showed a coulombic efficiency (Coulombs/removed IBP) of 40 mC/ppm of IBP. Carbon fibre, glassy carbon and TiO_2 showed a relatively constant current 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 TiO_2 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 TiO_2 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 TiO_2 (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.

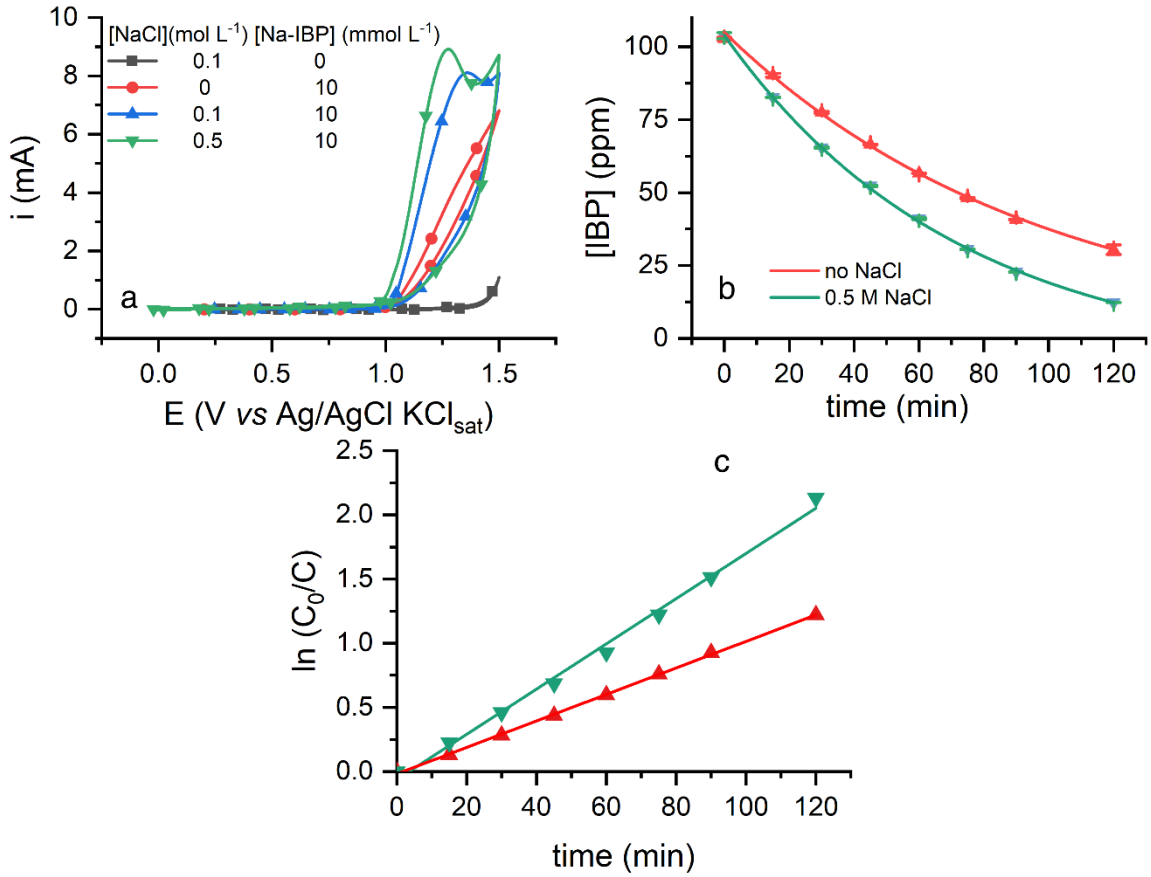
IBP removal using carbon fibre was slightly higher than published elsewhere using mesopore carbon and platinum as electrodes [44]. It is worth noting the different techniques employed, while the present work uses a potentiostatic regime, previous work used galvanostatic regimes. Therefore, their electrooxidation showed a coulombic efficiency 225 C/ppm, which is much higher than the charge consumed when the potentiostatic regime was used, as showed above.

