

Research article

Efficient electro-oxidation-based degradation of per- and polyfluoroalkyl (PFAS) persistent pollutants by using plasma torch synthesized pure-Magnéli phase-Ti₄O₇ anodes

Hela Rekik^a, Loick Pichon^b, Termeh Teymoorian^c, Hamed Arab^a, Sébastien Sauvé^c, My Ali El Khakani^{b,*}, Patrick Drogui^{a,*}

^a Institut National de la Recherche Scientifique (INRS) - Centre Eau Terre Environnement (ETE), 490 rue de la Couronne, Québec, QC, G1K 9A9, Canada

^b Institut National de la Recherche Scientifique, Centre Énergie, Matériaux et Télécommunications (EMT), 1650, Boulevard Lionel-Boulet, Varennes, J3X 1P7, QC, Canada

^c Université de Montréal, 2900, boul. Édouard-Montpetit, Montréal, QC, H3T 1J4, Canada

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ABSTRACT

Pure Magnéli-phase Ti₄O₇ were prepared by means of a Plasma Torch (PT) coating method and integrated into an advanced electro-catalytic oxidation (AEO) process in order to degrade perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) persistent pollutants present in waters. The X-ray diffraction analysis confirmed the polycrystalline nature of the pure Magnéli phase PT-Ti₄O₇ coatings (~100 μm thick). The Raman spectra of the PT-Ti₄O₇ coatings also exhibited the two characteristic peaks (at 138 and 183 cm⁻¹) of the PT-Ti₄O₇ Magnéli phase. Scanning electron microscopy revealed the nanostructured hierarchical morphology of the PT-Ti₄O₇ thus conferring them high surface area. The PT-Ti₄O₇ anodes are shown to achieve higher degradation efficiencies towards PFOA and PFOS in comparison with the conventional boron-doped diamond anodes. By investigating several AEO parameters (including current density, treatment time, nature of the anode material), we were able to optimise the AEO process. Thus, for both PFOA and PFOS (at an initial concentration of 500 ppb in synthetic wastewaters), degradation efficiencies as high as 96.6% and 99.7% were achieved, respectively, with a current density of 20 mA/cm², a treatment time of 120 min and PT-Ti₄O₇ mesh-type anodes. PFOA and PFOS can be degraded by both direct anodic electrochemical oxidation (*OH radicals) and indirect electrochemical oxidation via mediators, such as persulphate acid (H₂S₂O₈) generated by sulphate anodic oxidation. The degradation of both compounds followed pseudo-first-order kinetics. The reaction rate constant (k) for PFOS removal was 4.63 × 10⁻² min⁻¹, whereas 2.76 × 10⁻² min⁻¹ was recorded for PFOA removal. Subsequently, we have used the above optimal AEO operating conditions to treat real wastewater effluents (containing 17 types of PFAS molecules with a total content of 8500 ppb) and achieved a degradation rate of 39.1%–87.4% for eight of the 17 PFAS compounds. The degradation rate was found to be dependent on the chemical structure and chain length of each PFOA/PFOS component.

1. Introduction

Per and polyfluoroalkyl substances (PFAS, C_nF_{2n+1}-R) are a man-made chemicals that have been introduced to the world since 1930 (ITRC, 2020). Because of their high thermal and chemical stability, the PFAS have been widely used in a variety of application such as food packaging, non-stick cookware, waterproof makeup, aqueous fire-fighting foam, surface coatings, water-resistant fabrics, semiconductor

industry, etc. (Buck et al., 2011; Rekik et al., 2024; Tsang et al., 1998). PFAS compounds are known by their highly stable C-F bonds that replace of the typical C-H bonds in organic molecules (Fujii et al., 2007). Additionally, highly fluorinated aliphatic substances are a subset of fluorinated compounds that contain one or more carbon atoms on which all hydrogen substituents have been replaced by fluorine atoms resulting in the presence of the perfluoroalkyl moiety C_nF_{2n+1} (Buck et al., 2011). Thus, PFAS are extremely persistent in the environment and human

* Corresponding author.

** Corresponding author.

E-mail addresses: m.a.elkhakani@inrs.ca (M.A. El Khakani), patrick.drogui@ete.inrs.ca (P. Drogui).

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body and can be introduced in the environment through waste streams in different ways of making their removal very difficult. Due to their strong chemical stability, special procedures are generally required to handle this persistent class of contaminants (Tsang et al., 1998). A large portion of the PFAS persistent pollutants ends up in waste waters or can be a potential source of contamination of drinking waters. Unfortunately, the PFAS molecules are hardly removable by using traditional wastewater treatments and/or remediation methods. It is thus urgent to develop advanced and highly efficient technologies for the effective PFAS degradation and cleanup, in order to protect both human health and our environment.

While the PFAS related regulations are getting tighter, it is equally important to use affordable and scalable techniques for their massive treatment. Although there are many techniques and approaches for PFAS remediation, the advanced electrochemical oxidation (AEO) remains, to the best of our knowledge, the most appropriate and effective yet affordable and scalable approach. The choice of the AEO technique is justified by its robustness, ability to operate under severe conditions, and capacity to remove recalcitrant organic contaminants (Wang et al., 2020c). In general, the AEO process is based on the synergy between the anode oxidation reactions and the cathode reduction reactions. The goal of the AEO technique is the achievement of a degradation and ultimately a complete mineralization of the pollutants by exploiting and optimizing the redox reactions that produce a maximum of oxidant species (Coman et al., 2013; Nancharai et al., 2015). The oxidation of the PFAS occurs via the synergetic action of both direct anodic oxidation and indirect oxidation in the electrolytic reactor. First, the direct anodic oxidation takes place on the anode and drives a direct charge transfer reaction between the anode surface and the PFAS compound. To clearly understand the mechanism, a intermediation of the electrons endures the oxidation of the PFAS present in the effluent at a defined current density (Dombrowski et al., 2018). Secondly, the indirect oxidation is maintained by the in-situ produced oxidant species at the electrode surface such as hydrogen peroxide, hydroxyl radicals and persulphate (Dombrowski et al., 2018). Beside the redox reaction, the material used for the anodes is of paramount importance in the AEO pollutant removal rate (Brillas and Martínez-Huitle, 2015; Panizza and Cerisola, 2009). The elimination of PFAS by AEO has shown great promises, but finding the right anode is crucial to the process's effectiveness. The effective breakdown of PFAS is ensured by choosing the appropriate anode material that can perform efficiently while retaining scalability and economic viability.

The nature and properties of the anodes used in electro-oxidation processing are key for the successful degradation of pollutants in water. They must be chemically stable, highly-electrically conductive, non-polluting, and cost-effective (Särkkä et al., 2015). Boron-doped diamond (BDD) is well known to be a reliable anode, but it is also a highly expensive one. Their high manufacturing costs and difficulty in obtaining large surface areas are significant barriers to their scale-up (ELECTROCHEMICAL OXIDATION OF SULFIDE IONS IN SYNTHETIC SOUR, 2010; Kumar and Pan, 2020). Sub-stoichiometric titanium dioxide (TiO_{2-x}) anodes have emerged as a highly attractive alternative to BDD, as they were already used in many applications (Lan et al., 2013; Park et al., 2013). More precisely, the Magnéli phase ($\text{Ti}_n\text{O}_{2n-1}$; with $3 \leq n \leq 10$) materials, exhibit a pseudo-metallic electrical conductivity, in addition to their high chemical stability and strong corrosion resistance (Andersson et al., 1957; Liborio and Harrison, 2008; Walsh and Wills, 2010). Among the $\text{Ti}_n\text{O}_{2n-1}$ Magnéli phase compounds, Ti_4O_7 ($n = 4$) is the most interesting one because of its highest electrical conductivity (Gusev et al., 2007; Smith et al., 1998; Xu et al., 2016). Moreover, the Magnéli phase anodes can be generally produced at a much lesser cost than the BDD ones, making them highly cost-effective (Delegan et al., 2014). Different forms of Magnéli phase anodes, including Ti_4O_7 , have been reported to be effective for the degradation of various water pollutants including amoxicillin (Ganiyu et al., 2016), tetracycline (Liang et al., 2018), oxalic and terephthalic acids (Nayak and Chaplin, 2018),

p-methoxyphenol (Zaky and Chaplin, 2013), methyl orange (Wang et al., 2020a) and PFAS (Le et al., 2019; Li et al., 2021; Lin et al., 2018). So far, Ti_4O_7 electrodes have been mostly prepared in powder form and pressed into pellets (Arif et al., 2017; Li et al., 2010; Lin et al., 2020; Nayak and Chaplin, 2018; Zhu et al., 2013). Due to the rather poor latitude of the pelletizing process, the pellets cannot be scaled up into large size electrodes, and their nanostructure is barely controllable.

In the present work, we report on the use of a plasma torch (PT) based coating process to deposit Ti_4O_7 layers onto Ti substrates (both plate and mesh). Thus, by plasma spraying the Ti_4O_7 powder onto Ti substrates of desirable sizes and shapes, we were able to fabricate Ti_4O_7 anodes with controllable thickness, microstructure, and electrode size. The structure, morphology, and electrical conductivity of the PT-deposited Ti_4O_7 electrodes were systematically characterized. In a second step, the PT- Ti_4O_7 anodes were used into an electro-oxidative reactor to assess their capacity to produce hydroxyl radicals ($\cdot\text{OH}$) and persulphate ($\text{S}_2\text{O}_8^{2-}$). Finally, the degradation performance of our PT- Ti_4O_7 anodes was investigated against PFOA and PFOS pollutants in both synthetic and real wastewaters.

