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**Crossflow Electrochemical Filtration for Elimination of Ibuprofen
and Bisphenol A from Pure and Competing Electrolytic Solution
Conditions**

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Highlights

- Crossflow mode is effective in electrofiltration of ibuprofen and bisphenol A.
- Crossflow mode was successfully evaluated in different solution conditions.

- Crossflow mode exhibited great outcome eliminating ibuprofen and bisphenol A.
- Crossflow mode displayed superiority over dead-end mode in electrofiltration.

Abstract

For the first time, a crossflow electrochemical filtration system containing multiwalled carbon nanotubes (MWNTs) blended with buckypaper as a flat sheet dual membrane electrode was investigated for the removal of two contaminants of emerging concern, Ibuprofen and Bisphenol A. Breakthrough experiments revealed that a crossflow configuration could be highly efficient in eliminating both contaminants at applied DC potentials of 2 and 3 V over an extended period, from pure salt electrolyte as well as from synthetic secondary wastewater effluent.

The shear flow provided consistent surface coverage resulting in excellent sorption performance. The long residence time of the two contaminants within the membrane (18.3 seconds) was sufficient enough to allow for almost complete degradation of phenolic aromatic products and quinoid rings and the resulting formation of aliphatic carboxylic acids, which was more evident at a higher applied potential (3 V). The formation of the non-toxic aliphatic carboxylic acids is a clear indication of the superior electrochemical performance of the crossflow mode over the dead-end flow-through system. Moreover, this study provides an in-depth understanding of different factors such as filter surface area and residence time that can greatly affect the removal of the contaminants considered.

Keywords: Crossflow electrochemical filtration; Buckypaper; Ibuprofen; Bisphenol A;

Degradation

1. Introduction

Electrochemical filtration is an emerging technology that aims to advance both electrochemical degradation and adsorptive filtration. Advanced oxidation processes are a group of methods that rely mainly on in-situ generation of reactive species to remove harmful and persistent contaminants from water and wastewater [1-4]. Other processes rely on physicochemical properties of contaminants for their removal [5-8]. Electrochemical methods have shown to be of a variety of vital applications in water science and contaminants detection [9-15].

Electrochemical filtration combines the favorable outcomes of these processes and reduces their limitations, aiming for effective elimination of trace organic contaminants of a persistent and hazardous nature. The incorporation of electrochemistry with the sorption mechanism can reduce the membrane-fouling rate and increase sorption efficiency through the destruction of adsorbed organic foulants. This results in a reduced requirement for membrane regeneration through chemical or physical cleaning processes to maintain optimal permeability [16, 17].

There exists a vast body of research on crossflow filtration for water and wastewater treatment, and the enhancement of antifouling capacity during crossflow filtration [18-30]. The inclusion of electrical fields to contribute an increased antifouling capacity during crossflow micro- and ultra-filtration has also been extensively examined in previous studies [31-44]. In these studies, an original approach toward the role of electric fields in capacitive antifouling was detailed, aiming

to decrease the propensity toward micro- and ultra-membrane fouling and thus improve membrane expectancy and maintain permeate efficiency.

The application of crossflow filtration in the electrochemical degradation of emerging contaminants (ECs) of a particularly hazardous and persistent nature is a subject of evolving interest, which requires a more insightful understanding [45-48]. The advantage of using carbon-based electrodes is their high adsorption affinity toward organics at low or no voltage, resulting in higher filtration efficiency. In previous studies, it was shown that carbon nanotubes (CNTs) demonstrate excellent efficiency in the removal of emerging contaminants and viral and bacterial inactivation in dead-end electrochemical filtration processes [49, 50]. In our previous studies, the removal of potentially health affecting concentrations of ibuprofen, an anti-inflammatory drug found in natural water bodies and wastewaters, was investigated. In this study, we employed a conductive carboxylated multi-walled carbon nanotube (MWNTs-COOH) membrane electrode in a dead-end electrochemical filtration process [50]. Employing the same dead-end electrochemical filtration system under different applied conditions, bisphenol A, an endocrine-disrupting chemical reported to be released into natural water and wastewater from different industries, was also successfully removed [51].

In the current study, superconductive MWNTs blend buckypaper electrode membranes were used in a crossflow electrochemical filtration setup to study the removal of both ibuprofen and bisphenol A. The purpose of this study was to observe, for the first time, the electrochemical removal performance of both contaminants from pure electrolytic solutions in a crossflow filtration mode. Moreover, it aimed to observe the removal of these contaminants from a mixture of organics, free electrolytes, and competing electrolytic conditions using synthetic secondary wastewater (total organic carbon (TOC) of 34 mg/L), emulating challenges encountered in real-

life applications. The ultimate goal was to identify and highlight the differences between crossflow electrochemical filtration for the removal of these two contaminants, and previously reported outcomes from dead-end electrochemical filtration using CNTs based membrane electrodes. The study provides novel insight into the advantages of crossflow mode over conventional dead-end mode in the removal of contaminants, in particular, those of emerging concern. In addition, this study identified the influential factors that govern the efficacy of crossflow mode in electrochemical treatments. Critical factors such as molecule retention time, reactor hydrodynamics, and the nature of the membrane material are of significant importance for the effective removal of toxic aqueous contaminants. The study also provides recommendations for making electrochemical crossflow filtration an effective process for use in larger scale applications.