Based on the results, it was logical to select carbon fibre as the electrode material to further investigate. It clearly showed a good coulombic efficiency per ppm of IBP removed and the best performance after two hours of experiments. The cyclic voltammetry curves were performed with addition of 0.1 mol L^{-1} of NaCl, and at first the treatment experiment was performed with an absence of salt. Figure 4a shows the cyclic voltammogram of 10 mM of Na-IBP with no salt (red line). It shows a lower current at higher potential when compared with a cyclic voltammogram with 0.1 mol L^{-1} of NaCl (blue line). The latter also showed the oxidation peak at *ca.* 1.35 V *vs* Ag/AgCl. Further increasing of salt, *i.e.* addition of 0.5 mol L^{-1} of NaCl (green line), shifted the oxidation peak to lower potential, *ca.* 1.28 V *vs* Ag/AgCl and a higher current was observed.

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

The results suggest that the increase in ionic conductivity of the electrolyte – or treated water – improves the overall cell performance. This is evidenced by the oxidation peak shift to lower 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 10^{-4} s^{-1} (R^2 =
245 0.9993) and 3.0 10^{-4} 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 collaborators[32], 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

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

3.1.2 Electrooxidation of mixture of Ibuprofen and Diuron

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

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

Comparing the removal of IBP in mixture with Diuron with salt with the solution of IBP with salt, it was observed that the removal is higher in the latter. The results suggest a competition for the oxidation of both compounds that specifically diminished IBP oxidation. Overall, the removal of both compounds can be achieved using the addition of salt to the mixture. Figure 5b shows the best fits for pseudo-order reactions of IBP and Diuron decay in mixtures without and with NaCl. The rate constants for IBP alone in solution and in the mixture (both containing salt) were 3.0 10^{-4} (R^2 = 0.9944) and 2.0 10^{-4} s^{-1} (R^2 = 0.9997). In other words, it decreased 33% when Diuron was present. Moreover, the addition of salt to the mixture increased the IBP

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

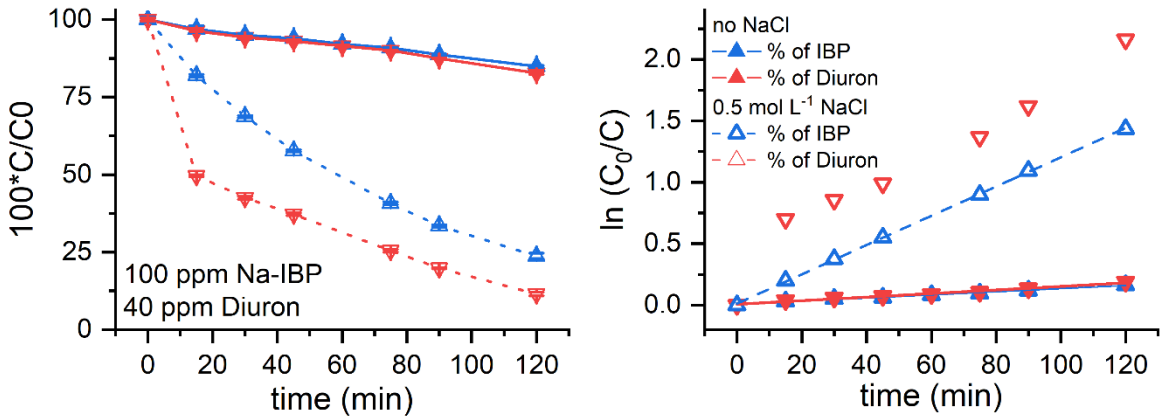


Figure 5. (a) Remaining percentage of IBP (up blue triangle) and Diuron (down red triagle) during chronoamperometry of carbon fibre in solution containing both 100 ppm Na-Ibuprofen and 39 ppm Diuron without (solid lines) and with 0.5 mol L^{-1} NaCl (dashed lines), stirring of solution during all time. (b) pseudo-first-order reaction analysis.