2. Materials and methods

2.1. Ti_4O_7 electrode preparation

The PT- Ti_4O_7 anodes were produced via the coating of Ti substrates by Ti_4O_7 films using a plasma torch system where Ti_4O_7 powder was used as a feedstock. Prior to their coating with Ti_4O_7 , the Ti substrates ($4 \times 9 \text{ cm}^2$) were first sand blasted to increase artificially their surface area, then cleaned with isopropanol and deionized water, and finally dried with nitrogen gas jet. The plasma torch system was operated at a DC current of 500 A and a DC voltage of $\sim 70 \text{ V}$, with an Ar/H_2 (90/10) carrier gas, resulting in a discharge that ionizes the gas and generates the plasma plume through which the powder is melted and projected towards the substrates. The PT system was fed by Ti_4O_7 powder at a feeding rate of $\sim 40 \text{ g/min}$. To achieve uniform coating of the Ti substrates, the PT nozzle was swept over the samples placed at a distance of $\sim 12 \text{ cm}$. The deposition time (or the number of PT-nozzle passes) was set to obtain Ti_4O_7 films with a thickness of $\sim 100 \mu\text{m}$. The crystalline structure of the feedstock powder and the PT-deposited films was determined by using a PANalytical X-Pert Pro X-ray diffractometer (XRD) operating with a Cu K source of 1.5418 Å). Raman spectrometer (Renishaw inVia Reflex) with a 523 nm laser excitation line (and 10% energy filter) was also used to characterize the Magnéli phase structures. The morphology and thickness of the PT-deposited films were determined by using a Jeol JSM-6300F scanning electron microscope (SEM). Finally, the electrical resistivity of the overall ($\text{Ti}_4\text{O}_7/\text{Ti}$) electrodes was measured by means of the four-point probe method.

2.2. Preparation of synthetic solutions

Different synthetic solutions were prepared by adding 1 mg/L of either PFOS or PFOA and a matrix of both PFOA and PFOS (each 0.5 mg/L) to a volume of 1.0 L of distilled water. The solution was kept under magnetic agitation until complete dissolution of the PFOS and PFOA. Sodium sulphate (Na_2SO_4 , 2.86 g/L) was added as supporting electrolyte in order to increase the conductivity of the synthetic solution. PFOA/PFOS and sodium sulphate were purchased from Sigma-Aldrich ($>98\%$ purity, a mixture of branched and linear isomers). The electrolyte concentration was selected based on the following considerations: the electrolyte concentration of 2.86 g/L was selected in order to be able to impose a current density varying from 5 to 50 mA/cm^2 . This electrolyte concentration aims to provide sufficient conductivity for efficient electrooxidation of PFAS while minimizing the potential difference existing between the electrodes connected to the power supply.

2.3. Real wastewater sampling and characterization

The real wastewater (RWW) used throughout this study was an effluent provided from a sampling campaign carried out by ALTRA SANEXEN company. Samples were collected and stored in polypropylene bottles and kept at 4 °C until use. The raw effluent had an initial content of COD of 588 mg/L, pH of 6.66 and conductivity of 451 ± 9 µS/cm. Basic information on the characteristics of raw real wastewater are shown in Table 1. Initial PFAS concentrations in RWW are presented in Table 2.

2.4. Electrochemical devices

The advanced electro-oxidation reactor was consisted of five rectangular electrodes placed vertically as a distance of 1.0 cm. Two different configurations of PT-Ti₄O₇ (three graphite (Gr) with similar size (4 cm width x 9 cm high)) serving as the anode and cathode, respectively. The electro-oxidation reactor was made of high-density polyethylene material (capacity 1.0 L) to minimize cross contamination of per- and poly-fluoroalkyl substances (PFAS) coming from the reactor walls. Using two peristaltic pumps, the electrolyte was recirculated through a 1500 ml beaker so then the process was performed in a dynamic-batch mode operation. The anodes were in two geometrical forms mesh and plate. A power supply (Sorensen DCS40-75E, Magna-Power Electronics Inc., Flemington, New Jersey, USA) was utilized to provide electrical power to perform electro oxidation at varying constant current density ranging of 5, 10, 15, 20, 30, 50 mA/cm² for a treatment time of 180 min. After identifying the optimal parameters for PFOA and PFOS electrochemical degradation, a transition to real wastewater samples had place, which were collected and characterized for their composition.

2.5. Experimental procedure

Three types of artificially contaminated effluent were prepared and subjected to electrolytic treatment: (i) effluent containing PFOA alone (1.0 mg/L); (ii) effluent containing PFOS alone (1.0 mg/L); and (iii) mixed effluent containing both PFOA (0.5 mg/L) and PFOS (0.5 mg/L). The tests performed separately on the three matrices allow to study the

Table 1
Characteristics of raw real wastewater.

Parameters	Values
pH	6.66 ± 0.01
Conductivity (µS/cm)	451 ± 9
COD (mg/L)	588 ± 1
TOC (mg/L)	180 ± 1
Al (mg/L)	0.03 ± 0.01
B (mg/L)	0.01 ± 0.01
Ba (mg/L)	0.07 ± 0.01
Ca (mg/L)	21.0 ± 0.04
Cu (mg/L)	0.003 ± 0.01
Fe (mg/L)	0.02 ± 0.01
K (mg/L)	43.7 ± 0.2
Mg (mg/L)	8.55 ± 0.01
Mn (mg/L)	0.01 ± 0.01
Mo (mg/L)	0.01 ± 0.01
Na (mg/L)	6.68 ± 0.01
P (mg/L)	0.09 ± 0.01
S (mg/L)	10 ± 1
Si (mg/L)	1.23 ± 0.01
Sr (mg/L)	0.9 ± 0.01
Zn (mg/L)	0.04 ± 0.01
F ⁻ (mg/L)	1.03 ± 0.00
Cl ⁻ (mg/L)	9.59 ± 0.05
NO ₂ (mg/L)	1.22 ± 0.01
SO ₄ ²⁻ (mg/L)	29.0 ± 0.2
NO ₃ ⁻ (mg/L)	27.0 ± 0.3
PO ₄ (mg/L)	0.16 ± 0.01

Table 2

Initial PFAS concentrations of real wastewater.

PFAS Compounds	Values (µg/L)
PFPrA (Perfluoropropionic acid)	61.2 ± 4.32
PFBA (Perfluorobutanoic acid)	94.9 ± 5.21
PFPeA (Perfluoropentanoic acid)	176.5 ± 7.61
PFHxA (Perfluorohexanoic acid)	420.5 ± 19.73
PFHpA (Perfluoroheptanoic acid)	42.7 ± 2.7
PFOA (Perfluorooctanoic acid)	63.8 ± 12.9
PFHxS (Perfluorohexanesulfonic acid)	119.8 ± 14.15
PFHpS (Perfluoroheptanesulfonic acid)	12.1 ± 2.96
PFOS (Perfluoroheptanesulfonic Acid)	406.2 ± 166
FBSA (Perfluorobutane sulfonamide)	49.2 ± 4.07
FHxSA (Perfluorohexanesulfonamide)	164.3 ± 19.77
5:3 FTCA acid (5:3 Fluorotelomer carboxylic acid)	63.2 ± 9.5
6:2 FTCA (6:2 fluorotelomer carboxylic acid)	6.92 ± 1.44
6:2 FTSA (6:2 Fluorotelomersulfonic acid)	1919 ± 229
5:3 FTB (5:3 fluorotelomer betaines)	253.6 ± 34.88
5:1:2 FTB (5:1:2 fluorotelomer betaines)	1591.4 ± 238
6:2 FTAB (6:2 fluorotelomer sulfonamide alkylbetaine)	3056.7 ± 550

competitiveness of PFAS degradation reactions with different molecular structures. The effluents were subjected to electrolytic treatment for a period varying between 60 min and 180 min, imposing different current densities between 10 and 50 mA/cm². Two different configurations of electrodes have been used PT-Ti₄O₇-Mesh and PT-Ti₄O₇-Plate.

Subsequently, RWW was subjected to treatment using the advanced electro-oxidation (AEO) process operated at 20 mA/cm² of current density during 120 min of electrolysis time. During these assays, the effectiveness of the process was evaluated by measuring the residual PFAS, COD and Fluoride concentrations.

2.6. Analytical techniques

2.6.1. Hydroxyl radical and total oxidant concentration measurements

Reactive oxygen species (such as hydroxyl radicals (*OH)) have been shown to bleach RNO (N, N-Dimethyl-4-nitroso-aniline) by chemical oxidation (García-Gómez et al., 2014). The hydroxyl radical production is equal to RNO disappearance rate. The bleachate rate was monitored by absorbance measurements of RNO at 440 nm using an UV-visible absorption spectrophotometer (UV M136, Varian, Australia) (Simonsen et al., 2010).

The indirect method of measuring oxidants by iodides is a chemical method able to determine the concentrations of oxidants produced during the EO reaction. The use of sodium sulphate during electrolysis generates S₂O₈²⁻ persulphate ions at the anode, while at the cathode and the use of graphite facilitates the oxygen reduction reaction (ORR), leading to the production of H₂O₂ (hydrogen peroxide). In the presence of oxidants, the iodide ions are oxidized into diode, giving the solution a yellow color. The entire solution is then dosed by a solution of thio-sulphate up to the equivalence which will allow to quantify the oxidants produced during the ECO (Davis et al., 2014; Koda et al., 2003; Rao et al., 2014).



To further understand the effect of S₂O₈²⁻ and H₂O₂ a UV spectrophotometer was employed (λ = 353 nm) (Simonsen et al., 2010). These resulting oxidants (persulphate) were quantified by titration during the EO reaction (Davis et al., 2014; Rao et al., 2014).