2. Materials and Methods

2.1. Materials

Highly conductive 20 gsm MWNTs blend buckypaper was purchased from Nanotech Labs, NC, USA, and was used as received. The MWNTs blend buckypaper used in this crossflow study was employed because it provided high durability for the shear flow under crossflow mode. The measured purity of the MWNTs buckypaper, as analyzed by Thermogravimetric analysis (TGA) was 92%. The specific surface area was measured by Brunauer–Emmett–Teller (BET) and determined to be 106.79 m²/g and have a total porosity of 0.4 cm³/gm. The geometrical surface area of the flat sheet used in the current study was 50 cm² for a loading of 102.5 mg/cm². This resulted in an enormous surface area of 109459.75 cm² and the total pore volume of 0.041 cm³ (Page S1, supplementary material). The SEM images of the MWNTs blend buckypaper

membrane (Figure S1, supplementary material), showed a rich collection of MWNTs of different diameters ranging from below 20 nm to above 250 nm. Ibuprofen ($C_{13}H_{18}O_2$) with 98% purity and a molecular weight of 206.29 g/mol and Bisphenol A ($C_{15}H_{16}O_2$) with 99% purity and a molecular weight 228.29 g/mol were purchased from Sigma-Aldrich, Oakville, ON, Canada. Sodium chloride with $\geq 99\%$ purity, was purchased from Sigma-Aldrich, Oakville, ON, Canada, and was used as a supporting electrolyte in background solutions. Magnesium sulfate, sodium bicarbonate, calcium chloride, potassium dihydrogen phosphate, ammonium chloride, and trisodium citrate were purchased from Fisher Scientific, Ottawa, ON, Canada, and were used to prepare synthetic secondary wastewater effluent.

2.2. Electrolyte solution

10 mM NaCl electrolytic solutions (pH 5.7 – 6) were used for the electrochemical crossflow filtration of ibuprofen and bisphenol A by a MWNTs blend buckypaper sheet with a geometric area of 50 cm² and 109459.75 cm² of total surface area (106.79 m²/gm x 0.1025 gm). NaCl was used as a background electrolytic species. The current densities were measured at 2.17×10^{-3} , 4.33×10^{-3} and 6.42×10^{-3} mA/cm², corresponding to 1, 2 and 3 V of applied DC potential during the study, respectively. The concentrations of ibuprofen and bisphenol A used in the study were 0.5, 1 and 10 mg/L for each chemical. The membrane conductivity before and after potential application was found to be around 2.3×10^5 to 2.4×10^5 μ S corresponding to 1, 2 and 3 V.

2.3. Crossflow electrochemical filtration setup

Crossflow electrochemical filtration experiments were conducted using a bench-scale, flat-sheet crossflow filtration holder, constructed in a similar method as previously described [41]. Flat

MWNTs buckypaper sheets—of identical area (50 cm^2) and thickness ($52.7 \text{ }\mu\text{m}$)—were used as anodes and cathodes. The electrode sheets were connected to the external terminals of an Agilent E364A power supply (Agilent Technologies, Rockaway, NJ, USA) using titanium sheets ($1 \text{ cm} \times 5 \text{ cm}$), for application of 1, 2 and 3 V of DC voltage. A porous Teflon rubber separator (2 mm thickness)—with the same geometric area as the buckypaper sheets—was used to separate the anode from cathode to prevent short-circuiting (Figure S15, supplementary material). The influent solution was driven from a feed reservoir into the cell holder via a 75211-10 model, 115 VAC Gear pump drive (Cole-Parmer Instrument Company, Vernon Hill, USA). The influent was driven from the feed container via the gear pump, through tubing and into the crossflow cell, where the influent solution made contact with the surface of the buckypaper membrane. The effluent was collected from the lower permeate outlet at the lower end of the holder, making sure that the solution had passed through the membrane and was subject to its adsorptive and electrochemical influence. The concentrate was rejected and was not recirculated to the feed reservoir in order to keep the feed concentration at a constant value during experiments. The pressure was adjusted to 20-25 psi, resulting in a permeate flow rate of $1 \pm 0.5 \text{ mL/min}$ during electrochemical filtration experiments, offering a permeate flux of $2.7 \times 10^{-3} - 8.2 \times 10^{-3} \text{ L m}^{-2} \text{ hr}^{-1}$. The flow rate was calibrated using a graduated measuring cylinder of $10 \text{ mL} \pm 0.1$ total volume at the permeate (effluent) outlet. 1 mL of effluent (permeate) samples were collected for analysis. The flow rate at the concentrate outlet was measured at 3-4 mL/min.

2.4. Buckypaper surface characterization and purity

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) were performed for buckypaper surface inspection and thickness determination using an FEI Inspect F-50 FE-SEM with EDAX Octane Super 60 mm^2 SDD and TEAM EDS Analysis System (Dawson Creek,

Oregon, USA). Thermogravimetric analysis using TA instruments qualified the stability and purity, Trios V3.3 (Waters LLC, New Castle, DE, USA) and the analysis protocol was performed as previously described [50]. Brunauer-Emmett-Teller (BET) was performed to quantify the membrane surface area and total pore volume using a Quantachrome Autosorb Automated Gas Sorption System (Autosorb 1, Boynton Beach, Florida, USA), under analysis conditions as previously described [50].

