

Review

Photocatalysis and Electro-Oxidation for PFAS Degradation: Mechanisms, Performance, and Energy Efficiency

Vincenzo Vietri ¹, Vincenzo Vaiano ^{1,*} , Olga Sacco ²  and Antonietta Mancuso ¹ 

¹ Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano, Salerno, Italy; vvietri@unisa.it (V.V.); anmancuso@unisa.it (A.M.)

² Department of Chemistry and Biology “Adolfo Zambelli”, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano, Salerno, Italy; osacco@unisa.it

* Correspondence: vvaiano@unisa.it

Abstract

The continuous emission of persistent and bioaccumulative pollutants into aquatic environments has become a critical global issue. Among these, per- and polyfluoroalkyl substances (PFASs) are of particular concern due to their exceptional stability, extensive industrial use, and adverse impacts on ecosystems and human health. Their resistance to conventional physical, chemical, and biological treatments stems from the strength of the carbon–fluorine bond, which prevents efficient degradation under standard conditions. This review provides a concise and updated assessment of emerging advanced oxidation processes (AOPs) for PFAS remediation, with emphasis on heterogeneous photocatalysis and electrochemical oxidation. Photocatalytic systems based on In_2O_3 , Bi-based oxyhalides, and Ga_2O_3 exhibit high PFAS degradation under UV light, while heterojunctions and MOF-derived catalysts improve defluorination under solar irradiation. Electrochemical oxidation—particularly using Ti_4O_7 reactive electrochemical membranes and BDD anodes—achieves near-complete mineralization with comparatively low specific energy demand. Energy consumption (E_{EO}) was calculated from literature data for UV- and simulated-solar-driven photocatalytic systems, enabling a direct comparison of their energy performance. Although solar-driven processes offer clear environmental advantages, they generally exhibit higher E_{EO} values, mainly due to lower apparent quantum yields and less efficient utilization of the incident solar photons compared to UV-driven systems. Hybrid systems coupling photocatalysis and electro-oxidation emerge as promising strategies to enhance degradation efficiency and reduce energy requirements. Overall, the review highlights key advances and future research directions toward scalable, energy-efficient, and environmentally sustainable AOP-based technologies for PFAS removal.



Academic Editors: Reyna Natividad, Alicia L. Garcia-Costa, Gabriela Roa-Morales, Ángeles Mantilla and Fiderman Machuca-Martínez

Received: 9 December 2025

Revised: 8 January 2026

Accepted: 12 January 2026

Published: 2 February 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

Keywords: per- and polyfluoroalkyl substances (PFAS); PFAS degradation; PFAS mineralization; advanced oxidation processes (AOPs); photocatalysis; electrochemical oxidation; energy efficiency

1. Introduction

The increasing release of anthropogenic pollutants into natural ecosystems represents one of the most pressing global environmental challenges of the twenty-first century. Per- and polyfluoroalkyl substances (PFASs) have recently gained significant global attention due to mounting environmental and public health concerns. These compounds constitute a vast and heterogeneous group of synthetic chemicals—comprising more than 4000 partially

or fully fluorinated structures—that may be linear, branched, or cyclic [1]. Their exceptional chemical and thermal stability, primarily attributed to the strength of the carbon–fluorine (C–F) bond (bond dissociation energy 485–582 kJ/mol), renders them highly resistant to degradation [2].

Since the 1950s, PFASs have been extensively used across numerous industrial and commercial sectors owing to their hydrophobic and oleophobic properties and their resistance to heat and chemical attack. They have been incorporated into adhesives, coatings, cosmetics, food packaging materials, pesticides, lubricants, and aqueous film-forming foams used for firefighting, where they typically represent 1–5% *w/w* [3,4]. The textile industry remains the largest consumer of PFASs and their precursors, followed by paper packaging and aftermarket consumer products [5].

Environmental monitoring has demonstrated the ubiquitous presence of PFASs in all environmental compartments—air, water, soil, and ice. Their release occurs via both direct emissions from manufacturing, industrial effluents, and wastewater treatment plants (WWTPs), which together account for over 80% of total PFAS inputs and indirect pathways such as long-range atmospheric transport and the degradation of precursor compounds [6]. WWTPs represent particularly critical point sources, as PFASs are not efficiently removed by conventional treatment methods and may even undergo transformation into shorter, more mobile derivatives [7]. Their detection in remote regions such as Arctic snow and Tibetan glaciers further underscores the global scale of PFAS dispersion [8,9].