2.6.2. PFOA, PFOS and PFAS measurements

PFAS analysis was carried out using an ultra-high-performance liquid chromatography coupled with high-resolution Q Exactive Orbitrap mass spectrometry (UHPLC-HRMS). Analysis was performed at a mass range of 150–1000 m/z, and both negative and positive electrospray ionization full scan acquisition modes. Thermo Hypersil Gold C18

columns were used for the chromatographic separation process. HPLC-water with 0.1% formic acid and acetonitrile with 0.1% formic acid served as mobile phases A and B, respectively. Before being injected into the LC-MS, all samples were diluted by 25 because of the high concentration of PFAS in the samples. The calculation of the removal efficiency was performed according to the following equation:

$$\text{Degradation efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (\text{Eq.3})$$

In the sample, the initial and final concentrations of PFAS are represented by C_0 and C_t , respectively.

3. Results and discussion

3.1. Characterization of Magnéli phase PT-Ti₄O₇ material

Fig. 1 (a) shows the X-ray diffraction (XRD) spectra of both the Ti₄O₇ powder feedstock (bottom) and the PT-Ti₄O₇ electrode made out of it (top). The XRD peaks exhibited by the feedstock powder correspond to the Ti₄O₇ pattern (JCPDS 050 0787), confirming the purity and high polycrystallinity of the used powder. For the obtained PT-Ti₄O₇ coatings (top spectrum of Fig. 1(a)), the majority of the diffraction peaks appear at the same positions as for the Ti₄O₇ feedstock powder, confirming the effective transfer of stoichiometry and polycrystalline structure to the films. The XRD peaks located at $2\theta = 20.8^\circ, 26.4^\circ, 29.6^\circ, 36.3^\circ, 40.5^\circ, 53.3^\circ$ and 55.1° , corresponding to the (10 $\bar{2}$), (1 $\bar{2}$ 0), (1 $\bar{2}$ 2), (120) (015), (3 $\bar{2}$ 2) and (14 $\bar{2}$) crystallographic plans of Ti₄O₇, respectively, are the most prominent ones. In comparison with the isotropically dispersed powder, the coatings are seen to be more crystallographically orientated. Such a preferential orientation is believed to result from the directional nature of the PT deposition process, which is expected to favor more mechanical stress relaxation in the in-plane direction of the coating than in its out-of-plane one. In the XRD spectrum of the PT-Ti₄O₇ films, few other peaks (identified by light-blue triangles) corresponding to Magnéli phases (Ti_nO_{2n-1}) with higher n values ($n > 5$) were also observed. Finally, one can also note the presence of two XRD peaks (appearing at $2\theta = 25.2^\circ$ and 27.5°) that can be associated with some anatase and rutile TiO₂ respective phases. The latter along with the high-order Magnéli phases possibly result from some surface oxidation of the coatings during their deposition under ambient atmosphere or post-exposure to air. Fig. 1a shows the Raman spectra of both Ti₄O₇ feedstock powder and PT-deposited Ti₄O₇ films. Our pure Ti₄O₇ phase

powder is shown to exhibit two distinct and intense characteristic peaks located at 138 cm^{-1} and 183 cm^{-1} . Three other broader and weaker peaks, located at $284, 465$ and 550 cm^{-1} , are also associated with the Ti₄O₇ phase. It is worth recalling that, in the very scarce literature on Raman characterization of Ti₄O₇, the sole peak generally used to identify the Ti₄O₇ phase is the one appearing at 138 cm^{-1} (Li et al., 2010; Watanabe, 2009; Watanabe and Ueno, 2006). The Raman spectrum of the PT-Ti₄O₇ coatings is seen to exhibit the two peaks (at 138 and 183 cm^{-1}) characteristic of the Ti₄O₇ Magnéli phase (the broader peak at 550 cm^{-1} is also present). In addition, one can also note the presence of another broad and less intense peak (centered around $\sim 425\text{ cm}^{-1}$), which is typically associated with TiO₂ rutile phase. All these Raman results are consistent with the XRD ones and confirm that the PT-deposited coatings predominantly consist of pure and polycrystalline Ti₄O₇ Magnéli phase. Finally, to assess the electrical conductivity of our PT-Ti₄O₇ based anodes, we have coated the titanium substrates by $\sim 100\text{ }\mu\text{m}$ thick Ti₄O₇ films on both faces and then measured the overall conductivity of the anodes, which was found to be of $(5600 \pm 140)\text{ S. cm}^{-1}$. Such a high conductivity of these double-face-coated [PT-Ti₄O₇/Ti/PT-Ti₄O₇] $4 \times 9\text{ cm}^2$ working anodes makes them highly suitable for use in electro-oxidation processing.

The micro/nano-morphology of the PT-Ti₄O₇ coatings was also examined by SEM. Fig. 2(a) shows a typical SEM cross-sectional view of the PT-Ti₄O₇ coating. The coatings have a typical thickness of $(105 \pm 7)\text{ }\mu\text{m}$ and show an excellent adhesion to the substrate (with a smooth and hardly distinguishable interface between the coating and the Ti-substrate; see Fig. 2(a)). Qualitative scotch-tape adhesion tests were performed, and no coating can be pulled out. Fig. 2(b-d) show typical top-views of the PT-Ti₄O₇ coating at increasing magnification scales. The PT-Ti₄O₇ surface is seen to consist of a dense coating with a pebbly morphology with a sort of hierarchical morphology. Indeed, different feature sizes ranging from few microns down to few 10 s of nm are seen.

The higher magnification SEM image (Fig. 2(d)) illustrates well the submicronic and even nanoscopic morphology of the PT-Ti₄O₇ coating along with an apparent micro/nanoporosity between the surface constituents. In fact, the microscopic features are seen to be covered with a sub-structure consisting of nanospherical particles and nanowiskers (yellow arrows of Fig. 2(d)). Such a hierarchical morphology of the PT-Ti₄O₇ coatings reveals their nanostructured nature, which would ensure them a very high surface area (an added value for their use in electro-oxidation applications).

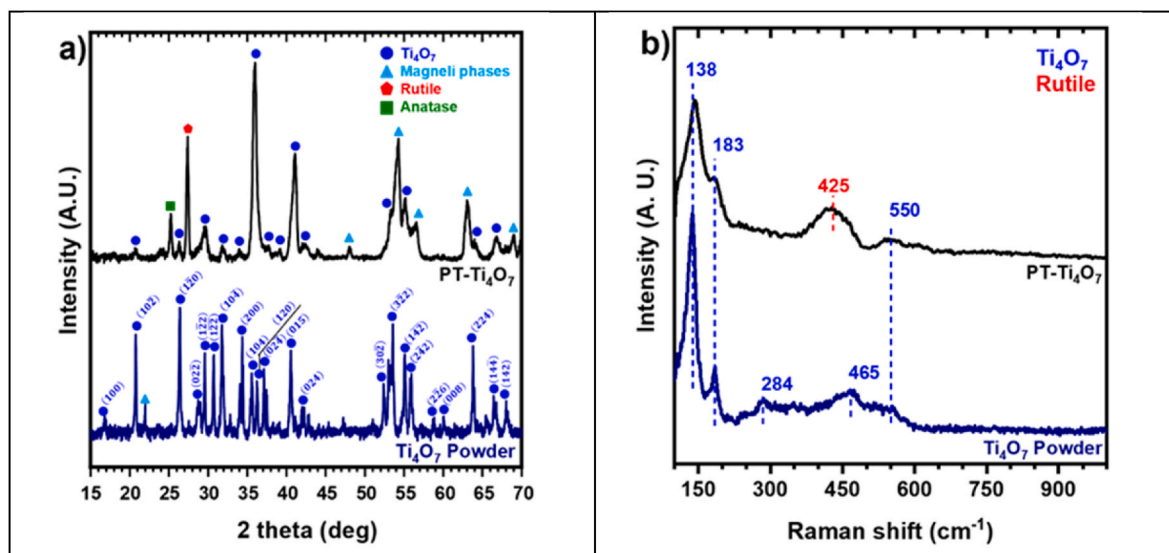


Fig. 1. Typical XRD (a) and RAMAN (b) spectra of the PT-Ti₄O₇ coatings along with those of the feedstock Ti₄O₇ powder.

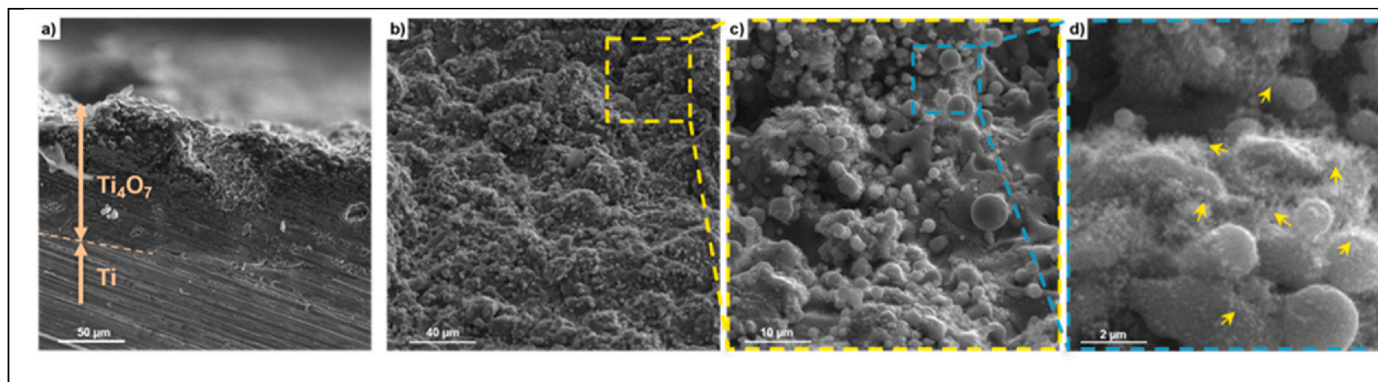


Fig. 2. Typical SEM images of the cross-sectional (a) and top (b) views of the Ti_4O_7 coatings (PT- Ti_4O_7). Higher magnification images (c–d) reveal the hierarchical nanostructure of the Ti_4O_7 films where nanowiskers (yellow arrows in (d)) cover the surfaces of the Ti_4O_7 micro-spheres.