2.5. Analysis and quantification

Individual concentrations of ibuprofen and bisphenol A were calculated from the absorbance values of samples before and after treatment, at 222 and 225 nm, respectively, using a UV/VIS Agilent Cary 8454 spectrophotometer (Santa Clara, CA, USA). In mixed samples of ibuprofen and bisphenol A (1:1), a major (220-226 nm) and a minor (273-285 nm) broad spectral peak was observed in one spectrum. The average wavelength of the major spectral peak (223 nm) was used to determine mixture concentrations. Liquid chromatography-mass spectrometry analysis was performed using a maXis impact MALDI Autoflex III-TOF (Bruker Daltonics Inc. Massachusetts, USA), in negative ESI mode, using 20 μ L of samples for analysis. The ESI source capillary voltage was 4500 V, nitrogen gas temperature was 350°C, and the flow rate was 8 L/min. The nebulizer pressure was maintained at 1 bar. The mass range was 50-1000 m/z with internal calibration using reference masses of 119 and 966 m/z in the Agilent reference-mass solution. The injection gradient was set to initial conditions of 5% acetonitrile with a 1 min hold, which was then increased to 100% at 8 min and held for 1 min. The column was re-equilibrated at 30% acetonitrile for 5 min before the next injection at a flow rate of 0.3 mL/min.

3. Results and discussion

3.1. Crossflow filtration and electrochemical filtration performance over time

Crossflow filtration and electrochemical filtration performance were evaluated over time for the removal of both ibuprofen and bisphenol A from pure 10 mM NaCl solutions (breakthrough experiments). Breakthrough plots were developed to observe the best sorption and electrochemical degradation outcomes for the two contaminants using MWNTs buckypaper membranes in a crossflow mode. Further, this allowed us to relate the findings to those previously reported in the dead-end process. Figure 1 shows the breakthrough plots for individual solutions of 1 mg/L ibuprofen and 1 mg/L bisphenol A in pure 10 mM NaCl solution. As seen in figure 1 A, ibuprofen sorption kinetics at 0 V were steady, starting at a C/C_0 value of 0.12 up to 20 minutes of operation time. This behavior is consistent with previous observations from the dead-end filtration of ibuprofen on MWNTs membranes showing C/C_0 starting at > 0 value. Such behavior indicates poor adsorption of ibuprofen on MWNTs membranes due to a lack of effective hydrophilic surface interactions between the molecule and MWNTs, and the presence of hydration shell formation at the polar groups [50].

However in the current study, sorption seems improved, and the C/C_0 started at a lower value (0.12 at 0 V for Figure 1 A), as compared to our previous observation for dead-end filtration of ibuprofen (0.33 at 0 V). This could be attributed to the shear flow, which is most likely providing better and more consistent coverage of the molecules at the buckypaper surface, as compared to the flow through in dead-end filtration. Additionally, the large surface area (109459.75 cm²) of the buckypaper membrane (10-11 fold larger than MWNTs flow through filters used in previous dead-end studies) provides more sorption sites. However, and despite this enormous surface area, breakthrough starts at around 25-30 minutes, indicating that active sorption sites are limited.

Therefore, breakthrough starts earlier than expected. When 1 V of DC potential was applied (Figure 1 A), a slight increase in adsorption capacity was observed, which can be attributed to electrostatic interactions taking place between the positively charged surface and the negatively charged deprotonated ibuprofen molecules (pKa, 4.9) at pH 5.7-6. Bisphenol A sorption kinetics at 0 and 1 V (Figure 1 B) show that near complete removal of the molecule could be observed within 10 minutes of sampling time.

The filtration kinetics were almost identical for bisphenol A at applications of 0 and 1 V, indicating that adsorption is likely through hydrophobic surface interactions, due to the neutrality of the molecule. The sharper plateauing for ibuprofen adsorption (Figure 1 A), as compared to bisphenol A (Figure 1 B) at 0 and 1 V, indicates faster adsorption kinetics for ibuprofen. Although the reason for the faster ibuprofen adsorption at 0 V is not apparent, it can be better explained in the case of the application of 1 V, namely due to the electrostatic surface interactions. Despite the previously reported effect of the large specific surface area of CNTs on increasing anode potential and thereby increasing the magnitude of electrooxidation [16, 52, 53], the contribution of 1 V of applied DC potential is yet to result in significance in the current study. The difference between flux values for 0 V and the application of 1 V for ibuprofen removal is $0.12 \mu\text{g m}^{-2} \text{hr}^{-1}$ (Figure S7 A, supplementary material), and the difference in bisphenol A removal is $0.04 \mu\text{g m}^{-2} \text{hr}^{-1}$ (Figure S7 B, supplementary material). The higher flux value for ibuprofen (pKa, 4.9), as contrasted with bisphenol A (pKa 9.6 -11.3), can only, as reported previously here, be attributed to the incorporation of electrostatic surface interactions toward the adsorption of the former. In our previous dead-end studies, we could not conclude any electrochemical activity when a 1 V DC potential was applied, which was mainly due to the

higher oxidation potential of ibuprofen and bisphenol A as compared to anode potentials corresponding to 1 V of applied potential.

The overall behavior in the case of applications of both 0 and 1 V is in agreement with our previous observations using dead-end filtration, indicating the absence of electrochemical activity when 1 V is applied.

