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# **Optimizing electrochemical degradation of**

# 2 perfluorooctanoic acid in landfill leachate using

# **ceramic carbon foam electrodes by coupling CFD**

# 4 simulation and reactor design

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25

# 26 Abstract

Perfluorooctanoic acid (PFOA), a persistent and bioaccumulative pollutant classified as a 27 28 'forever chemical', poses a global environmental and health risk due to its widespread use and resistance to degradation. The development of effective and efficient removal technologies is 29 crucial to mitigate its long-term impacts. In this study, we present a novel approach to address 30 the growing concern of emerging contaminants, particularly PFOA, in landfill leachate. We 31 investigate the use of ceramic carbon foam electrodes (CCFE) as a cost-effective and efficient 32 alternative to traditional electrode materials for the electrochemical degradation of PFOA. 33 34 Micro-computed tomography was used to reconstruct the actual three-dimensional geometries of the samples in which porosities were calculated. We also coupled computational fluid 35 dynamics simulations of the actual geometries and optimised the working conditions to 36

minimise pressure drop and improve treatment efficiency. Our design significantly reduces 37 energy requirements by operating at lower potentials, a critical factor in sustainable waste 38 management practices. The optimised CCFE system demonstrated superior performance in 39 the degradation of PFOA in landfill leachate, offering a promising solution for the treatment of 40 emerging contaminants. This study not only provides a viable method for mitigating the 41 environmental impact of PFOA, but also sets a precedent for the development of low-energy, 42 high-efficiency treatment technologies for various persistent pollutants. In addition, the 43 proposed solution, as part of closed-loop water systems, will enhance water reuse and 44 45 recycling, thereby preserving and regenerating natural water bodies.

46 Keywords

47 PFAS, electrochemical oxidation, advanced oxidation process, electrode stability

48

# 49 **1. Introduction**

The global increase in the volume and complexity of waste poses serious risks to ecosystems 50 and human health (Clift et al., 2018; Falandysz et al., 2022). These growing waste streams are 51 a combined source of emerging contaminants, including per- and polyfluoroalkyl substances 52 (PFAS) (Reinhart et al., 2023). Due to the strong carbon-fluorine (C-F) bond, the persistent 53 nature of PFAS allows them to persist in the environment, accumulate in soil and water, and 54 55 thereby enter the food chain (Wee and Aris, 2023; Zafeiraki et al., 2019), raising significant 56 health concerns. These concerns include the potential for both chronic and acute adverse human health effects, such as developmental problems, liver damage and an increased 57 likelihood of cancer (Goodrich et al., 2022), as well as effects on wildlife (De Silva et al., 2021; 58 Zafeiraki et al., 2019). Although many environmental contaminants are regulated and 59 managed, effective control measures for PFAS and similar emerging contaminants remain 60 inadequate. In particular, there is an urgent need for cost-effective technologies to remove 61 persistent contaminants before they are released to the environment (Brunn et al., 2023; 62

Falandysz et al., 2022), especially from landfill leachates (Pierpaoli et al., 2021b). Efforts to 63 remove PFAS from water include activated carbon adsorption and various physical and 64 chemical treatments such as reverse osmosis, nanofiltration, ultrafiltration, oxidation and ion 65 exchange, as well as biological treatments including biodegradation and constructed wetlands 66 (EUN et al., 2022; Lu et al., 2023). Despite their effectiveness, these treatments are costly and 67 result in PFAS-containing waste, which poses disposal challenges. Innovative technologies, 68 such as electrochemical methods, offer promising alternatives for the treatment of PFAS-69 contaminated waters (Pierpaoli et al., 2021b; Xiao et al., 2023). These methods are valued for 70 their versatility and cost-effectiveness, using electrons to directly or indirectly oxidise 71 72 contaminants. A major focus is the use of three-dimensional electrodes, which come in various forms such as meshes, foams and porous solids, and are effective in increasing the rate of redox 73 74 reactions. The movement of mass towards the electrode surfaces involves migration, convection and diffusion. The role of mixing in this context is twofold. Firstly, it helps to 75 uniformise the concentration of reactants within the solution, ensuring a consistent and 76 77 homogeneous mixture; secondly, it helps to reduce the thickness of the Prandtl layer 78 immediately adjacent to the electrode surface.