3.2. In-situ ROS generation

The first objective was to evaluate the efficacy of the electrolytic reactor (comprised of PT- Ti_4O_7 (anode) and graphite (cathode)) to produce reactive oxygen species (i.e.: H_2O_2 , $\text{H}_2\text{S}_2\text{O}_8$, $\bullet\text{OH}$, etc.). $\text{H}_2\text{S}_2\text{O}_8$ and $\bullet\text{OH}$ can be simultaneously generated at the anode while using some catalytic electrodes having high oxygen overvoltage including PT- Ti_4O_7 (Guelfi et al., 2019; Oturan et al., 2017; Silva Barni et al., 2020). Sulphate ions can be oxidized into persulphate in solution, whereas hydroxyl radicals ($\bullet\text{OH}$) can be generated on the surface of such electrodes by anodic oxidation of water. At the same time, H_2O_2 can be generated at the cathode (such as graphite) by oxygen reduction (Daghrir et al., 2013; Kiendrebeogo et al., 2022).

3.3. Electrochemical generation of hydroxyl radicals and persulphates

The production of $\bullet\text{OH}$ was evaluated by bleaching of RNO (Kiendrebeogo et al., 2022). Different current densities (10, 20, 30, and 50 mA/cm^2) and treatment times (10–60 min) were imposed during electrolysis of RNO for two configurations of anodes (PT- Ti_4O_7 Mesh versus PT- Ti_4O_7 -Plate electrodes). It is worth noting that RNO is selectively bleached by oxidation with hydroxyl radicals and cannot react with persulfate (Simonsen et al., 2010). One mole of RNO reacts with 1 mol of hydroxyl radical, so that the RNO disappearance rate corresponds to the hydroxyl radical production rate.

Fig. 3 presents the residual RNO concentration against time while

using PT- Ti_4O_7 -Mesh versus PT- Ti_4O_7 -Plate electrodes, respectively. The initial concentration RNO was 4×10^{-3} M. The decrease of RNO concentration is quite linear using PT- Ti_4O_7 -Mesh electrode, compared to the curves recorded with PT- Ti_4O_7 -plate electrodes. After 60 min of electrolysis, the residual concentrations of RNO varied from 4×10^{-3} M and 4.24×10^{-4} M while using PT- Ti_4O_7 -Mesh electrodes for current densities ranging between 10 and 50 mA/cm^2 . By comparison, the residual concentrations of RNO varied from 4.0×10^{-3} M and 5.68×10^{-4} M while using PT- Ti_4O_7 -Plate electrodes. Overall, RNO concentration decays at all the applied current density and anode configurations namely mesh and plate. Also, it can be found from Fig. 3 that higher current density slightly leads to faster degradation of RNO, which agrees with kinetic constants. Moreover, kinetic constants are illustrated in Fig. 4. The hydroxyl radical production rate ($V_{(\bullet\text{OH})}$) is equal to RNO can be written as follows:

$$V_{(\bullet\text{OH})} = \frac{d[\text{RNO}]}{dt} = -k_1 \cdot [\text{RNO}] \quad (\text{Eq.4})$$

In this equation, [RNO] is the concentration of RNO and k_1 is the first-order reaction rate constant. Bleaching of RNO could be correlated to production of OH radicals. According to Marthe et al. the complete removal of RNO at the highest current density, a notably higher production rate than a previous study using different conditions (Kiendrebeogo et al., 2022). The integration of equation (4) leads to:

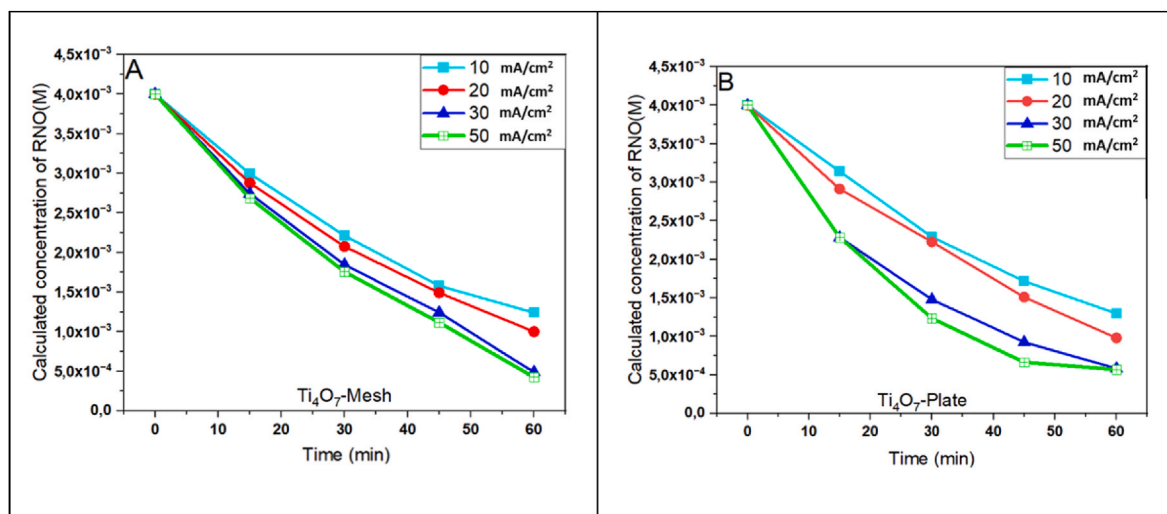


Fig. 3. Effect of applied current: 10, 20, 30, and 50 mA/cm^2 on the time course of RNO concentration decay using PT- Ti_4O_7 -Mesh (A) and PT- Ti_4O_7 -Plate (B) anodes and graphite cathode in 2.86 g/L Na_2O_4 .

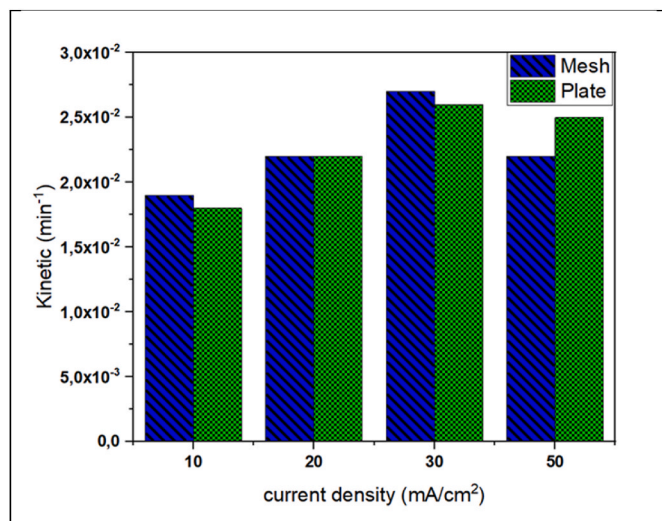


Fig. 4. Apparent rate constants for the bleaching of RNO by EO process at different applied current density using Mesh and plate PT-Ti₄O₇ anodes.

$$\ln\left(\frac{[RNO]_0}{[RNO]_t}\right) = k_1 \cdot t \quad (\text{Eq.5})$$

Where $[RNO]_0$ and $[RNO]_t$ represent respectively the initial concentration of RNO and the residual concentration of RNO at time t . As expected from RNO bleaching results, increasing current density led to an increase in the generation of hydroxyl radicals ($\bullet\text{OH}$) (Kjendrebegoo et al., 2022; Muff et al., 2011). As it can be observed in Fig. 5 the amount of produced hydroxyl radical during 1 h of process increases from $5,8 \times 10^{-5}$ M to $1,36 \times 10^{-4}$ M and $5,08 \times 10^{-5}$ M to $1,3 \times 10^{-4}$ M for mesh and plate, respectively. Such increase can be explained by greater flow of electrons through electrode-electrolyte interface at higher applied current density. Interestingly, the generation of $\bullet\text{OH}$ and degrading RNO simultaneously shows the weak interactions between $\bullet\text{OH}$ and Ti₄O₇ surface, which can be considered as a great advantage. In particular, several investigations have shown that PT-Ti₄O₇ anodes a higher O₂ overvoltage than anodes made of platinum and lead dioxide (PbO₂) or tin dioxide (SnO₂). As effect of anode geometry on production of hydroxyl radicals, the slight difference may arguably from different flow dynamics.