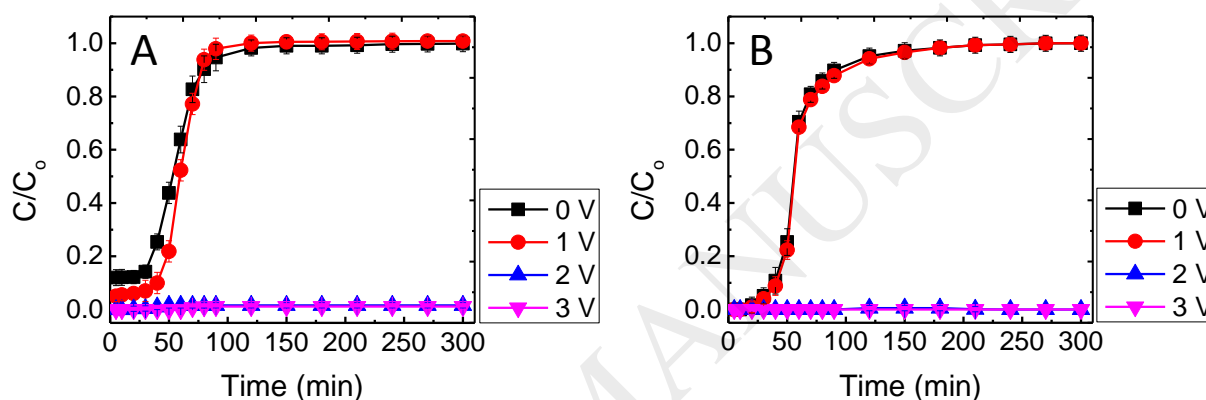


Figure 1. (A) Breakthrough plots for the removal of 1 mg/L Ibuprofen from 10 mM NaCl and (B) for the removal of 1 mg/L bisphenol A from 10 mM NaCl, under 0, 1, 2 and 3 V of applied DC potential, applied pressure is 20 psi, permeate flow rate is 1 mL/min and all experiments performed at room temperature.

Previously reported values for electrode potential obtained from our dead-end studies were 0.33 – 0.35 V vs. Ag/AgCl of anode potential corresponding to 1 V of applied potential. The oxidation potentials for ibuprofen and bisphenol A were determined to be 1.13 and 0.75 V, respectively.

The filtration kinetics at 2 and 3 V of applied potential for both contaminants show nearly complete removal at up to 300 minutes of sampling time. This outcome demonstrates the outstanding electrochemical performance of the MWNTs blend buckypaper in a crossflow

configuration. Increasing the applied voltage from 1 V to 3 V increased flux values by around $4.3 \mu\text{g m}^{-2} \text{hr}^{-1}$ (Figure S7, supplementary material), which can be confidently attributed to electrooxidative degradation. The nearly similar outcomes at 2 and 3 V DC potential application confirm that electrooxidation pathways are analogous at these voltages, which are due to the contribution from direct electrolysis and indirect oxidation by oxidative intermediates (e.g. superoxide and reactive chlorine). Previous superoxide assays from dead-end electrochemical filtration showed the formation of the reactive anion radicals on MWNTs at 2 and 3 V of applied DC potential. Moreover, it was reported that carbon-based electrodes could provide electrocatalytic reductive sites for the efficient production of reactive oxygen species (ROS) from diatomic oxygen with high oxidative power [50, 54]. The enormous surface area (109459.75 cm^2) and the high conductivity (274 – 703 mA corresponding to 1 – 3 V) of MWNTs buckypaper, are essential factors in providing superior electrochemical performance at the membrane surface at an affordable rate.

Figure 2 (A and B) shows the breakthrough plots for the treatment of the 1 mg/L (1:1) ibuprofen/bisphenol A mixture from 10 mM NaCl solution (Figure 2 A), and from synthetic secondary wastewater of the same composition as previously reported (Figure 2 B). The synthetic secondary wastewater was composed of 33 mg/L $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ (as a carbon source), 311 mg/L NaCl, 18 mg/L MgSO_4 , 25 mg/L NaHCO_3 , 22 mg/L CaCl_2 , 2.3 mg/L KH_2PO_4 and 8.5 mg/L NH_4Cl , giving a pH of 7.4 and a TOC of 34 mg/L [50, 55, 56]. The breakthrough trends are similar to those of individual molecules, shown in Figure 2 A, with breakthrough starting at 10-20 minutes at 0 V and 25-30 minutes at 1 V. For Figure 2 B, a breakthrough started at 10-20 minutes at 0 and 1 V. Remarkably, and despite the high TOC concentration of the synthetic

secondary wastewater (TOC 34 mg/L), the overall breakthrough behavior is very similar to the case of electrofiltration of 10 mM NaCl.

While in our previous studies on dead-end mode filtration, the breakthrough performance clearly deteriorated with synthetic wastewater of the same composition, due to the incorporation of high TOC content and the filtration kinetics started at higher C/C_0 values. This can, again, be explained in terms of better surface coverage through the crossflow shearing mechanism, and the larger membrane surface area of the buckypaper membrane employed in the current study, as compared to constructed MWNTs filters used in dead-end studies. Comparing the performance of pure 10 mM NaCl (Figure 2 A) to that from synthetic secondary wastewater effluent (Figure 2 B) at 1 V of applied DC potential, there is a slight shift to a higher C/C_0 with the mixture of synthetic secondary wastewater. This results in flux dropping by $-0.09 \mu\text{g m}^{-2} \text{hr}^{-1}$ from 0-1 V (Figure S7 D, supplementary material) and an earlier breakthrough (figure 2 B), in addition to a reduction in flux by 25%, as compared to the mixture of pure 10 mM NaCl. This may be related to the competing effect of citrate molecules (33 mg/L) which constitute a significant portion of the synthetic secondary wastewater, and which contain three carboxylate groups per each molecule. The presence of citrate resulted in a somewhat rapid blocking and consumption of surface sorption sites, motivated by electrostatic interactions, as compared to the electrolytes free of organics (Figure 2 A). However, despite the presence of 33 mg/L of citrate in the solution, the surface sorption sites within the larger membrane surface area were not exceedingly depleted by the effect of the competing citrate molecules.