The adsorption and electrochemical oxidation (EO) of perfluorooctanoic acid (PFOA) using 79 unconventional materials have received considerable attention due to their low cost, high 80 efficiency and environmental friendliness. While no adsorption of PFOA was observed on the 81 negatively charged silica surface, PFOA and other PFASs were found to sorb to the alumina 82 surface (positively charged), forming a hydrated layer, suggesting that the adsorption process 83 appears to be driven by electrostatic interactions between the PFAS functional group (negative) 84 and the mineral surface (Hellsing et al., 2016). Hydrotalcite is a layered double hydroxide 85 (LDH) with the general formula Mg6Al2CO3(OH)16-4H2O and has been shown to have 86 extraordinary adsorption capacities for PFOA, of the same order as anionic exchange resins 87 (above 100 mg/g) (Alonso-de-Linaje et al., 2021). Similarly, Wang and Shish showed how 88 PFOA adsorption on crystalline alumina is influenced by the pH of the solution and how it 89 90 decreases with increasing ionic strength of the cations, due to the compression of the electrical

double layer, as both Ca and Mg can form bridges with PFOA anions in solution (Wang and 91 Shih, 2011). In fact, PFOA adsorption on inorganic oxide materials is mostly driven by 92 electrostatic interactions (Chen et al., 2021). Al oxides and hydroxides, such as those derived 93 from aluminium-based drinking water treatment residuals, have also been shown to strongly 94 adsorb PFOA, with the capacity decreasing with increasing pH (Zhang et al., 2021). Open-cell 95 foams have attracted considerable attention for various applications, such as catalytic 96 substrates in combustion, reformers and converters to control pollutant emissions. They have 97 also been of interest in the energy sector, particularly for heat transfer applications and as 98 99 catalytic substrates in combustion devices, fuel reforming systems and emission control. The appeal of open-cell foams lies in their light weight, high surface to volume ratio and excellent 100 fluid permeability, making them suitable for a wide range of engineering applications. The 101 102 microstructural geometry of open-cell foams induces a tortuous flow path, resulting in high activity per unit volume, which is particularly advantageous for the aforementioned 103 104 applications. Researchers have used CFD simulations to study flow regimes within ideal foam 105 structures and the transition from laminar to fully turbulent regimes. Indeed, understanding the pressure drop and flow type as a function of flow rate within such a porous structure is 106 107 crucial. The Reynolds number has been used to define the flow regime, with smaller pore sizes 108 resulting in lower Reynolds numbers, leading to laminar flow.

The aim of our study was to explore the use of ceramic carbon foam electrodes (CCFE) as a 109 cost-effective replacement for traditional electrode materials in the electrochemical 110 111 degradation of PFOA found in landfill leachate. We focused on selecting a more affordable material and free from critical raw materials (CRMs) compared to traditionally available 112 options such as boron-doped and metal oxide-coated titanium electrodes (Pierpaoli et al., 113 2020). Additionally, we optimized the flow and operational conditions using computational 114 fluid dynamics (CFD) simulations, with a particular emphasis on minimizing energy 115 116 consumption.

# 117 2. Materials and methods

### 118 2.1 Chemicals and Materials

Perfluorooctanoic acid (PFOA) standard, an analytical standard grade, was purchased from 119 120 DR Ehrenstorfer (Germany). Eluent additive to HPLC method: ammonium acetate was suitable for mass spectrometry (LiChropur<sup>TM</sup>, Merck Company), while methanol (MeOH), was 121 hypergrade for LC-MS (LiChrosolv<sup>®</sup>, Merck Company). Phosphate buffer solution (PBS, 0.1 122 M) was prepared as described in our previous work (Pierpaoli et al., 2021b). Purified water 123 (ultrapure water, resistivity 18.2 MΩ cm at 25°C) was obtained via a Direct-Q® Water 124 Purification System, and used to dilute 1:1 the landfill leachate and spike at different 125 concentrations (0.001, 0.1 and 10 mg L<sup>-1</sup>) with PFOA. Ceramic carbon foam electrodes (CCFE) 126 127 were supplied by Ferro-Term (Poland). Briefly, CCFE were prepared from a mixture of ceramic powder, hard coal and carbon binder, suspended in an aqueous silicic acid sol solution. The 128 129 solution is then used to coat polymer foams, which, after drying, are fired at a temperature of 600-1000°C in an oxygen-free atmosphere. 130

## 131 2.2 CCFE Chemical and morphological characterization

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy were 132 133 performed using a Phenom XL microscope (Thermo Fisher Scientific) with a beam acceleration voltage of 10 kV, operating in high vacuum mode and with a secondary electron detector (SED). 134 Raman spectroscopy was used to study the molecular composition of CCFE. The system 135 136 consists of a TE-cooled to -60° CCD camera detector (Andor iDus-420-BR-DD, Ireland), a f/2.2 spectrograph with volume phase holographic (VPH) transmission grating (HT-137 spectrometer, EmVision llc., USA) with dedicated fibre-optic contact probe (EmVision llc., 138 139 USA) and an excitation laser module with central wavelength of 830 nm (Innovative Photonic 140 Solutions, USA). Micro-computed tomography ( $\mu$ CT) was used for 3D reconstruction of the actual geometry of the samples. The equipment used was a GE phoenix vltomelxs with an X-141 142 ray power set at 30 W (100 kV, 300  $\mu$ A) and an exposure time of 5000 ms for each radiogram. Additional information on µCT are reported in the supplementary materials. Two copper 143 filters, each with a thickness of 0.5 mm, were used. ICP-OES (Inductively Coupled Plasma -144

145 Optical Emission Spectrometer, Optima 8300 PerkinElmer) analyses were performed on the 146 PFOA solutions, on the LL solution (after 30 minutes the CCFE electrode was in contact with 147 the spiked LL and after full EO test). A constant voltage was then applied and the test was run 148 for 3 hours. The samples collected were 10 mL of liquid for each analytical step. Prior to 149 analysis, the samples were filtered at 45  $\mu$ m and 0.1 ml of concentrated HNO<sub>3</sub> (ACS acid grade 150 at 65%) was added to prevent precipitation of metals. Each CCFE was used once.