Concentrations of PFASs in aquatic environments typically range from nanograms per litre (ng/L) to micrograms per litre (µg/L), although sub-ng/L levels have been reported in some remote areas [10]. A global survey (2004–2010) detected perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA)—two of the most studied PFASs—in all surface water samples collected from 41 cities across 15 countries, reaching concentrations of 70.1 ng/L and 1630.2 ng/L, respectively [11].

In Italy, PFOA concentrations as high as 200 ng/L have been recorded in the Po River [12], while PFOS, PFOA, and related compounds have been found in surface waters near Milan and Trissino (Vicenza) [13,14]. A national survey conducted by Greenpeace in 2024 detected at least one PFAS compound in 206 out of 260 municipal drinking water samples analyzed across all Italian regions [15]. In October 2025, the study was expanded to bottled waters, identifying trifluoroacetic acid (TFA)—one of the most ubiquitous PFASs—in six of the eight most consumed brands [16].

The environmental fate and transport of PFASs are governed by molecular chain length and functional group chemistry. Long-chain PFASs ($C > 8$) display a strong tendency to bioaccumulate, especially in aquatic organisms and sediments. In response to stringent regulations limiting their use, industry has progressively shifted toward short-chain (C_4 – C_6) and ultra-short-chain (C_1 – C_3) substitutes such as PFBS and PFBA [17]. However, these shorter analogues, though more mobile, exhibit comparable persistence and toxicity, making them equally challenging to treat [7].

Both long- and short-chain PFASs have been detected in human serum and are associated with various adverse health outcomes, including elevated cholesterol, thyroid dysfunction, ulcerative colitis, kidney and testicular cancers, and gestational hypertension. Their mechanisms of toxicity remain under investigation, but PFASs are strongly suspected of acting as endocrine disruptors, developmental and reproductive toxicants, and potential carcinogens. [3]. Regulatory authorities have responded by tightening exposure limits. In 2024, the U.S. Environmental Protection Agency (EPA) reduced the advisory limits for PFOA and PFOS to 0.004 ng/L and established maximum contaminant levels (MCLs) of 0.010 ng/L for PFNA, PFHxS, and HFPO-DA (GenX chemicals) [18]. The European Union subsequently classified PFASs as persistent organic pollutants (POPs) and introduced dual

limits for drinking water, 0.5 µg/L for total PFASs or 0.1 µg/L for the sum of 20 specified compounds (EU Directive 2020/2184, <https://eur-lex.europa.eu/eli/dir/2020/2184/oj/eng>, accessed on 8 November 2025), with comparable measures now enforced in Canada, the United Kingdom, Germany, Sweden, Norway, and Australia [3]. Despite substantial analytical advances enabling detection at picogram-per-litre (pg/L) concentrations, significant knowledge gaps persist regarding the transformation pathways, degradation intermediates, and long-term toxicity of novel and replacement PFASs. Detection techniques now reach picogram-per-litre (pg/L) sensitivity, improving global monitoring capabilities [19]. However, key knowledge gaps persist regarding transformation pathways, degradation intermediates, and the long-term toxicity of newer PFASs [20]. PFASs are notoriously resistant to removal by conventional physical, chemical, or biological processes. In particular, adsorption and membrane filtration primarily relocate the contaminants from water to solid or concentrated phases without achieving mineralisation [21]. To overcome these limitations, research has focused on advanced oxidation processes (AOPs), with particular emphasis on heterogeneous photocatalysis and electro-oxidation techniques, which offer the potential for complete mineralization. This review provides an updated overview of the environmental and human health implications of PFASs, with particular emphasis on emerging technologies for their degradation. Special attention is devoted to heterogeneous photocatalytic and electrochemical oxidation systems, which have shown great potential for complete PFAS mineralization. By critically comparing their efficiencies and energy requirements, this review aims to identify sustainable, energy-efficient, and environmentally benign approaches for PFASs remediation in aquatic environments.

2. Methods for PFASs Removal

2.1. Conventional Wastewater Treatment Methods

Conventional wastewater treatments are primarily designed to remove suspended solids and reduce total organic load, yet they are largely ineffective in addressing highly persistent contaminants such as PFASs [22].

The chemical resilience of PFASs, stemming from the exceptional strength of their carbon–fluorine bonds, prevents significant degradation under the biological and physico-chemical conditions typical of traditional treatment systems [23].

Among conventional methods, the activated sludge process remains the most widely employed. This technique relies on aerobic microorganisms to biodegrade organic pollutants. Although efficient for readily biodegradable compounds, its performance is severely constrained for PFASs due to their low bioavailability, hydrophobic nature, and inability of microbial enzymes to cleave C–F bonds [23]. As a result, PFASs can pass through treatment plants virtually unchanged or even form shorter-chain transformation products through partial defluorination, which are typically more mobile and equally persistent.