When 2 and 3 V of DC potential were applied, near complete removal of the contaminants from 10 mM NaCl was observed up to 300 minutes of operation time (Figure 2 A). In the case of electrofiltration from synthetic wastewater at 2 V (Figure 2 B), a slight deterioration can be

observed starting at 120 minutes and increasing until 270 minutes of operation time. However, such deterioration did not result in significant reduction in flux values at applications of 2 and 3 V in both cases of removal from 10 mM NaCl and synthetic wastewater ($5.5 - 5.6 \mu\text{g m}^{-2} \text{hr}^{-1}$) (Figure S7 C and D, supplementary material). The similar flux values confirm that major degradation pathways are through indirect oxidation by the interaction of ibuprofen and bisphenol A with oxidative intermediates (i.e. superoxide and reactive chlorine) in bulk. This observation agrees with our previous observations during dead-end studies. In our previous dead-end studies, it was observed that bisphenol A is more readily oxidizable at 2 and 3 V as compared to ibuprofen, mainly due to the lower oxidation potential of the former [50, 51]. Similar outcomes for the removal from pure NaCl solution and synthetic wastewater also show that production of reactive species is considerably efficient in both solution conditions.

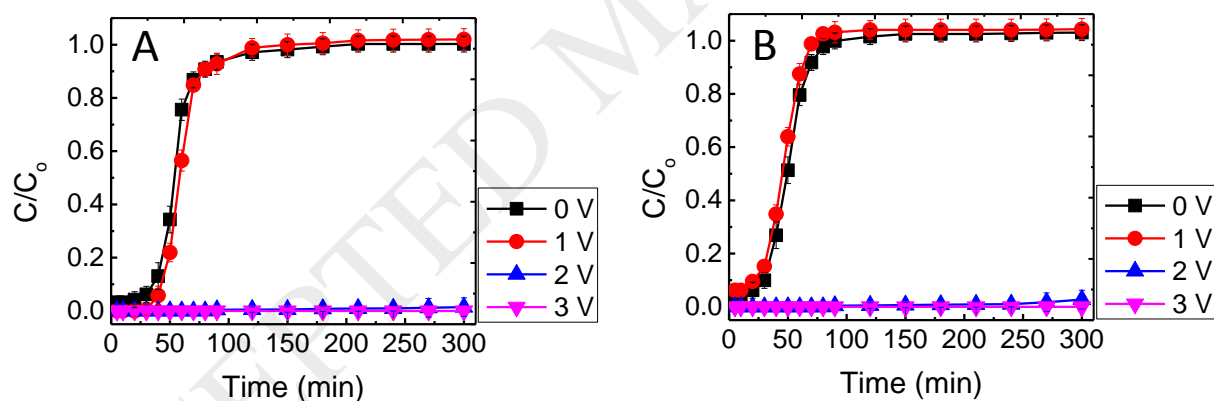


Figure 2. (A) Breakthrough plots for the removal of 1 mg/L Ibuprofen and bisphenol A (1:1) mixture from 10 mM NaCl and (B) from synthetic secondary wastewater (TOC 34 mg/L, pH 7.4), under 0, 1, 2 and 3 V of applied DC potential, applied pressure is 20 psi, permeate flow rate is 1 mL/min and all conducted at room temperature.

The fact that the deterioration is very slight ($C/C_0 = 0.01 - 0.035$) may, again, be due to the combination of efficient surface coverage by the shear flow, the high conductivity, and the

enormous surface area, all which contribute to great electrochemical performance as compared to the flow-through mechanism in dead-end studies. On the other hand, it was previously reported that using conductive carbon-based CNTs as a cathode material contributes toward improving anode performance. This is mainly due to the larger specific surface area of CNTs as compared to conventional metallic electrodes, which, in turn, leads to a significant reduction of the cathodic charge transfer resistance and reflects an increased anode potential. Therefore, the magnitude of electrooxidation at the anode surface would be of a greater extent [16].

3.2. Qualification of Ibuprofen and bisphenol A (1:1) mixture removal, and by-products characterization by liquid chromatography mass spectrometry

Ibuprofen and bisphenol A mixture samples were analyzed by LC-MS before and after crossflow electrochemical filtration treatment to obtain an insight into the effectiveness of the process of eliminating the two target molecules and reducing their toxicity. A sizeable initial concentration of 20 mg/L of a 1:1 ibuprofen and bisphenol A mixture in 10 mM NaCl was used to enhance electrochemical reaction kinetics, obtain a significant by-product spectrum, and to avoid spectral noise interference from any background species. Figure 3 shows the LC-MS analysis for the ibuprofen and bisphenol A mixture before and after treatment under 2 and 3 V of applied DC potentials, at 5, 150, and 300 minutes of operation time.