## 151 2.3 CCFE Electrochemical characterization

Electrochemical measurements, including Tafel plots, electrochemical impedance 152 spectroscopy (EIS), and potential versus current, were performed before and after electrolysis 153 in a three-electrode system in a beaker with a working electrode (CCFE) measuring 7.5 x 7.6 x 154 2.5 cm, while the counter (cathode) and reference electrodes were a steel grid and Ad/AgCl 155 156 wire, respectively. Tafel measurements were recorded from 0 to 4 V at a scan rate of 10 mV/min. A current-potential curve for the CCFE in LL was obtained in the range of -1.5 V to 4 157 V at a scan rate 20 mV/s. EIS was performed in the frequency range from 1 MHz to 100 mHz, 158 at open circuit potential and with an amplitude of 20 mV. Electrochemical measurements were 159 carried out with a potentiostat-galvanostat (VMP-300, Bio-Logic, France) controlled by EC-160 Lab software. The electrolyte used for electrochemical measurements was 0.1 M PBS. 161

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# 163 2.4 Reactor and monitoring system design

The electrochemical reactor and monitoring cell were designed and realized by additive 164 165 manufacturing in PETG. Monitoring cell geometry was optimized by CFD simulation, as well 166 as the residence time was estimated to minimize the time between two subsequent samples. The monitoring cell includes 4 low-cost Electrical Conductivity, dissolved  $O_2$  (DO), redox 167 potential, pH sensors (Table S1), which have been calibrated against a laboratory grade digital 168 169 multimeter (HQ40D, Hach), equipped with HQ2200 (pH); IntelliCAL LDO101 (DO); PT1000 (conductivity) and IntelliCAL MTC101 (redox) probes manufactured by Hach (Germany). The 170 171 optical cell (Fig. 1B) includes a small cell (10 mm x 10 mm and 6 mm of optical path length) comprised of two quartz glasses. From one of the two sides, the water sample was illuminated 172

with a halogen source through an optical fibre and a collimator, and the resulting spectra were 173 passed through collimator and an optical fibre and acquired using a portable UV-VIS 174 spectrometer (Ocean Optics FX). For the monitoring and optical cells, two peristaltic pumps 175 regulated the flow. All optical and chemical measurements were conducted under static 176 177 conditions, meaning there was no flow during these measurements. Leachate was directed to the measurement cells at five-minute intervals for sensor analysis. Additionally, samples taken 178 at specific time intervals - 0, 5, 15, 30, 60, 90, 120, and 150 minutes - were specifically 179 designated for analysis using ultra-high performance liquid chromatography tandem mass 180 181 spectrometry with electrospray ionisation (UHPLC-ESI-MS/MS). The electrochemical reactor was designed as a parallelepiped chamber to facilitate flow through the CCFE electrode, with 182 the inlet and outlet positioned at diametrically opposed openings in the reactor (Fig. 1C). For 183 184 each experiment, the system was allowed to stabilise for 30 min before a constant voltage was applied. This stabilisation period ensured that the adsorption on the electrode reached a steady 185 state. A constant potential was then maintained for 180 minutes in each experiment, with the 186 187 current measured continuously throughout the process.



189 Fig. 1. – (A) Setup for the EO tests; (B) Optical cell;(C) EO reactor

The energy consumption per unit mass of PFOA removed (EC<sub>PFOA</sub>) for the electrochemical
mineralization process at a giving reaction time t (h) was calculated as [29]:

192 
$$EC_{PFOA} = \frac{E_{cell}lt}{\Delta[PFOA]_t V}$$
 Eq. 1

where  $E_{cell}$  is the cell potential (V), I the applied electric current (A),  $\Delta$ [PFOA]<sub>t</sub> (mg L<sup>-1</sup>) the variation of [PFOA] after a certain time t (h), and V the solution volume (L).