Similarly, physical separation processes such as coagulation–flocculation, sedimentation, and filtration can only partially remove these pollutants [10,24]. Adsorption on activated carbon takes advantage of the high surface area and porosity of carbon materials. Although this system can effectively reduce the concentration of various micropollutants, it only transfers contaminants from the aqueous phase to a solid matrix, thus generating secondary waste requiring further management [25]. In recent decades, membrane-based technologies, such as nanofiltration (NF) and reverse osmosis (RO), have been increasingly adopted for advanced wastewater treatment. These systems are capable of removing a broad spectrum of micropollutants, yet they are associated with high energy consumption and the problem of concentrate disposal [26].

Thus, while conventional and established advanced methods contribute to the removal of refractory pollutants, none provide definitive solution.

2.2. Advanced Oxidation Processes (AOPs)

AOPs have emerged as a promising class of treatment technologies designed to overcome the limitations of conventional methods in degrading recalcitrant pollutants, like PFASs. However, the application of AOPs to PFAS remediation poses specific challenges associated with the exceptional strength of the carbon–fluorine (C–F) bond, which strongly limits the effectiveness of conventional oxidative pathways [27].

AOPs rely on the in situ generation of highly reactive and non-selective radical species, most commonly hydroxyl radicals ($\bullet\text{OH}$), which can oxidize a wide range of organic contaminants. In the case of PFASs, however, $\bullet\text{OH}$ radicals alone often show limited reactivity toward the fluorinated carbon backbone, and purely oxidative mechanisms are frequently insufficient to achieve complete defluorination, requiring the involvement of additional reactive species or synergistic oxidation–reduction pathways [20,28]. Under favourable conditions, AOPs can promote partial transformation of PFAS molecules and, in some cases, lead to mineralisation into CO_2 , H_2O , and fluoride ions.

According to the activation pathways of oxidants and the underlying degradation mechanisms, AOPs can be broadly classified into chemical and non-conventional processes. Chemical AOPs include ozone-based, catalytic, and electrochemical oxidation systems, while non-conventional AOPs encompass microwave-, ultrasound-, and plasma-assisted processes [29]. Among chemical AOPs, methods combining oxidants such as hydrogen peroxide (H_2O_2) or ozone (O_3) with UV irradiation or suitable catalysts are widely employed. Hydrogen peroxide is less oxidizing than ozone but is comparatively inexpensive, which often makes it attractive despite the need for higher oxidant dosages and longer irradiation times in UV/ H_2O_2 systems [30]. In contrast, ozone exhibits a stronger oxidizing potential and can enhance PFAS transformation, although its application is frequently constrained by higher energy demand and operational costs [31].

Moreover, the efficiency of AOPs applied to PFASs is often limited by low apparent quantum yields and inefficient utilization of generated radicals, particularly under environmentally relevant conditions. This has motivated increasing interest in advanced AOP configurations that promote the generation of reductive species (e.g., hydrated electrons) or exploit synergistic mechanisms, such as persulfate activation or combined photocatalytic–electrochemical systems, to improve defluorination efficiency and energy performance [27].

2.2.1. Heterogeneous Photocatalysis

Photocatalysis represents an advantageous and promising approach for treating refractory pollutants in wastewater, principally because it relies on sustainable energy and mild conditions, as it directly exploits light energy to drive redox reactions. Unlike conventional chemical treatments, photocatalytic processes can be powered by sunlight, making them environmentally friendly, cost-effective, and aligned with the principles of green chemistry. Photocatalysis exploits the use of semiconductors as catalysts, TiO_2 is one of the most common examples. Two types of photocatalysis can be distinguished: homogeneous photocatalysis, where the reactants, products, and catalyst are in the same phase; heterogeneous photocatalysis, where the reactants are in the liquid or gas phase while the catalyst is in the solid phase. In particular, heterogeneous photocatalysis approach offers several advantages, mainly because the photocatalyst, being in the solid state, can be easily recovered and reused. The core mechanism of heterogeneous photocatalysis can be described in three steps:

1. **Light absorption and electron–hole pair generation:** When a semiconductor photocatalyst is irradiated with photons ($h\nu$) of energy equal to or greater than its band gap (E_g), an electron (e^-) is promoted from the valence band (VB) to the conduction band (CB). This process leaves behind a positively charged “hole” (h^+) in the valence band, creating an electron–hole pair.