3.2 The ion-exchange column component

Although the removal of compounds was observed organic carbon did not decay at the same rate as the parental compound. For instance, 108 ppm IBP as starting solution without NaCl shows 81 ppm of TOC, and after electrochemical treatment, the TOC decayed to only 74 ppm, while IBP decayed to 29 ppm. It is clear that the electrooxidation of IBP does not lead to complete mineralisation of the organic carbon, and products of the oxidation were still present in solution. To help the removal of the remaining parental compound (IBP or Diuron) and also of any generated product, which are likely charged species, a mixed bed strong acid/strong 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.

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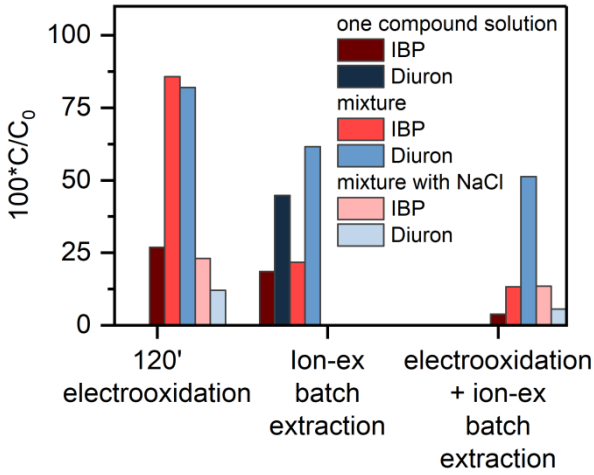

Figure 6. Remaining % of IBP (red) and Diuron (blue) using electrooxidation for 120 minutes, ion-ex batch extraction and ion-ex batch extraction after the electrooxidation, of solutions containing only one compound (darker colours), mixture of both compound (middle shade colours) and mixture of both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

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

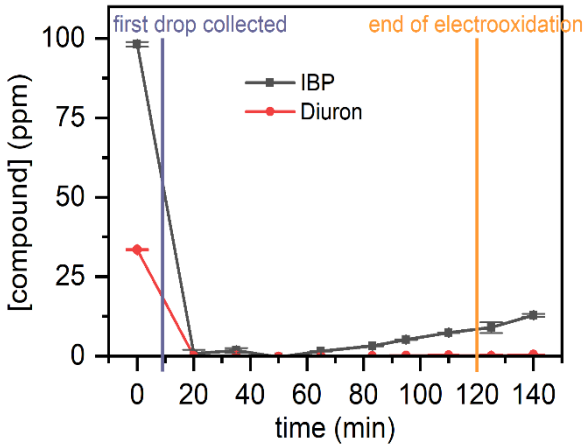

Figure 7. IBP and Diuron concentration over time after flow through proof-of-concept device. Electrochemical cell using carbon fibre as positive electrode at 1.5 V *vs* Ag/AgCl coupled with SA/SB ion-exchange column. Electrooxidation for 5 minutes before flow of 0.7 mL min^{-1}, first drop was collected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

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

4. Conclusions

The removal of micropollutants was evaluated by electrooxidation, ion-exchange resin and the coupling of both technologies. Carbon fibre showed the best performance with comparatively good coulombic efficiency and high Ibuprofen removal among the four electrode materials evaluated (stainless steel, carbon fibre, glassy carbon and TiO_2). The addition of NaCl improved the overall performance which was related to the increase in ionic conductivity and generation of chlorine species.

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

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

Conflicts of interest

"Authors declare no conflicts of interest".

Contributors

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

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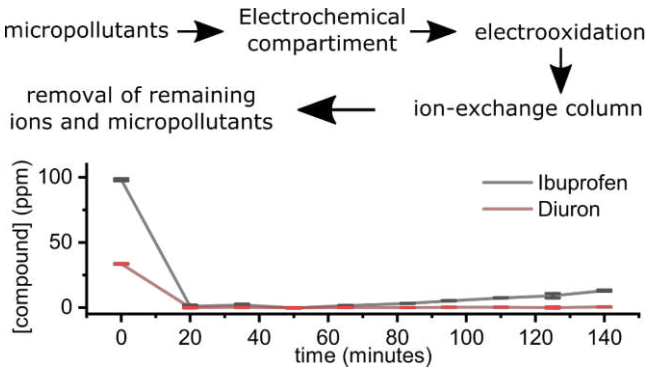
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