## 195 2.5 Adsorption experiments

Adsorption isotherm experiments were carried out in 120 mL HDPE vessels containing 100 mL solution. The initial concentrations of PFOS varied from 0.02 mg L<sup>-1</sup> to 0.5 mg L<sup>-1</sup> and from 10 mg L<sup>-1</sup> to 125 mg<sup>-1</sup> to achieve two adsorption isotherms at low and high concentrations. The vessels were shaken for 24 h. The amount of PFOS adsorbed by the CCFE and the single-point adsorption coefficients  $K_d$  (L g<sup>-1</sup>) were calculated from

201 
$$q_t = \frac{C_0 - C_t}{C_s}$$
 Eq. 2

$$202 K_d = \frac{q_e}{c_e} Eq. 3$$

where  $q_t$  and  $q_e$  (µmol g<sup>-1</sup>) are the concentrations of solutes adsorbed on the adsorbents at time t (min) and at equilibrium, respectively.  $C_0$  (µmol L<sup>-1</sup>) is the initial solute concentration.  $C_t$  and  $C_e$  (µmol L<sup>-1</sup>) are the solute concentrations in the aqueous phase at time t and at equilibrium, respectively.  $C_s$  (g L<sup>-1</sup>) is the mass of the CCFE.

The solid–liquid sorption distribution coefficient,  $K_d$  (mL g<sup>-1</sup>), was calculated as the ratio between the PFOA concentration sorbed in CCFE,  $C_s$  (mg g<sup>-1</sup>), and its concentration in the aqueous phase at equilibrium,  $C_{eq}$  (mg L<sup>-1</sup>):

210 
$$K_d = \frac{C_s}{C_{eq}}$$
 Eq. 4

C<sub>eq</sub> values were directly determined by UPLC–MS/MS and the corresponding concentrations
of PFASs sorbed by CCFE, whereas Cs was calculated by the following equation:

213 
$$C_s = \frac{(C_{in} - C_{eq})V}{m_{CFFE}}$$
 Eq. 5

- where  $C_{in}$  (mg L<sup>-1</sup>) corresponds to the initial concentration of PFOA added to the CCFE, V (mL)
- is the volume of solution and  $m_{CCFE}$  (g) refers to the dry mass of the CCFE.
- 216 The Freundlich model is quantitatively described by the following equation:
- 217  $C_s = K_f C_{eq}^n$  Eq. 6

218 Where  $K_f$  is the Freundlich constant, related to the adsorption capacity of the adsorbent and 219 the intensity of adsorption and n is the Freundlich exponent, a dimensionless constant that 220 represents the heterogeneity of the adsorption sites on the solid surface. The  $K_f$  and n221 parameters of the Freundlich equation were calculated by non-linear least squares fitting of 222 the sorption isotherms.

## 223 2.6 UHPLC – MS/MS and chemical analysis

An UHPLC-ESI-MS/MS Nexera XR coupled with LC/MS-8050 (Shimadzu Company), was 224 used to determine PFOA concentration. Process control samples were filtrated via 225 polypropylene (PP) 0.45 µm pore size syringe filters (Whatman®) and directed to UHPLC-226 227 ESI-MS/MS analysis. Modified and adjusted to the study purposes EPA 537.1 method was applied. Shim-pack SP-C18, 2.1 x 150 mm, and 2.7 µm was used as an analytical column, with 228 229 a constant flow applied at 0.3 ml min<sup>-1</sup>. The sample injection volume was 1 or 5 µL (depending on the spiking level). The calibration curve was plotted using 5-level calibration (linearity in 230 the ranges of 1–100 µgL<sup>-1</sup> and 1-10 mgL<sup>-1</sup>). The method detection limit (MDL) and method 231 quantification limit (MQL) were 1 and 3 µgL<sup>-1</sup> for the landfill leachate matrix. For this method, 232 no analyte pre-concentration was applied. Additional details are reported in the 233 supplementary materials. The composition of the landfill leachate was analysed using the 234 methods described in detail in our previous work (Fudala-Ksiazek et al., 2018; Szopińska et al., 235 236 2021; Wilk et al., 2022).

### 237 2.7 CFD simulation

A aomprehensive review on modelling turbulent flows in porous media, among which metal
foams, has been done by Wood, He and Apte (Wood et al., 2020). Briefly, in porous media,
four distinct flow regimes can be identified: (a) Darcy, (b) Forchheimer, (c) unsteady laminar

(transitional), and (d) fully-turbulent regime (Dybbs and Edwards, 1984). The transition
between these regimes is described by the pore-based Reynolds number, given by the formula:

243 
$$Re_p = \frac{UL_p}{v}$$
 Eq. 7

In which  $L_p$  is assumed equal to the diameter of the average pore size, U is the intrinsic average velocity and v the kinematic viscosity.

Firstly, by considering a 20 x 20 x 60 mm representative elementary volume (REV), steady Reynolds-averaged Navier–Stokes (RANS) simulations were performed at various Re number. The REV was obtained by  $\mu$ CT of the real sample and subsequent the mesh was reconstructed by voxel segmentation. Meshing (4.5×10<sup>6</sup> elements) and CFD simulations were performed with COMSOL Multiphysics 6.1.