In this study also the persulphate production has been thoroughly evaluated with two different electrodes (PT-Ti₄O₇-Mesh versus PT-

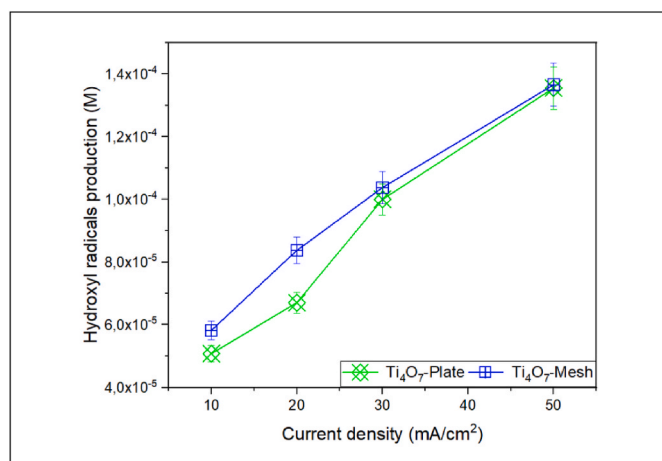


Fig. 5. Effect of the current density on the concentration of $\bullet\text{OH}$ during the electrolysis, the inset figures represent the first-order reaction kinetics analysis of RNO. $[\text{Na}_2\text{SO}_4] = 2.86$ g/L.

Ti₄O₇-Plate electrodes), as part of the experimental inquiry. There is no statistically significant difference between the $\text{S}_2\text{O}_8^{2-}$ production rates of these two anodes, according to our rigorous review of the data (Fig. 6). This result implies that the mesh and plate reactors are equally efficient from the standpoint of persulphate generation. These findings show that the $\text{S}_2\text{O}_8^{2-}$ production is not influenced by the electrode configuration itself. This conclusion is attributed to the electrode material. PT-Ti₄O₇-Mesh versus PT-Ti₄O₇-Plate electrodes are made with the same material of Ti₄O₇. However, the production is influenced by the electrolyte and reactant concentration. The concentration of persulphate precursor species and the supporting electrolyte can be influencing $\text{S}_2\text{O}_8^{2-}$ production than the electrode configuration. As the concentrations are high, the electrode configuration has less impact on the overall reaction rate. The slight difference between the mesh and the plate electrodes is due to their geometry. However, in the next experiments, mesh was used as an anode and graphite as a cathode. The turbulence-enhancing characteristics of mesh anodes reduce concentration gradients close to the electrode surface (Cai and Guo, 2021). Also, the PT-Ti₄O₇-Mesh speeds up the electrochemical processes by lowering the thickness of the diffusion boundary layer, which makes it possible for reactants to get to the electrode more quickly (Kislyi et al., 2023). For high-speed kinetics applications like water electrolysis, increased mass transfer is essential for increasing power density and operating effectiveness. This impact is particularly helpful in operations where increased performance and overall efficiency are achieved through improved mass transfer. This increased mass movement is especially important for applications such as water electrolysis, where quick kinetics are necessary to get the greatest operational results and energy efficiency (Wang et al., 2015).

3.4. PFOA and PFOS degradation

To illustrate the effectiveness and usefulness of AEO technology for the destruction of persistent PFAS pollutants, two model chemicals, PFOS and PFOA, were chosen as illustrative examples. The mass transfer coefficient can be firstly calculated for the characterization of electrolytic cell during PFOA and PFOS degradation using PT-Ti₄O₇-Mesh and PT-Ti₄O₇-Plate anodes, respectively. It can be calculated from the data of material balance. The material balance on PFOS and PFOA gives as follows: [Rate of disappearance of PFOS/PFOA] = [Rate of reaction]

$$-V \frac{dC}{dt} = k_m \cdot A \cdot C \quad (\text{Eq.6})$$

where k_m is the mass transport coefficient (m min^{-1}), A is the surface of

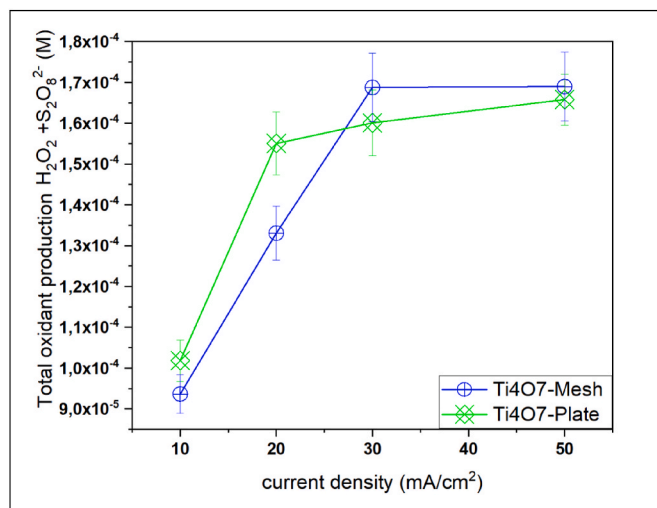


Fig. 6. Effect of applied current: 10, 20, 30, and 50 mA/cm² on the persulphate production using PT-Ti₄O₇ anodes and graphite cathode in $[\text{Na}_2\text{SO}_4] = 2.86$ g/L.

the anode electrode, C the concentration of PFOS or PFOA, t the reaction time (min) and V the working volume of the system (m^3). The integration of the equation (Eq. (6)) leads to the following equation:

$$-\ln\left(\frac{C}{C_0}\right) = k_m \frac{A}{V} t \quad (\text{Eq.7})$$

The equation (Eq. (7)) is analogue to equation (Eq. (8)) mentioned above:

$$-\ln\left(\frac{C}{C_0}\right) = k_2 t \quad (\text{Eq.8})$$

$$\text{With } k_2 = k_m \frac{A}{V} \quad (\text{Eq.9})$$

k_2 represents the reaction rate constant, and it is calculated from the slope value of the plot (t) versus $-\ln(C/C_0)$ of equation (Eq. (8)) (see supplementary data). Fig. 7 presents the variation of mass transport coefficient in function of current density using PT-Ti₄O₇-Mesh and PT-Ti₄O₇-Plate anodes. The decomposition reaction rate constant (k_2) of PFOA by the electrochemical oxidation using PT-Ti₄O₇-Plate anode varied from 0.0025 to 0.0086 min^{-1} . By comparison, using PT-Ti₄O₇-Mesh anode, the degradation reaction rate constant (k_2) of PFOA varied from 0.0019 to 0.0135 min^{-1} . The mass transfer coefficients (k_m) (Fig. 7) for both PFOS and PFOA exhibited a distinct trend with varying current densities and electrode configurations. With the mesh electrode, k_m for PFOS increased steadily from $1.85 \times 10^{-4} \text{ m min}^{-1}$ at 10 mA/cm^2 to $3.02 \times 10^{-4} \text{ m min}^{-1}$ at 30 mA/cm^2 (calculated from equation (Eq. (9))), indicating enhanced mass transfer at higher current densities. A similar trend was observed for PFOA, with k_m rising from $2.09 \times 10^{-5} \text{ m min}^{-1}$ at 10 mA/cm^2 to $6.36 \times 10^{-4} \text{ m min}^{-1}$ at 30 mA/cm^2 , suggesting a more pronounced effect of current density on PFOA mass transfer. Notably, the mesh electrode consistently demonstrated higher k_m values for both PFOS and PFOA compared to the plate electrode across all current densities tested. For instance, at 30 mA/cm^2 , the k_m for PFOA with the mesh electrode ($6.36 \times 10^{-4} \text{ m min}^{-1}$) was nearly an order of magnitude higher than that with the plate electrode ($1.08 \times 10^{-4} \text{ m min}^{-1}$). According to the mass transfer results, it's has been obvious that PT-Ti₄O₇-Mesh is a better choice for the degradation of PFAS contaminants. For instance, at a current density of 30 mA/cm^2 , the mass transfer coefficient k_m using PT-Ti₄O₇-Mesh anode was 2.4 times higher than that recorded using PT-Ti₄O₇-Plate anode. During PFOA degradation, the mass transfer followed the same trend than that recorded for PFOS. At a current density of 30 mA/cm^2 , the mass transfer coefficient k_m using PT-Ti₄O₇-Mesh anode was six times higher than

that recorded using PT-Ti₄O₇-Plate anode. The Ti₄O₇-Mesh anode demonstrated a better efficiency in mass transfer than the PT-Ti₄O₇-Plate anode. The PT-Ti₄O₇-Mesh anode improved the mass transfer by promoting a uniform distribution of liquid flow. It is interesting to compare the constant rate of PFOA/PFOS degradation with those obtained under different experimental conditions. The rate constant of organic degradation has been determined by Lin et al. (2012) while studying electrochemical oxidation of perfluorooctanoic acid (PFOA) using a Ti/SnO₂-Sb anode (Lin et al., 2012). They reported a degradation rate constant of 0.064 min^{-1} and a half-life of 10.8 min for PFOA degradation at 100 mg/L initial concentration and 10 mA/cm^2 as current density. The rate constant for the decomposition of PFOA through electrochemical oxidation in this study ranged from 0.0025 to 0.0086 min^{-1} when using a PT-Ti₄O₇-Plate anode, and from 0.0019 to 0.0135 min^{-1} with a PT-Ti₄O₇-Mesh anode. These values were obtained at an initial PFOA concentration of 1 mg/L. In comparison, Lin et al. (2012) documented a markedly higher rate constant of 0.064 min^{-1} for PFOA degradation employing a Ti/SnO₂-Sb anode. However, it is crucial to note that their experiments were conducted with an initial PFOA concentration of 100 mg/L, which is 100 times greater than the concentration used in the present study.

The substantial disparity in the observed rate constants can be primarily ascribed to the significantly elevated initial PFOA concentration utilized by Lin et al. (2012). According to the rate law equation, the rate constant is directly proportional to the concentration of reactants. Consequently, the higher initial concentration of PFOA in their study likely accelerated the reaction rate, resulting in a higher rate constant. Furthermore, variations in the anode materials and other reaction parameters, such as current density and pH, could have contributed to the differences in rate constants between the two studies.