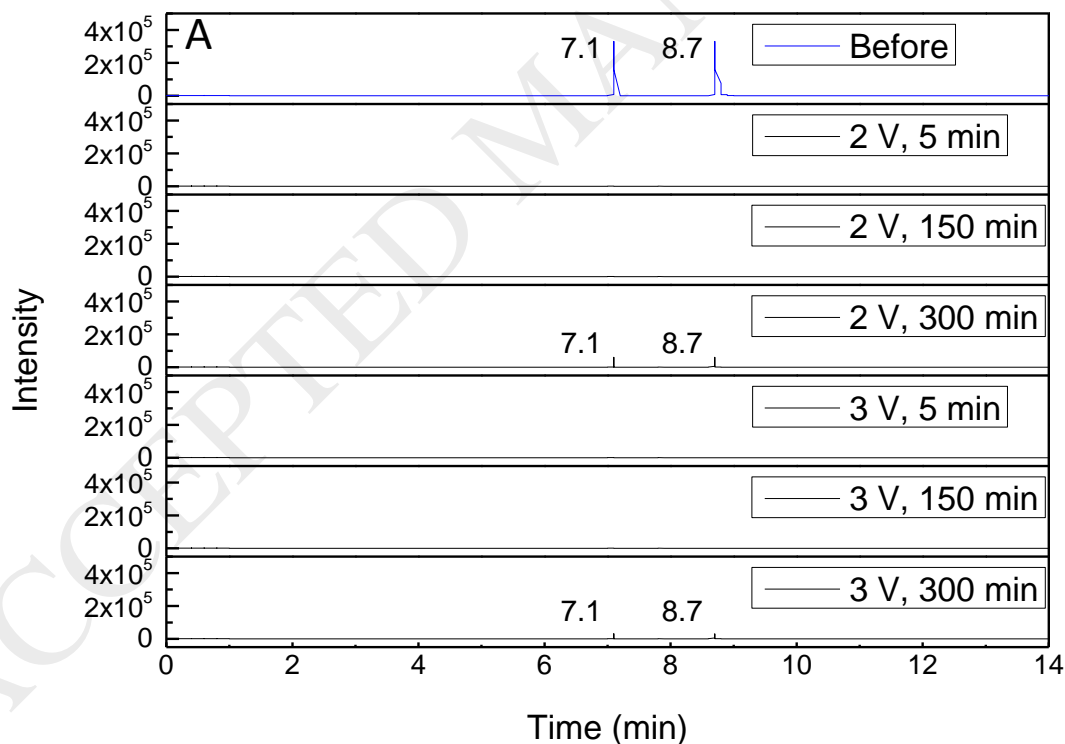
Figure 3 A shows the overlaid LC chromatograms in which two significant peaks were detected in the sample before treatment (blue trace) at retention times (RT) of 7.1 and 8.7 minutes, assigned to ibuprofen and bisphenol A, respectively. After treatment under 2 V, the two peaks were not detected in the samples obtained at 5 and 150 minutes of operation time, while traces of ibuprofen and bisphenol A could be detected only in the samples obtained at 300 minutes.

Under 3 V, similar observations were found with fewer traces observed only after 300 minutes. Figure 3 B shows the mass spectra corresponding to Figure 3 A, confirming the complete removal of ibuprofen (m/z 205) and bisphenol A (m/z 227) within 150 minutes of electrochemical filtration. Nine other MS peaks were detected in samples after treatment at m/z 59, 73, 89, 103, 107, 109, 115, 157 and 171 (Figure S8 to S11, supplementary material). The peaks at m/z 107 and 109 were only detected after treatment under 2 V and were predicted to correspond to the formation of p-benzoquinone (m/z 107), hydroquinone, and catechol (m/z 109). Several authors previously detected and reported the formation of hydroquinone and p-benzoquinone from the degradation of ibuprofen and bisphenol A [57-61].

Ambuludi, Panizza, Oturan, Özcan and Oturan [57] detected the formation of p-benzoquinone from the oxidation of ibuprofen through the hydroxyl radical attack on the parent molecule and a consecutive hydroxylation in an electro-Fenton process. Cui, Li and Chen [58] detected the formation of hydroquinone and benzoquinone during the electrochemical degradation of bisphenol A using different electrode materials in a batch electrolysis process. The authors attributed the formation of such single-ring aromatic products from bisphenol A to: the first step of Isopropylidene bond cleavage, resulting in the splitting of the molecule, followed by further hydroxylation to phenolic intermediates, and the deprotonation of hydroquinone to benzoquinone. Moreover, the formation of hydroquinone and benzoquinone is an indication of a formation of phenolic derivatives that could herald the formation of unstable polymeric compounds during bisphenol A electrolysis [62-66]. Muruganathan, Yoshihara, Rakuma and Shirakashi [59], Zhang, Sun and Guan [60], Cui, Li and Chen [58], Gözmen, Oturan, Oturan and Erbatur [62] and Katsumata, Kawabe, Kaneco, Suzuki and Ohta [67] all reported the formation

of hydroquinone and benzoquinone from the degradation of bisphenol A, which is reported to be followed by the formation of simple aliphatic carboxylic acids.