The v<sup>2</sup>-f model (Durbin, 1991), a higher order turbulence model, suggested to be particularly suitable for turbulent flow in coarse porous media (Kazerooni and Hannani, 2007), has been chosen. Then CFD simulation at different flow rates have been performed, in order to obtain the averaged values for permeability to describe the macroscopic model. Permeability,  $\kappa$ , is given by the Eq. 8

256 
$$\kappa = u_{out} \mu \frac{L}{\Delta p}$$
 Eq. 8

257 Where  $\mu$  is the dynamic viscosity,  $u_{out}$  the outlet fluid velocity in the flow direction, *L* the side 258 length and  $\Delta p$  the pressure drop across the REV.  $\kappa$  has been calculated for low velocities 259 (equivalent to Re<sub>p</sub> < 12), for which we found a linear relation was still valid.

Secondly, the reactor reported in Fig. 1c has been simulated, using a porous media characterized by porosity  $\varepsilon_p$  and permeability  $\kappa$  as the CCFE with the additional Forchheimer coefficient equal to:

$$\beta = \frac{\rho \varepsilon_p c_f}{\sqrt{\kappa}}$$
 Eq. 9

Having  $\rho$  the fluid's density and C<sub>f</sub> the dimensionless Friction coefficient (Amiri and Vafai, 1998), equal to 0.23 (Amiri and Vafai, 1998).

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## 267 3. Results and discussion

## 268 3.1. Landfill leachate characterization

The landfill leachate (LL) was taken from the municipal solid-waste plant (MSWP) 'Eko Dolina 269 270 Lezyce' located in the Pomerania region (northern Poland) from the cell operated during a period where there was no waste segregation (from 2003 to 2011). This may cause various 271 micropollutant presence in the samples (including contaminants from the perfluorinated 272 organic compounds). The samples of raw LL were collected to polyethylene bottles in August 273 2022 and transported to the laboratory (at  $4 \pm 1^{\circ}$ C), where their physicochemical properties 274 were immediately evaluated. The basic composition of the landfill leachate is summarised in 275 Table S2. 276

# 277 3.2. Setup characterization and parameter optimization

278 CCFE is characterized by a three-dimensional connected mesh structure and high porosity, small flow resistance and it is electrically conductive. The fabrication of CCFE is conducted via 279 a multi-stage procedure. The process starts with the application of a ceramic suspension, 280 281 comprising alumina, sintering coal, and a blend of additives, onto an elastic polymer foam. 282 This slurry is employed to impregnate the polymeric foam, which acts as a foundational skeleton for the ensuing structure. Following the application of the slurry, the foam filters are 283 284 subjected to a drying phase. Then, filters are placed in a kiln and exposed to elevated temperatures. During the firing phase, the organic skeleton within the filters is incinerated, 285 resulting in an interconnected, porous ceramic matrix. This structure is then sintered to 286 287 enhance its mechanical strength and durability. Concurrently, caking coal, is added. The 288 heating process induces the caking coal to initially attain a plastic state, facilitating its 289 adherence to and encapsulation of the ceramic component grains. As the temperature 290 increases, the caking coal undergoes sintering, forming a sturdy ceramic-carbon composite material (Asłanowicz et al., 2019; Karwiński et al., 2013). 291

The resulting solid matrix is a heterogenous composite rich of Al, C, Si oxides (Fig. 2D,E). Fig. 2A presents the 3D reconstruction of the microtomography of the entire CCFE (REV1) employed in the experiments. For more detailed observations of inner pores, a smaller sample

295 (REV2) was reconstructed at a higher resolution, as illustrated in Fig. 2B. In addition, the diameters of inner pores and voids were analysed based on microphotographs taken by SEM 296 297 (Fig. 2C). From SEM/EDX analysis (Fig. 2D) it is possible to see that the composition of the 298 raw CCFE accounts mostly of Al, C, Si and Na (Fig. 2E). The total porosity is a complex outcome 299 influenced by the sacrificial polymeric structure, which is skeletal and characterized by a high void content, along with the presence of inner pores. The volume of inner pores has been 300 calculated for both REV samples, and the distribution is depicted in Fig. 2F. The inner pore 301 302 diameters, shown in Fig. 2G, were in the range of tens of micrometers, and the distribution of 303 void diameters, as shown in the same figure, had a median diameter of approximately 3.8 mm. 304 Full porosity calculations for both samples based on 3D reconstructions are shown in Table 1. The total porosity of the REV1 sample was 72.4%, while that of the REV2 sample was 79.6%. 305 306 The differences in porosity between the samples are attributed to the different volumes used for calculations and the different resolutions (voxel size) obtained. In addition, the surface area 307 308 of the samples that were counted is given in Table S3.