2. **Charge carrier separation and migration:** The photogenerated electrons and holes must separate and migrate to the surface of the photocatalyst. The efficiency of this step is critical, as many electron–hole pairs tend to quickly recombine, releasing their energy as heat or light and reducing the overall efficiency [32].
3. **Surface Reactions:** Once the charge carriers reach the surface, they drive redox reactions: holes act as strong oxidants, either directly attacking adsorbed molecules or reacting with water generating hydroxyl radicals ($\bullet\text{OH}$) (Equation (1)), while electrons typically reduce molecular oxygen to form superoxide radicals ($\bullet\text{O}_2^-$) or other reactive species (Equation (2)).



To enhance photocatalytic performance, several strategies can be adopted during catalyst design. Among these, deliberate morphological and structural modifications are particularly effective. Morphological features govern surface atomic arrangements, thereby tuning the density and coordination of active sites as well as the specific surface area [33]. Such modifications can shorten charge-carrier transport pathways and effectively suppress electron–hole recombination, ultimately enhancing overall photocatalytic efficiency [6,34]. In addition, structural modifications, such as the creation of oxygen or halogen vacancies, can generate active sites, promote reactive oxygen species formation, and facilitate pollutant adsorption [35]. Another approach is the doping of semiconductor materials, which involves the introduction of foreign atoms—metallic or non-metallic—into their crystal lattice, causing the modification of the electronic structure of the photocatalyst, for instance by narrowing the band gap to extend light absorption into the visible range [36]. Furthermore, coupling different semiconductors to construct photocatalytic heterostructures is a widely adopted approach. In such systems, the photocatalyst combines materials with distinct band structures, and the resulting band alignment at the interface generates an internal electric field. This interfacial field enhances charge separation and promotes the directional migration of photogenerated electrons and holes, thereby improving overall photocatalytic efficiency [6]. Finally, the combination of semiconductors with carbonaceous materials, such as carbon nanotubes or reduced graphene oxide, has also proven effective. These materials act as electron acceptors and transporters, thereby prolonging the lifetime of photogenerated e^- – h^+ pairs [18].

The performances of different photocatalytic systems for PFAS degradation are summarized in Table 1.

Table 1. Performances of various photocatalytic systems for the degradation of PFASs. C_0 , initial PFAS concentration; sp., spontaneous; Deg. eff., degradation efficiency; Defl. eff., defluorination efficiency.

Photocatalyst	Light	PFAS C_0	Catalyst Dosage	pH	Time	Deg. eff.	Defl. eff.	Ref.
Zn^{2+} - Bi_2WO_6	Visible 150 W	PFHxA 5 mg/L	0.4 g/L	-	45 min	57%	-	[37]
$\text{Bi}_3\text{O}(\text{OH})(\text{PO}_4)_2$	UV	PFOA 54 mg/L	1.8 g/L	~4.0	1 h	>99%	-	[38]
BiOCl	UV	PFOA 20 mg/L	1 g/L	sp.	0.5 h	99.99%	-	[39]
FeO/CS (1:1)	Solar	PFOA (pre-adsorbed) 0.2 mg/L	1 g/L	7.0	4 h	95.2%	57.2%	[40]
$\text{BiOI}0.95\text{Br}0.05$	UV 300 W	PFOA 20 mg/L	0.4 g/L	-	2 h	100%	65% in 3 h	[41]
In_2O_3 microspheres	UV 15 W	PFOA 30 mg/L	0.5 g/L	~3.9	20 min	100%	-	[42]

Table 1. Cont.