Watanabe, Harada, Matsui, Miyasaka, Okuhata, Tanaka, Nakayama, Kato, Bamba and Hirata [68] attributed the formation of a catechol group from bisphenol A firstly to the creation of phenolic derivatives at an m/z of 149, which upon further oxidation yields a 1,2-quinone group. Such phenolic derivatives at m/z 149 were detected in our previous study on dead-end electrochemical filtration of bisphenol A. Thus the formation of the m/z 109 (catechol) suggests the same oxidative sequence in the current study. Figure 4 shows a suggested common degradation pathway for both ibuprofen and bisphenol A, based on our detected products.



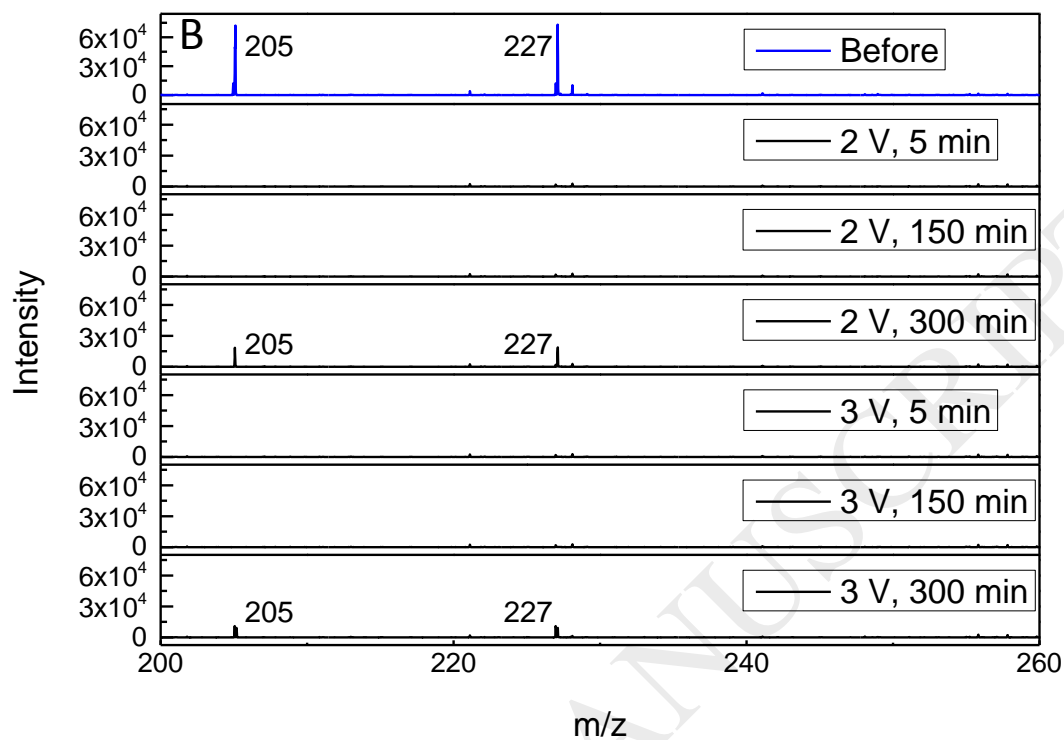


Figure 3. LCMS for the treatment of 20 mg/L Ibuprofen and bisphenol A (1:1) mixture from 10 mM NaCl, where (A) are the overlaid LC chromatograms for mixture before treatment (Blue trace) and after treatment (Black traces) and (B) is MS spectra for mixture before treatment (Blue trace) and after treatment (Black traces). Applied voltages were 2 and 3 V of applied DC potential, applied pressure of 20 psi, and a permeate flow rate of 1 mL/min, all conducted at room temperature.