Fig. 2. – A) 3D visualization of a reconstructed larger sample; B) 3D visualization of a reconstructed
smaller sample with marked void and a magnified semi-transparent image showing pores; C) Cross-

- 312 section of sample observed by SEM; D) Map of elements on the cross-section of the sample observed
- 313 by SEM and EDX; E) Elemental analysis of the sample; F) Volume distribution of pores and (G)
- 314 diameter distribution of pores and voids of the REVs.
- 315

# 316 3.3. PFOA oxidation in landfill leachate

A current-potential curve for the CCFE in LL was obtained by scanning from -1.5 V to 4 V (vs Ag/AgCl 3M KCl). From Fig. 3A it is possible to observe two linear trends from which two potentials, 2.5 V and 4 V, have been selected to perform the EO experiment under potentiostatic conditions.



Fig. 3. - A) Potential vs current for CCFE in LL; B) PFOA adsorption isotherms at high and low (inset) concentrations for the CCFE electrode; C) PFOA degradation rate as function of the flow rate. Zeroorder rate constants for; D)  $N-NH_4^+$ ; E)  $N-NO_2^-$  and F)  $N-NO_3^-$  as function of the flow rate. "ns": not significant for p > 0.05.

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The adsorption of PFAS on various carbonaceous and inorganic materials has been extensively described and reviewed elsewhere (Du et al., 2014; Valencia et al., 2023). C<sub>s</sub> vs. C<sub>eq</sub> plots were used to construct sorption and then fitted to both Freundlich and linear models, which are commonly used for hydrophobic compounds (Hinz, 2001) and have been previously applied to describe PFAS sorption in sediments (Du et al., 2014; Hellsing et al., 2016; Higgins and Luthy,

2006). For low PFOA concentrations (0.02-0.5 mg L<sup>-1</sup>), a linear relationship was observed with 332 a K<sub>d</sub> of 0.05 mL/mg, while for higher PFOA concentrations (10-125 mg L<sup>-1</sup>), the Freundlich 333 isotherm fit the experimental results with a K<sub>f</sub> of 0.078  $mg^{(1-n)}mL^n g^{-1}$  (Fig. 3B). A comparison 334 335 with similar adsorbents by composition is given in Table S4. The first order rate constants of PFOA as a function of both initial concentration and flow rate are shown in Fig. 3C. It can be 336 observed that at lower concentrations, the slower the flow through the CCFE, the higher the 337 rate constant. While this may seem counterintuitive, since a higher flow rate implies a higher 338 339 mixing rate, which has been reported in the literature to enhance PFOA oxidation (Asadi 340 Zeidabadi et al., 2023), it also implies a lower residence time in the reactor and a lower contact 341 time with the CCFE surfaces. Since PFOA oxidation is mostly driven by direct electron transfer, rather than the action of the •OH radical (Pierpaoli et al., 2021b), where the limiting step is 342 343 provided by the electrode active surface, the higher velocity through the CCFE results in a lower rate. Furthermore, we observed that no degradation occurs at the lower potential of +2.5 V 344 (Fig. S1). A zero-order reaction was observed for ammonium removal, as it may be mainly 345 346 driven by the indirect pathway through reaction with chlorine (Li and Liu, 2009), which is 347 abundant in LL. Fig. 3D shows the variation of the ammonia rate constant as a function of the flow rate. While the NH<sub>4</sub><sup>+</sup> concentration decreases as the EO process progresses, the N-NO<sub>2</sub><sup>-</sup> 348 and N-NO<sub>3</sub><sup>-</sup> concentrations increase, also clearly at zero order, as ammonia is partially 349 converted to nitrate ions (Anglada et al., 2011; Pierpaoli et al., 2021a). While a correlation 350 between flow rate and N-NH4<sup>+</sup> removal rate is not visible, it is for the N-NO<sub>2</sub><sup>-</sup> and N-NO<sub>3</sub><sup>-</sup> rates, 351 as they increase with increasing flow but they are less affected from the presence of PFOA, due 352 to competitive direct oxidation on the surface electrode. The COD is slightly affected by the EO, 353 since its degradation is accompanied by the release of carbon from the electrode (Fig. S2). 354

The optical transmittance of the LL was measured using the designed optical cell, with a halogen lamp as the source, in the ranges 350-550 nm and 670-950 nm. The 550-670 nm interval was discarded due to the presence of the lamp emission peak which saturated the spectroscope. When a potential of +4 V was applied, the transmittance in the range 400-550 nm decreased, which may be due to carbon loss from the electrode to the LL. Additionally, a

slight increase in transmittance was observed in the range 670-780 nm when a potential of 360 +2.5 V was applied. An increase was also observed in the blank sample without the application 361 of a potential. This increase is likely due to the sedimentation and/or adsorption of particles 362 and compounds (Fig. S3). Fig. S4 shows the correlation between the parameters estimated by 363 the chemical/physical monitoring cell. A general decrease in LL pH is observed, along with a 364 slight increase in electrical conductivity. The oxidation reduction potential decreases abruptly 365 from positive  $(84\pm18)$  mV to negative  $(-66\pm12)$  mV just 15 minutes after the application of the 366 367 potential difference, and slowly increases with time to  $(-43\pm24)$  mV at 150 minutes. Oxygen is 368 rapidly depleted as it is consumed in the cathode, reaching its minimum after one hour of 369 treatment. However, a higher flow rate supports the LL reoxygenation (see Fig. S<sub>5</sub>). The specific energy consumption for PFOA removal, as described in Eq. 1, decreases with 370 371 increasing PFOA concentration, in a log-log correlation (Fig. S6).