According to the mass transfer results, PT-Ti₄O₇-Mesh anode has been selected for the next step of this study. Fig. 8 shows the residual concentrations of PFOA and PFOS against time while they are separately treated in synthetic solution. It's interesting to note that under the same experimental conditions, PFOS degraded slightly faster than PFOA (Fig. 9). It displayed a greater removal rate for PFOS with a starting concentration of 1 mg/L (Fig. 8B). The PFOS content was reduced by 99.7% after 30 min. However, the PFOA concentration was only lowered by 96.6%. The degradation of half-time for PFOS was 60 min, which was more than twice in term of degradation as long as that for PFOA (Fig. 8A). There are multiple pathways involved in the degradation of PFOS and PFOA by persulfate and hydroxyl radicals. These oxidants have the potential to cause PFOS to defluorinate and break down into shorter-chain PFAS molecules. $\text{S}_2\text{O}_8^{2-}$ has the ability to initiate a

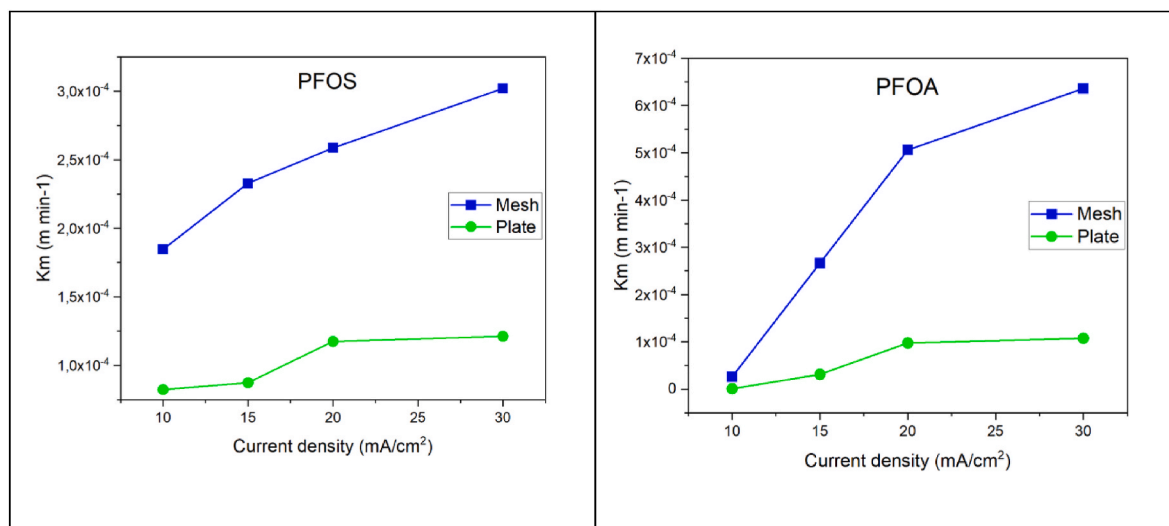


Fig. 7. Variation of mass transport coefficient in function of current density in the matrix of PFOA and PFOS.

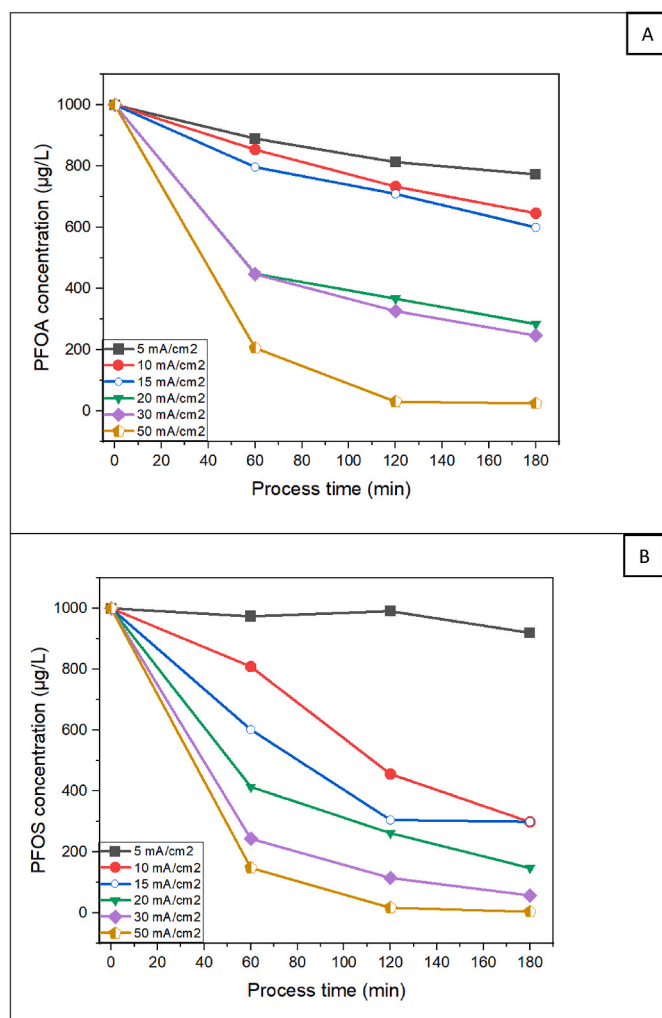


Fig. 8. Degradation of PFOA (a) and PFOS (b) in synthetic water by electrochemical oxidation (using PT-Ti₄O₇-Mesh anode) [PFOS]₀ = 1 mg/L; [PFOA]₀ = 1 mg/L.

decarboxylation reaction, which in fact begins with a fluoride elimination process that eventually results in the degradation of PFOA (Bruton and Sedlak, 2017). Persulfate's complicated process of degrading PFOA involves multiple reaction stages. A perfluorooctanoic carboxyl radical is first produced by $S_2O_8^{2-}$ attacking the ionic PFOA. This radical subsequently goes through decarboxylation to yield a perfluoroheptyl radical. The perfluoroheptyl radical is then hydrated to produce a perfluorinated alcohol, which is then eliminated from HF to produce its acid fluoride. After that, the acid fluoride is hydrolyzed to produce a PFCA that has one fewer CF_2 unit. The resultant PFCA then reacts with $S_2O_8^{2-}$ in a way comparable to that of PFOA. This reaction then repeats itself until all of the PFCAs are fully mineralized (Zhang et al., 2019). According to the previous persulfate production, it can be seen that the rate of PFOA decomposition increased as $S_2O_8^{2-}$ dosages increased (Lee et al., 2009). In order to understand way more the mechanism in experiments utilizing PT-Ti₄O₇ electrodes, the electrochemical breakdown of PFOS begins with a single electron transfer from the PFOS from the head group of $C_8F_{17}SO_3$ to an anode (Zhang et al., 2019), producing C_8F_{17} radicals that will react with $\bullet OH$ to generate $C_8F_{17}OH$. This PFOS by-product ($C_8F_{17}OH$) proceed decomposition into $C_8F_{16}COF$ and then rapidly hydrolyze to $C_7F_{15}COO^-$ (Pica et al., 2019). $C_7F_{15}COO^-$ proceed a decarboxylation which result in the elimination of CF_2 units until complete mineralization (Zhang et al., 2019) Greater PFOS degradation efficiency results from increased PFOS affinity and a lower energy barrier for direct electron transfer, which are both facilitated by the higher proportion of Ti^{3+} ions in Ti₄O₇ (Wang et al., 2022).

Based on our experimental results and existing literature, the following general degradation pathway for PFOA and PFOS under electrooxidation conditions is proposed. The process typically begins with the oxidation of the terminal functional group, leading to decarboxylation in PFOA (Eq. (10)) and desulfonation in PFOS (Eq. (18)). This is followed by a stepwise loss of CF_2 units through oxidation (Eq. (11), Eq. (12), Eq. (13) for PFOA and Eq. (19), Eq. (20) and Eq. (21) for PFOS) (Sirés et al., 2014). As the degradation progresses, shorter chain perfluorinated carboxylic acids (for PFOA) or sulfonic acids (for PFOS) are formed as intermediates (Deng et al., 2021; Gar Alalm and Boffito, 2022; Smith et al., 2023). For instance, PFOA degradation may produce perfluoroheptanoic acid (PFHpA) (Eq. (14)), perfluorohexanoic acid (PFHxA) (Eq. (15)), and perfluorobutanoic acid (PFBA) (Eq. (16)), while PFOS degradation may yield perfluoroheptanesulfonic acid (PFHpS) (Eq. (22)), perfluorohexanesulfonic acid (PFHxS) (Eq. (23)), and perfluoropentanesulfonic acid (PFPeS) (Eq. (24)) (Smith et al., 2023). These shorter-chain intermediates continue to be oxidized. With sufficient treatment time, complete mineralization to fluoride ions, CO_2 , and