Photocatalyst	Light	PFA _S C ₀	Catalyst Dosage	pH	Time	Deg. eff.	Defl. eff.	Ref.
Fe/TNTs@AC	Solar	PFOA 0.2 mg/L	1 g/L	~7.0	4 h	90.1%	62% in 4 h	[43]
Bare Fe ⁰ NPs	UVC 4.24 mW/cm ²	PFOA 0.5 mg/L PFOS 0.5 mg/L PFNA 0.5 mg/L (mix in real wastewater)	0.1 g/L	3.0	2 h	46% 88% 90%	-	[44]
Fe ₃ O ₄ @SiO ₂ -BiOBr	UV and Visible (DBD)	PFOA 20 mg/L	0.1 g/L	4.28	1 h	92.9%	32.8%	[45]
20% In-MOF/BiOF	UV 500 W	PFOA 15 mg/L	0.5 g/L	-	2.5 h	100%	34% (in 3 h)	[46]
3% Pt/In ₂ O ₃ nanorods	UV500 W	PFOA 200 mg/L	0.4 g/L	-	1 h	98%	-	[47]
In-Ga ₂ O ₃ hierarchical nanosheets	UV 200 W	PFOA 20 mg/L	0.5 g/L	4.5	1 h	100%	57% (in 4 h)	[43]
(4%) MnOx/In ₂ O ₃ -Ov-rich sub-micro rods	Solar 500 WUV500 W	PFOA 50 mg/L	0.5 g/L	-	3 h 10 min	99.8% 98%	17.4% 95.7% in 4 h	[48]
(2%) Pb-TiO ₂	UV 400 W	PFOA 50 mg/L	0.5 g/L	53	2 h 15 min	100% 100%	40.7% -	[49]
ZnO/rGO	Solar	PFOA 100 mg/L	1 g/L	7	1 h	90.9%	-	[50]
Bi ₄ O ₅ I ₂ + Bi ₅ O ₇ I	Solar 700 W	PFOA 1 mg/L	0.5 g/L	~6.8	2 h	94%	65%	[51]
Needle-like β-Ga ₂ O ₃	UV 14 W	PFOA 0.5 mg/L	0.5 g/L	~4.8	1 h	100%	-	[52]
2% rGO/BiOCl	UV 125 W	PFOA PFOS 10 mg/L	1 g/L	-	1 h	90.1% 66.2%	-	[32]
BiOCl@PMoV (0.9 g/L persulfate)	UV 300 W	PFOA 100 mg/L	1.5 g/L	3	6 h	95.0%	44.4%	[53]
Bi/TiO ₂	UV 400 W	PFOA 50 mg/L	0.1 g/L	3	0.5 h	99.3%	55.3% (in 2 h)	[54]
MXene/TiO ₂	UV	PFOA 20 mg/L	0.13 g/L	5.2	9 h	94.6%	58.4%	[55]
Palm kernel shell activated carbon- Fe ₂ O ₃ /SnO ₂	Visible 250 W	PFOA 20 mg/L	10 mg/L	5	6 h	92.4%	51.2%	[56]
2% ReS ₂ -TiO ₂	UV	PFOA 2 mg/L	-	3	2 h	98%	75%	[35]
BN/BiOI-2:1	UV	PFOA PFOS C7 Gen-X F-53B 6:2 FTS F-53	1.5 g/L	3	2 h 2 h 6 h 6 h 6 h 6 h 6 h	100% 100% 77% 7.3% 100% 100% 67.6%	45.4% in 6 h (PFOS)	[57]
BiOI/ZnO 4:1	Solar 500 W	PFOA 10 mg/L	-	-	1 h	100%	100% (in 5 h)	[58]
ZnO/BiOI 4:1					3 h	100%	100% (in 5 h)	
Magnetic modified clay + Na ₂ SO ₃ + KI (Photoreductive system)	UV	PFOA 1 mg/L	2.5 g/L MMC, 50 mM Na ₂ SO ₃ , 10 mM KI	12	48 h	100%	66.5 ± 1.1%	[59]
Fe-BTC/BiOCl BTC: iron-based metal-organic framework (MOF)	Visible 5 W	PFOA 10 mg/L	0.2 g/L	-	0.5 h	98.7%	31.1%	[60]
30% In ₂ O ₃ / BiOCl	UV 500 W	PFOA 20 mg/L	0.2 g/L	5	2 h	-	84%	[61]

Perfluorooctanoic acid (PFOA) is most often used as a model pollutant. Currently, the most promising photocatalytic systems achieve treatment times as short as 30 min, under UV irradiation, whereas the use of simulated solar light generally requires longer exposure times. Among the semiconductor materials investigated, indium oxide (In₂O₃), bismuth oxyhalides (e.g., BiOCl, BiOI), and gallium oxide (Ga₂O₃) have emerged as the most effective photocatalysts for PFOA degradation. These materials exhibit distinct optical properties that largely determine their activation regime: UV-driven photocatalysts

such as In_2O_3 and Ga_2O_3 typically possess wide band gaps in the range of ~ 3.0 – 4.9 eV, limiting their excitation to high-energy photons. In contrast, bismuth-based oxyhalides and related heterojunction or composite systems designed for solar activation display narrower band gaps, generally between ~ 1.8 and 2.8 eV, enabling more efficient absorption in the visible region.

In addition to band gap considerations, photocatalytic performance is strongly influenced by the effective photon flux reaching the reaction medium, which depends not only on the nominal power of the light source but also on reactor configuration, optical path length, catalyst loading, and solution properties. As a result, systems operated under simulated solar irradiation often require longer treatment times despite favourable band gap alignment, highlighting the critical role of irradiation conditions in determining overall photocatalytic efficiency.