## 372 3.4. Uniform corrosion rate and local corrosion susceptibility evaluation

To evaluate the susceptibility of uniform corrosion rate, the electrodes underwent cyclic 373 polarization and electrochemical impedance spectroscopy measurements before and after an 374 electrolysis event. Three external environmental factors were identified as important for 375 material degradation rate and electrolytic efficiency: electrolyser polarization conditions, 376 hydrodynamic fluid flow through the electrochemical cell, and the concentration of 377 contaminant species in the electrolyte. It is important to note that even a single electrolysis 378 379 cycle can lead to a deterioration in the corrosion resistance of the CCFE electrodes being 380 studied. This can be observed through changes in the electrode's kinetics. Tafel extrapolation 381 can be used to estimate the corrosion current  $(i_0)$ , which is directly proportional to the 382 corrosion rate. Notably, the electrolysis voltage has a visible effect on the cathodic slope, indicating that both studied polarization conditions: +2.5 and +4.0 V lead to io increase by two 383 orders of magnitude, higher at higher polarization voltages (Fig. 4.3A,D). The charge-transfer 384 385 mechanism shifts from anodically controlled to cathodically controlled after electrolysis.



Fig. 4. – (A-C) cyclic polarization curves and (D-F) EIS spectra recorded for CCFE electrodes. (G) Al,
Fe, Mg, Mn concentrations, determined by ICP-OES, before and after both pre-conditioning in PBS
and in LL. (H) difference in elemental composition, determined by EDX and (I) Raman spectra of the
CCFE before and after EO tests.

It is known that some of the electro-oxidized species are adsorbing at the electrode surface, 392 acting as a passive film and effectively blocking the electrode towards consecutive oxidation 393 394 processes. This characteristic process may lead to a secondary decrease in electrode susceptibility to corrosion, which should be explained by the passivation mechanism. As an 395 example, an effect of Perfluorooctanoic acid (PFOA) was used in different concentrations 396 397 ranging from 0.001 to 10 mg/L (Fig. 4B,E). Here, at the highest concentrations, the corrosion current i<sub>0</sub> was the lowest, which, however, has an expected negative influence on the electro-398 oxidation efficiency. Notably, there was no shift in the corrosion potential observed, as would 399 be in the case of the classic passive layer. The CCFE corrosion susceptibility was studied at 400

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401 various hydrodynamic flows, ranging from 250 to 1025 mL/min (Fig. 4.C,F). It is seen that 402 regardless of the flow rate the mechanism of the corrosion process is quite similar, and the 403 corrosion rate is not driven by the diffusion limitation. In other words, despite the flow rate 404 studied the electrochemical process under investigation is activation-controlled, and the 405 electron transfer is slower compared to the diffusion. This observation is connected to the foam 406 shape of the studied electrodes. It should be noted that the lowest  $i_0$  was identified for the 407 sample studied at the lowest flow rates.

408 Part of the Al and Fe content of the CCFE is leached into the PBS prior the electrochemical 409 oxidation test, during the Tafel characterization (Fig. 4G). Moreover, a decrease of Mg and Mn 410 from LL are observed (Chen et al., 2022). The reason may be due the formation of magnesium hydroxide, Mg(OH)<sub>2</sub>, especially in alkaline conditions, which can precipitate, since it becomes 411 412 less soluble as the pH increases (Pilarska et al., 2017; Weijma et al., 2022); however, since the pH increases during the process, it may be possible that Mg may be adsorbed/electrodeposited 413 on the electrode or in general, metals can have a rapid aggregation in aqueous solution due to 414 415 large Van der Waals forces, and decreasing the adsorption potential (Qasem et al., 2021). In 416 fact, according to the reduction at the cathode, the heavy metals solid gathers at the cathode and form a layer on its surface (Tran et al., 2017). Indeed, a reduction was detected on Cr and 417 418 slightly on Ni (Fig. S7). Additionally, the EDX analysis reveals a loss of carbon content and an enrichment of other elements (Fig. 4H). The Raman spectra collected before and after the EO 419 process show distinct peaks on top of the D peak, broadening of the D peak, and an increase in 420 421 background fluorescence, possibly due to the loss of carbon from the Al-rich structure (Fig. 4I). The sharper peaks that arise are at approximately 1395 cm<sup>-1</sup> and 1420 cm<sup>-1</sup>, which most likely 422 correspond to C–O stretching and CH<sub>2</sub> scissor bending, respectively. Additionally, there is a 423 weak, broad band near the G peak at about 1760-90 cm<sup>-1</sup>, which is likely attributable to C=O 424 stretching, suggesting oxidation. 425

In summary, the most notable factor affecting the corrosion rate is the electrode modificationunder electrolysis, which leads to surface area development and modification of the redox

428 mechanism. The variation in polarization voltages and flow rates is noticeable but does not429 exceed one order of magnitude.