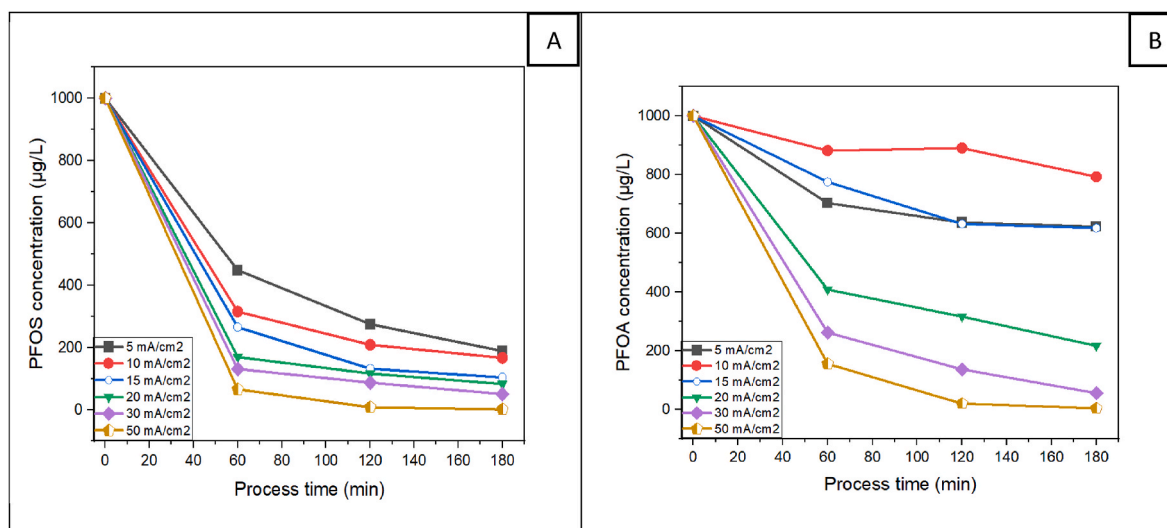
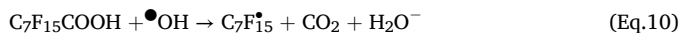


Fig. 9. Electrochemical degradation of PFOS (a) and PFOA (b) in a mixture solution (using PT-Ti₄O₇-Mesh anode); [PFOS]₀ = 0.5 mg/L; [PFOA]₀ = 0.5 mg/L.

sulphate (in the case of PFOS) (Eq. (25) and Eq. (26)) is possible (Deng et al., 2021; Gar Alalm and Boffito, 2022). It's worth noting that the exact pathway and distribution of intermediate products can vary depending on specific electrooxidation conditions, such as electrode material, applied potential, and electrolyte composition.

Proposed mechanism for PFOA (C₇F₁₅COOH) degradation:

Initial decarboxylation:

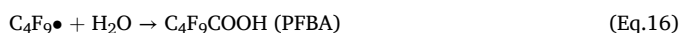


Stepwise loss of CF₂ units:



(This process continues)

Formation of shorter-chain perfluorinated carboxylic acids:

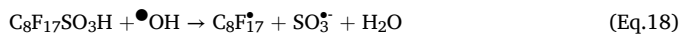


Mineralization:



Proposed mechanism for For PFOS (C₈F₁₇SO₃H) degradation:

Initial desulfonation:

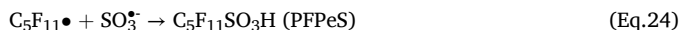
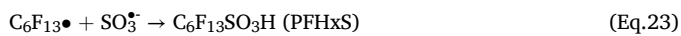
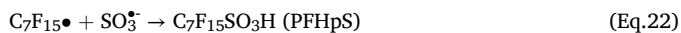


Stepwise loss of CF₂ units:



(This process continues)

Formation of shorter-chain perfluorinated sulfonic acids:



Mineralization:



Since PFOA and PFOS are frequently discovered together at contaminated sites, it is important to understand how they degrade when present in a mixture solution. It's interesting to note that when PFOA and PFOS were present in the same solution and treated with AEO, the rate of PFOS degradation was greatly slowed down. During the first hour of degradation with EO PFOS attend >90% of degradation at the highest current density 50 mA/cm² (Fig. 9A). However, after 1 h of EO PFOA degradation was 80%. Overall, when both are present in the same solution, PFOS breaks down more quickly than PFOA (Yang et al., 2013). This occurrence happens as a result of PFOS having the potential to defluorinate, which causes PFOA to develop during the breakdown process. This causes some of the PFOS to change into PFOA, which may explain why PFOA degrades more slowly overall and why the combined PFOS and PFOA remain in the solution throughout the breakdown process (Fig. 9B) (Kim et al., 2019; Yang et al., 2020).

To further investigate the electrochemical degradation efficiency of

PFOA and PFOS in a separated solution, we calculated the Faradaic efficiency for each compound. The Faradaic efficiency represents the ratio of the actual amount of substance degraded to the theoretical amount that could be degraded based on the charge passed through the system (Panizza and Cerisola, 2009). The following equation was used to determine the Faradaic efficiency (η) of the degradation:

$$\eta = \frac{n \times F \times z}{I \times t}$$

Where n is the number of moles of the species degraded, F is Faraday's constant (96,500 C/mol), and z is the number of exchanged electrons during electrolysis, I is the current intensity in ampere and t is the time in seconds.

The electrochemical degradation of PFOS and PFOA reveals intriguing insights into their removal efficiencies and faradaic efficiencies. The faradaic efficiency for PFOS is 0.0022%, while for PFOA, it is slightly higher at 0.0025%, indicating that only a small fraction of the electrical current is utilized for direct degradation in both cases. Despite these low faradaic efficiencies, the degradation rates are remarkably high, with PFOS achieving a 97% removal rate compared to 91% for PFOA. It is worth noting that, PFOA and PFOS degradation are mainly attributed to anodic oxidation (owing to the formation of hydroxyl radicals on the surface of PT-Ti₄O₇-anode). First, PFOA/PFOS must be transported toward the anode electrode surface, and then be oxidized there. The PFAS degradation may be subjected either to current control or mass transfer control. In fact, at the start of the electrolysis, the PFOA/PFOS concentration was relatively high and accordingly the PFOA/PFOS reduction rate was subjected to current control. As the PFOA/PFOS concentration was lowered to a certain level, the PFAS reduction rate was subjected to the mass transfer control (Panizza et al., 2001). In that case, only a fraction of current intensity (or charge loading) supplied was used to oxidize PFOA/PFOS, while the remaining charge loading was wasted for parasitic reactions (such as of oxygen generation). It was the reason for which the faradaic yields were very low in spite of relatively high percentages of PFOA and PFOS abatements recorded during electrolysis. Overall, these findings highlight the need for further optimization of the electrochemical process to enhance energy efficiency while maintaining high removal rates for these persistent contaminants, as emphasized by (Wang et al., 2020b) in their work on enhanced PFOA degradation.

3.5. Application to real wastewater treatment

The effectiveness of the electro-catalytic oxidation (AEO) process in treating real wastewater effluent contaminated by PFAS (around 8502 μg L⁻¹ of total PFAS) was evaluated at a current intensity of 20 mA/cm² using PT-Ti₄O₇-Mesh anode electrodes and a retention time of 120 min (best conditions determined above in synthetic effluent). The application of these parameters to real wastewater requires careful consideration. The objective was to test the effectiveness of the electrolytic reactor for a mixture of PFAS compounds in real wastewater, along with other co-occurring contaminants. In addition to PFOS and PFOA, the raw wastewater contained different PFAS (PFHx, PFHpS, FHxSA, PFPrA, PFBA, PFPeA, PFHpA, FBSA, etc.).

Fig. 10 indicate the percentages of PFAS removal in real wastewater sample after electrochemical treatment. In order to better illustrate and compare the different abatements, two groups of PFAS were defined according to their percentage of degradation. The first group includes PFAS compounds for which more than 20% of degradation was recorded. The second group of PFAS pollutants includes the most difficult degradable compounds with final abatement inferior to 20% (Fig. 11). PFOS and PFOA are included in the first group of PFAS pollutants having more than 20% of degradation (Fig. 10). After an electrolysis time of 120 min, the residual PFOS concentrations decreased from 406 to 28.14 μg/L (86% of PFOS removal), whereas PFOA decreased from 64 to 39

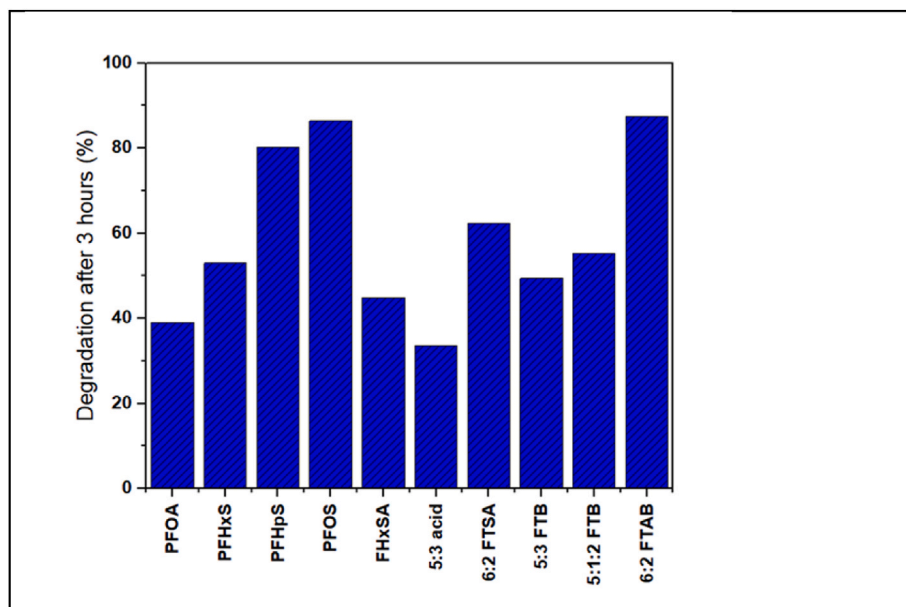


Fig. 10. PFAS compounds exhibiting greater than 20% degradation during electrooxidation treatment.