Most of the studies report a general mechanistic pathway for the photocatalytic degradation of PFOA. The process often begins with hole-mediated decarboxylation. In fact, in most cases, $\bullet\text{OH}$ are not the primary reactive species responsible for initiating the cleavage of PFAS C–F bonds [38,43]. Although $\bullet\text{O}_2^-$ are frequently identified as key reactive species during PFAS degradation, their role is not associated with direct oxidative decarboxylation, as their redox potential is insufficient to oxidize perfluorinated carboxylic acids. Instead, $\bullet\text{O}_2^-$ is believed to participate in secondary reaction pathways, including radical propagation steps and the transformation of intermediate species [32,37,46,47]. Subsequent oxidative reactions drive stepwise chain shortening through the elimination of HF and the formation of shorter-chain perfluorocarboxylic acids. This cycle repeats until complete mineralization into fluoride ions (F^-) and CO_2 is achieved.

A critical prerequisite for efficient heterogeneous photocatalysis is the adsorption of PFAS onto the catalyst surface, which concentrates the pollutant in proximity to photo-generated reactive species. The mode of adsorption strongly influences the efficiency of degradation. For example, In_2O_3 catalysts enable tight bidentate or bridging coordination (Figure 1) between PFOA's carboxylate head group and the catalyst surface, which facilitates direct hole-driven decomposition [48].

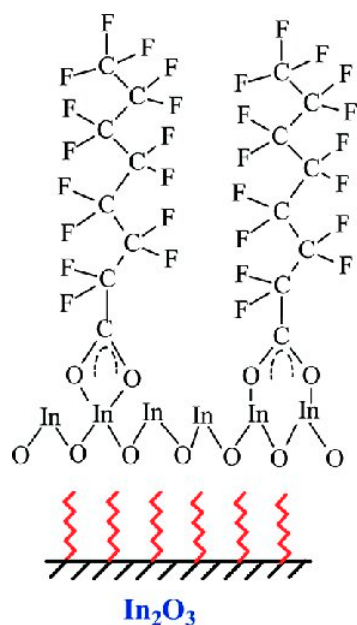


Figure 1. Schematic representation of the PFOA adsorption configurations on In_2O_3 . Reprinted with permission from [62]. Copyright 2012 American Chemical Society.

Zhang et al. (2012) [62] synthesized In_2O_3 with controlled morphology, identifying porous microspheres as the optimal structure. This catalyst achieved complete decomposition of PFOA within 20 min under UV light, with a kinetic constant of 7.94 h^{-1} , nearly 75 times higher than TiO_2 (P25). Similarly, BiOCl achieved 99.99% PFOA degradation within 30 min UV irradiation. The efficacy of bismuth oxyhalides is often linked to their wider band gap, producing a more positive valence band potential and stronger oxidation ability of photogenerated holes. Furthermore, BiOX crystal structure (Figure 2), consisting in alternating $[\text{Bi}_2\text{O}_2]^{2+}$ layers interleaved with two sheets of halide ions generates an internal static electric field oriented perpendicular to the $[\text{Bi}_2\text{O}_2]^{2+}$ and $[\text{X}]^-$ layers [63]. Such built-in fields efficiently drive the separation of photogenerated charge carriers [39].

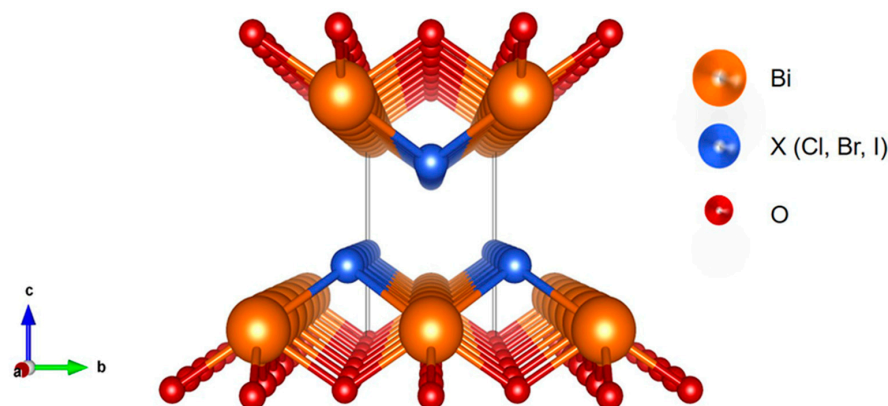


Figure 2. Crystal structure of bismuth oxyhalide (BiOX , $\text{X} = \text{Cl}$, Br , and I) [63]. Reprinted from Frontiers. Copyright © 2022 Castillo-Cabrera, Espinoza-Montero, Alulema-Pullupaxi, Mora and Villacís-García [63] under the terms of the Creative Commons Attribution License (CC BY).