## 430 3.5. CFD Simulation

The initial step in CFD simulation involved reconstructing the imported REV of the CCFE to eliminate the internal porosity and simplify the geometry through castellation for import into the software. After that, high-order turbulence model (v<sup>2</sup>f) has been employed to solve the model. This helps obtain permeability and porosity values, which are then used in an approximate model of the full reactor (Fig. 5A).



Fig. 5. – (A) schematic representation of the procedure towards the EO reactor CFD simulation. (B)
Velocity magnitude across the REV for three selected inlet velocities. (C) EIS results at different flow
rates and (D) EEC used to fit the experimental data. (E) Rct and F as function of the flow rate. (F)
Velocity magnitudes in the CCFE cross-section at half depth resulting from the simplified CFD

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441 simulation of the EO reactor. (G) Relative concentrations within the CCFE volume as function of the

442 *time for an instantaneous release.* 

Fig. 5B shows the change in the flow field through the CCFE porosity with increasing velocity. 443 The CFD simulation investigated velocities ranging from 1 to 250 cm min<sup>-1</sup>. Meanwhile, EIS 444 445 was performed on the CCFE electrode using the setup depicted in Fig. 1. The resulting impedance spectra at various flow rates (ranging from 250 to 1250 mL min<sup>-1</sup>) are shown in Fig. 446 5C and fitted with the equivalent electrical circuit (EEC) presented in Fig. 5D. It is noteworthy 447 that  $R_{ct}$  increases as the flow rate increases, specifically for Q > 625 mL min<sup>-1</sup>, which is the 448 threshold at which the Forchheimer contribution (Eq. 9) becomes relevant (Fig. 5D). The 449 increased pressure drop and flow resistance associated with the Forchheimer term (F) affect 450 451 the transport of species towards the electrode surface, which in turn affects charge transfer 452 kinetics and subsequently the charge transfer resistance of the electrode. The simulation yielded values for porosity and permeability of 0.83 (similar to the total porosity ratio obtained 453 by  $\mu$ CT) and 6.4 × 10<sup>-7</sup> m<sup>2</sup>, respectively. These values were used to create a simplified model of 454 the reactor. The flow is described by the Navier-Stokes equation in the free region and a 455 Forchheimer-corrected version of the Brinkman equations in the CCFE region. The simulation 456 457 results at the flow rates used in the EO tests are shown in Fig. 5F. An increasing heterogeneity of velocity intensity can be observed at the centre of the CCFE electrode as the flow rate 458 increases. By simulating an instantaneous release of a given species at the inlet, it is possible 459 460 to observe concentration peaks at the outlet at 4, 8, and 23 seconds for the three flow rates (Fig. 5G). The latter flow rate has the lowest coefficient of variation (calculated as Fig. S8) and 461 is more constant over time (see inset), suggesting better mixing and concentration uniformity 462 within the CCFE electrode. 463

#### 464 4. Conclusions

465 This study explores the use of CCFE for the electrochemical oxidation of PFOA in landfill 466 leachate. The process parameters, such as applied potential and flow rate, were optimized, and 467 an automated platform was developed to monitor the process, supported by CFD simulations. 468 The PFOA adsorption onto CCFE is comparable to that on Al-rich sediments, and it provides a

valuable support for its electrochemical oxidation. Lower flow-through rates improve PFOA 469 oxidation, while the opposite is true for the oxidation of N-NH<sub>4</sub> to N-NO<sub>3</sub> by N-NO<sub>2</sub>. PFOA 470 follows a first-order kinetic due to direct electron transfer being the leading mechanism. In 471 contrast, N-NH<sub>4</sub> oxidation is driven by the indirect reaction with the electrogenerated chlorine, 472 resulting in a zero-order kinetic fashion due to the abundance of chlorides in LL. The results 473 of the CFD simulation indicate that at lower flow rates, the concentration at the CCFE electrode 474 cross-section is more uniform under Darcy flow conditions. Electrode stability was assessed 475 using electrochemical methods, and the leaching of carbon and aluminium was confirmed by 476 477 EDX and ICP-OES. Additionally, the removal of some metals in the solution, such as Mg and Mn, from LL and their possible deposition onto the electrode surface were detected by means 478 of Raman investigations. By coupling spectroscopic methods with electrochemical ones, it is 479 480 possible to observe that the transmittance through the LL increases at potentials up to 2.5 V without the oxidation of PFOA. However, at 4 V, PFOA is oxidised, resulting in a decrease in 481 transmittance in the 480-550 nm interval. Additionally, CFD simulations can be used to 482 483 optimize reactor geometry and operational parameters to develop a viable technology for PFAS 484 control.

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