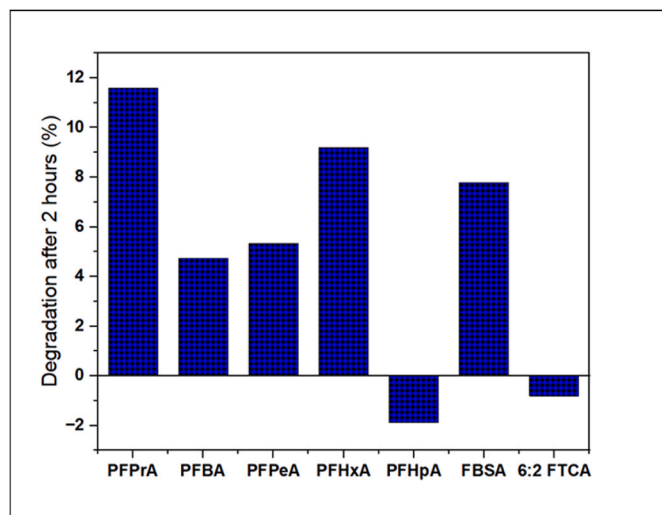


Fig. 11. PFAS compounds exhibiting less than 20% degradation during electrooxidation.

$\mu\text{g/L}$ (39% of PFOA removal). In spite of a mixture of PFAS in real wastewater, the percentage of PFOS degradation was quite the same percentage recorded (86%) in synthetic effluent. By comparison, the percentage of PFOA degradation in real wastewater was 1.6 times lower than that obtained (64%) in synthetic effluent. The competitive reactions did not affect PFOS degradation (compared to PFOA) owing to its molecular structure easier to oxidize.

The high rate of PFOS degradation (86.4%) was consistent with earlier research using comparable electrooxidation process. These works reported that PFOS degradation rates ranging between 88% and 90% (Houtz and Sedlak, 2012; Zhuo et al., 2011). The first group of PFAS pollutants was comprised of PFHpS and 6:2 FTAB for which at least 80% of degradation was recorded. Final abatements ranging between 35% and 60% were also recorded for the following compounds: PFHxS, 5:3 acid, 6:2 FTSA, 5:3 FTB, 5:1:2 FTB. Finally, it is worth noting that the best rates of PFAS degradation in this first group were obtained with perfluoroalkyl sulfonic acid compounds, PFHxS (53.0%), PFHpS (80.2%), and PFOS (86.4%). The observed differences in degradation

rates among various PFAS compounds can be attributed to several key factors. The search results indicate that the molecular structure and functional groups of the PFAS play a crucial role. Perfluoroalkyl sulfonic acids, such as PFOS, PFHxS, and PFHpS, which contain a sulfonate group (SO_3^-) are generally more susceptible to be oxidized compared to carboxylate-based PFAS like PFOA. This is because the sulfonate group can undergo desulfonation reactions during the degradation process, facilitating the further breakdown of the molecule (Hori et al., 2006; Ochoa-Herrera et al., 2008). Additionally, the carbon-sulfur bond in these sulfonic acid compounds requires less energy to degrade than the carbon-carboxylate bond found in PFOA (Ochoa-Herrera et al., 2008).

Fig. 11 presents the second group of PFAS pollutants for which less than 20% of abatement was recorded. The percentages of PFAS degradation varying between 4% and 12% for the following compounds: PFPrA, PFBA, PFPeA, PFHxA and FBSA. However, negative abatements were recorded for PFHpA (−1.89%) and 6:2FTCA (−0.82%), indicating that these compounds were formed as by-product during the application of electro-catalytic oxidation (AEO) process (Gomez-Ruiz et al., 2017). The production of byproducts such as 6:2 FTCA and PFHpA emphasises the need for additional research into the processes of degradation and the possible environmental effects of these by-products (Gomez-Ruiz et al., 2017; Kim et al., 2021).

The electrooxidation process demonstrated effectiveness in reducing organic contaminants in wastewater contaminated with PFAS, with COD reduced from 588 mg/L to 468 mg/L (20.4% reduction) and TOC decreased from 180 mg/L to 146 mg/L (18.7% reduction). The similarity in reduction percentages suggests consistent degradation of organic compounds. The Faradaic efficiency for PFOA degradation was exceptionally low, primarily due to the small fraction of the electrical current used for direct PFOA degradation. This low efficiency can be attributed to the complex nature of the wastewater matrix, where multiple competing reactions occur simultaneously (Ma et al., 2015). Analysis revealed the presence of shorter chain perfluorinated carboxylic acids as final transformation products, indicating partial PFOA degradation without complete mineralization. Specifically, the production of by-products such as 6:2 fluorotelomer carboxylic acid (6:2 FTCA) and perfluoroheptanoic acid (PFHpA) was observed. The presence of these compounds provides valuable insights into the degradation pathway of PFOA. For instance, the formation of PFHpA suggests the stepwise removal of CF_2 units from the PFOA molecule, while the presence of 6:2 FTCA indicates potential defluorination processes

occurring during electrooxidation (Godoi et al., 2021). These by-products align with the proposed degradation pathway for PFOA, which involves successive oxidation steps (Zhuo et al., 2012). The fluoride concentration increased from an initial value of 1.03 mg/L to a final value of 2.8 mg/L (2.7 times higher than initially measured in the raw effluent). This increase in fluoride concentration is an indicator of PFAS degradation during the electrooxidation process. The observed rise in fluoride levels can be attributed to the breaking of carbon-fluorine bonds in PFAS molecules, releasing fluoride ions into the solution. This defluorination process is a crucial step in PFAS degradation and is often used as a measure of treatment efficiency. The increase to 2.8 mg/L suggests that a substantial portion of the PFAS compounds were degraded. However, it's important to note that the extent of fluoride release may not directly correlate with complete mineralization of PFAS, as some fluorine-containing intermediates or shorter-chain PFAS may still be present in the treated water. The incomplete mineralization and presence of transformation products highlight the challenges in achieving complete PFAS destruction through electrochemical oxidation. This is particularly evident in complex wastewater matrices, where competing reactions and the presence of other organic compounds can interfere with the degradation process. The low COD and TOC reduction levels observed in our study (20.4% and 18.75%, respectively) further emphasize these challenges, as they indicate that a significant portion of organic compounds, including PFAS and their transformation products, remain in the treated water. It is worth underlying that, in addition to PFAS present in the raw effluent, other pollutants such as surfactants could be found in this type of effluent and they constitute the majority of the COD (Aboulhassan et al., 2006). During electrolysis, COD pollutants can be subjected to two different paths in anodic oxidation: electrochemical conversion or electrochemical combustion (Drogui et al., 2001; Grimm et al., 1998). Electrochemical conversion only transforms the non-biodegradable organic pollutants into biodegradable compounds, whereas electrochemical combustion yields water and carbon dioxide, and no further treatment is then required. To improve the treatment efficiency, future research could focus on optimizing reaction conditions, exploring enhanced catalytic activity, and developing strategies to minimize energy consumption while maximizing PFAS degradation. Additionally, coupling electrochemical oxidation with other treatment methods, such as foam fractionation, may provide a more comprehensive approach to PFAS remediation in contaminated water (Radjenovic and Sedlak, 2015).

4. Conclusion

The electrooxidation (EO) process using a plasma torch Magnéli phase PT-Ti₄O₇ anode has demonstrated feasibility as a technology for the treatment of water contaminated by PFAS. Using sodium sulphate (Na₂SO₄) at a concentration of 2.86 g/L as the supporting electrolyte and applying a current density of 20 mA/cm² during a 2-h electrolysis time ensures a high degradation efficiency of PFAS compounds, reaching up to 86% for PFOS and 64% for PFOA in synthetic water. However, the degradation of PFAS compounds in real wastewater was lower, with a 40% removal rate observed for PFOA. Further research is needed to fully understand the performance and limitations of this EO process using Magnéli phase PT-Ti₄O₇ anodes for the remediation of PFAS-contaminated waters, particularly in addressing the differences in degradation efficiency between synthetic and real-world wastewater matrix. Likewise, the identification of by-products needs to be rigorously verified and a mechanism of PFOA/PFOS degradation should be proposed. The total organic (TOC) should be measured to evaluate the degradation level and see if PFAS other organic pollutants are completely or partially transformed into water and carbon dioxide.

CRedit authorship contribution statement

Hela Rekik: Writing – original draft, Investigation,

Conceptualization. **Loick Pichon:** Writing – original draft, Methodology, Investigation. **Termeh Teymoorian:** Visualization, Validation, Investigation. **Hamed Arab:** Writing – original draft, Investigation. **Sébastien Sauvé:** Supervision, Funding acquisition, Formal analysis. **My Ali El Khakani:** Writing – review & editing, Supervision, Funding acquisition. **Patrick Drogui:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships, which may be considered as potential competing interests: Pôle Recherche Innovation Matériaux Avancés (PRIMA) Research and innovation project in advanced materials.

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Abbreviation

AEO	Electro-catalytic oxidation
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
XRD	X-ray diffractometer
Ppb	Part per billion.
Min	minutes
PFAS	Per and polyfluoroalkyl substances
BDD	Boron-doped diamond
TiO _{2-x}	Sub-stoichiometric titanium dioxide.
Ti _n O _{2n-1}	The Magnéli phase
•OH	hydroxyl radicals
S ₂ O ₈ ²⁻	Persulphate
DC	Direct current
SEM	Scanning Electron Microscope
Na ₂ SO ₄	Sodium sulphate
RWW	Real WasteWater
COD	chemical oxygen demand.
TOC	Total Organic Carbon
RNO	N, N- Dimethyl-4-nirtoso-aniline.
UHPLC-HRMS	Ultra high-resolution Q Exactive Orbitrap mass spectrometry
SnO ₂	Tin dioxide
PbO ₂	platinum and Lead dioxide

Data availability

Data will be made available on request.

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