Composite systems can also offer synergistic effects. A p–n heterojunction of 30% $\text{In}_2\text{O}_3/\text{BiOCl}$ achieved a defluorination rate of 84% within 2 h under UV light, accompanied by a total organic carbon (TOC) removal efficiency of 82.9% [61]. The built-in electric field at the heterojunction interface promoted efficient charge separation, with holes transferred to BiOCl and electrons to In_2O_3 , thereby facilitating both oxidative and reductive pathways. Mechanistic analysis revealed $\bullet\text{OH}$ is not the main oxidizing species, and $\bullet\text{O}_2^-$ and h^+ play a major role. According to Hu et al. (2025) [61], the degradation pathway is divided into three routes (Figure 3). In route 1, photogenerated holes (h^+) at the photocatalyst surface oxidize the carboxylate group of PFOA, leading to the formation of a carboxyl radical ($\text{C}_7\text{F}_{15}\text{COO}\bullet$), which undergoes a Photo–Kolbe decarboxylation to generate the perfluoroheptyl radical ($\text{C}_7\text{F}_{15}\bullet$). This radical subsequently reacts with molecular oxygen through a sequence of oxidative transformation steps, forming oxygenated perfluorinated intermediates that ultimately yield perfluoroheptanoic acid (PFHpA). In route 2, ROS generated in the system are proposed to facilitate $\alpha\text{-C-F}$ bond cleavage, leading to the formation of oxygenated fluorinated carboxylate intermediates. Rather than a direct nucleophilic attack by a single well-defined radical species, these steps are better described as ROS-assisted transformations, consistent with the experimentally observed faster degradation under acidic conditions. Subsequently, route 2 give rise to two distinct pathways: In route 2a, decarboxylation produces highly unstable fluorinated alcohol-type intermediates, which readily eliminate HF to form fluorinated aldehydes (e.g., $\text{C}_6\text{F}_{13}\text{CHO}$). In route 2b, oxygenated fluorinated intermediates undergo direct HF elimination, generating carbonyl-containing species such as perfluoro-2-oxohexanoic acid. These intermediates subsequently decarboxylate to form the same fluorinated aldehydes obtained via route 2a. These aldehydes are further transformed through oxidative reactions involving $\bullet\text{OH}$ and $\bullet\text{O}_2^-$, ultimately yielding PFHpA. Overall, all the routes result in the loss of one CF_2 unit

relative to the parent PFOA molecule. The proposed degradation mechanism therefore involves a stepwise chain-shortening process, in which successive cycles progressively reduce the perfluorinated carbon chain until complete mineralisation is achieved.