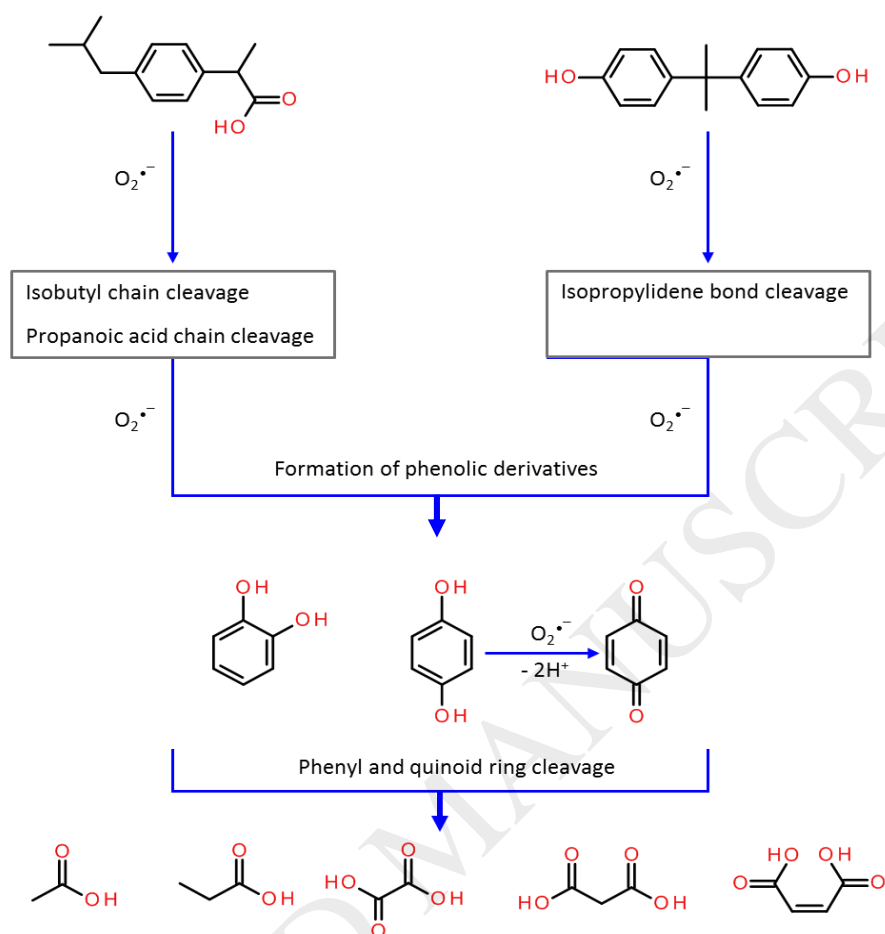


Figure 4. Possible degradation pathway for ibuprofen and bisphenol A during crossflow electrochemical filtration.

As reported, the formation of single-ring phenolic products could be a common outcome of the oxidative degradation of ibuprofen and bisphenol A. The fact that these phenolic products could only be detected in the samples obtained from the treatment under 2 V, while at 3 V they were not detected (Figure S10, supplementary material), is a clear indication of the effect of increased voltage toward faster degradation kinetics. This result also indicates a more efficient transformation of the parent molecules and their phenolic products during treatment using the current crossflow configuration and applied conditions. Moreover, the longer residence time of

18.3 seconds (corresponding to an average flow rate of 1 mL/min), compared to the lower residence times in our previous dead-end study on bisphenol A degradation, is another critical factor in further degradation to the point of the first formation of aliphatic by-products in the current study.

The degradation pathway starts with cleavage of aliphatic chains in ibuprofen (isobutyl and propanoic acid chains) and bisphenol A (Isopropylidene group) by the effect of superoxides or other possible ROS. Further hydroxylation would take place at the phenyl and quinoid rings, resulting in ring cleavage and subsequent formation of simple aliphatic carboxylic acids. The aliphatic carboxylic acids detected in the current study were acetic acid (m/z 59), propanoic acid (m/z 73), oxalic acid (m/z 89), malonic acid (m/z 103), and maleic acid (m/z 115). The formation of these aliphatic acids also suggests a possibility of further complete mineralization of ibuprofen and bisphenol A into the final products of carbon dioxide and water. The observed spectral trend of increased intensity of these acids at 3 V as compared to 2 V also indicates their faster and more intense production when voltage was raised from 2 to 3 V (Figure S8 to S10, supplementary material).

Other possible chlorinated products could be formed, as indicated by the formation of m/z 157 and m/z 171 only in the samples treated under 3 V (Figure S11, supplementary material). These m/z values were also detected from our previous dead-end electrochemical filtration treatment of bisphenol A under 3 V and low flow rate. The m/z values of 157 and 171 suggest that reactive chlorine interactions with bisphenol A is of significantly slow kinetics and requires high input voltage as compared to ROS (superoxide) interactions.

3.3. Energy consumption for crossflow electrochemical filtration

The energy consumption per volume treated for crossflow electrochemical filtration was calculated for the removal of individual and mixture solutions of ibuprofen and bisphenol A. The energy consumption values were found to be around 7.5 KWh m⁻³, corresponding to 2 V of applied potential and 17 KWh m⁻³, corresponding to 3 V (Figure S12, supplementary material). These values put crossflow electrochemical filtration within previously reported energy consumption ranges of the state-of-the-art electrochemical oxidation processes, yet below maximum reported values (0.1- 40 KWh m⁻³)[16]. This makes crossflow a highly competitive process for removal of trace contaminants, given the substantial advantages of crossflow electrochemical filtration, such as: the significant antifouling capacity, the more efficient solute transfer under hydrodynamic flow, and the higher time efficiency in removing trace organic contaminants, which are hardly removed by conventional electrooxidation processes and require long operation hours for satisfactory outcomes. However, comparing the energy consumption of crossflow electrochemical filtration to previously reported values for dead-end electrochemical filtration shows higher values for the former, and as such, is the only limitation for crossflow process as compared to dead-end [16, 50, 51]. This is attributed to the large-blend buckypaper membrane filter surface area employed in the current study, the high conductivity, and the long solute retention.

4. Conclusion

A superconductive MWNTs blend buckypaper membrane was successfully employed in an electrochemical filtration treatment for two emerging contaminants, ibuprofen and bisphenol A, using a flat sheet crossflow configuration. The removal of the two target molecules was

evaluated individually and in a mixture of 1:1 equimolar composition. It was shown that the crossflow configuration shows excellent potential in eliminating the two contaminants in individual and mixture solutions. The superior electrochemical efficiency of the crossflow mode in the elimination of the two contaminants was mainly attributed to the shear flow, which likely leads to a consistent surface coverage and the excellent conductivity of the MWNTs blend buckypaper membrane when 2 and 3 V DC potentials were applied. The long residence time of 18.3 seconds led to a significant degradation outcome of the two contaminants and their toxic aromatic products, at both 2 and 3 V of applied DC potential. The LCMS analysis showed complete removal of the two target contaminants, and the total degradation of their phenolic products into aliphatic carboxylic acids at 3 V. This outcome offers a significant indication that there is a possibility of complete degradation into the final products of carbon dioxide and water during the process.

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