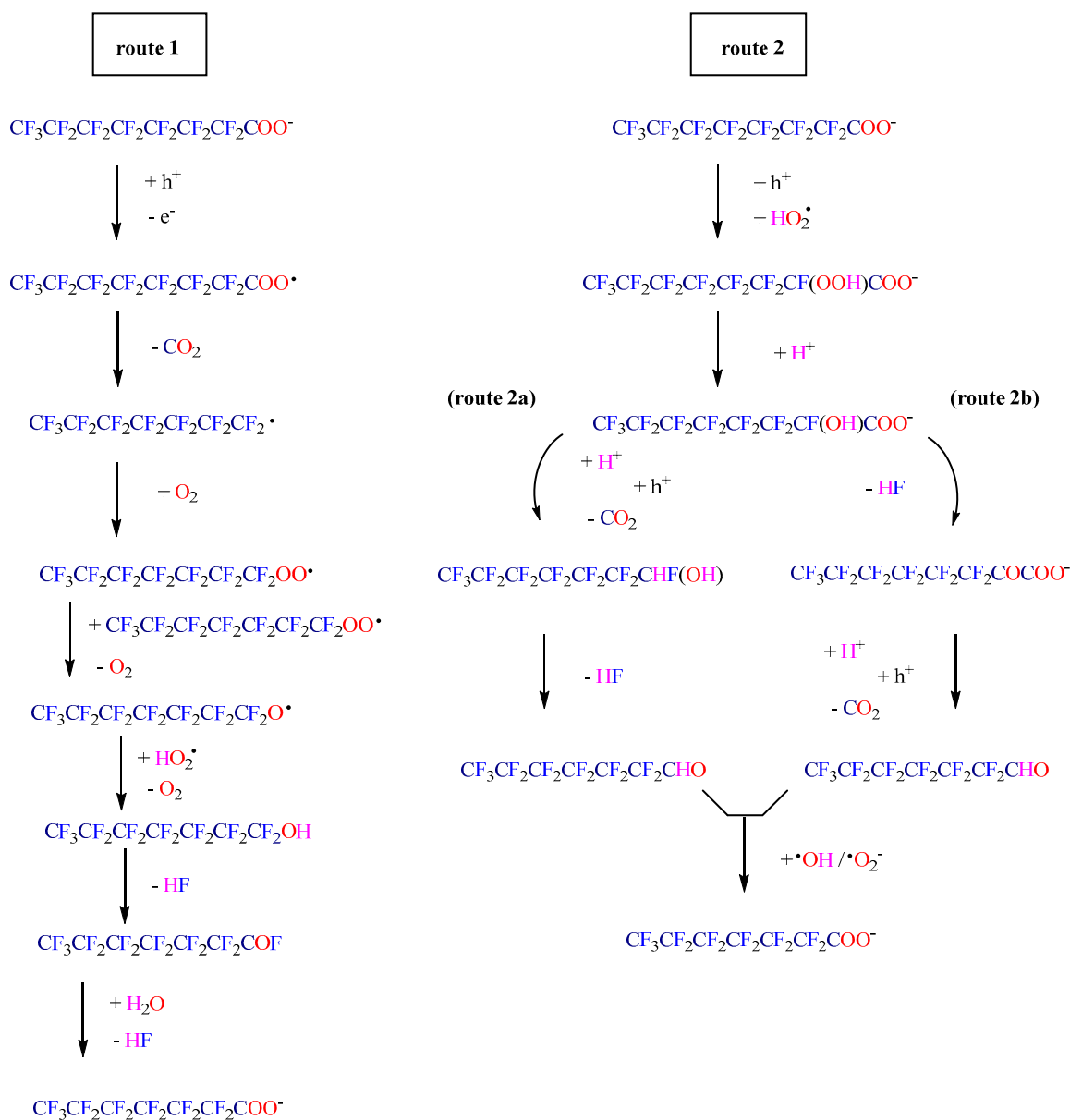


Figure 3. Possible pathways of PFOA degradation by p-n type $\text{In}_2\text{O}_3/\text{BiOCl}$ heterojunction [61].

2.2.2. Electrochemical Oxidation (EO)

Electrochemical oxidation has gained increasing attention as a versatile and efficient process for the treatment of persistent pollutants. This treatment is carried out by applying an electrical potential to an electrochemical cell equipped with one or more electrode pairs. The generation of oxidizing species occurs directly at the surface of the anode when an electric current is applied [64]. Two main mechanisms are typically distinguished in electrochemical oxidation: direct oxidation and indirect oxidation. In direct oxidation, pollutants are adsorbed onto the anode surface and undergo electron transfer reactions, leading to their degradation or mineralization. In indirect oxidation, reactive species are electrochemically generated and subsequently attack pollutants in the bulk solution [65]. The choice of electrode material is crucial for EO efficiency. Research on electrocatalytic

materials mainly focuses on the development of anodic materials that are efficient, stable, and cost-effective.

Key strategies to improve anode performance include:

- **Surface doping with functional species**, aimed at optimizing the crystalline phase and increasing particle compactness, which enhances the ability of the anode to generate surface-adsorbed reactive oxygen species.
- **Metal doping**, which can improve electron transfer kinetics.
- **Construction of three-dimensional nanostructures**, capable of increasing the number of active sites and thereby improving mass transfer and adsorption efficiency.
- **Introduction of functional interlayers**, which strengthen the adhesion between the active layer and the substrate, resulting in improved anode stability [66].

Non-active anodes, which tends to promote indirect oxidation, implying the generation of $\bullet\text{OH}$ strongly adsorbed on the electrode surface, usually demonstrate the highest potential for complete mineralization [64]. This category include:

- **Boron-doped diamond (BDD)** electrodes are among the most widely studied materials. They possess a wide potential window, high oxidation potential (around 2.7 V vs. SHE), excellent chemical stability, rapid charge-transfer kinetics, and minimal adsorption of intermediates. These features allow BDD to achieve high mineralization rates. However, the high cost of fabrication and the challenges of scaling up production hinder large-scale applications [67].
- **Among metal oxides-based electrodes, SnO_2 -based** ones are semiconductors with a wide bandgap, whose conductivity and performance can be significantly improved through doping. Nevertheless, SnO_2 electrodes may suffer from short operational lifetimes if not properly modified, and the presence of sulfate ions in the electrolyte can block active sites, lowering hydroxyl radical generation [66]. **PbO_2 -based** electrodes are low-cost and simple to fabricate, with high conductivity. Their main drawback lies in the risk of Pb^{2+} leaching. Also in this case, doping can improve electrode stability, increase electroactive surface area, and mitigate Pb release, but concerns remain regarding their safe long-term application [66].
- **Magnéli-phase Ti oxides** are sub-stoichiometric titanium oxides that combine high electrical conductivity, good chemical stability, and relatively low production cost, since TiO_2 is a cheap precursor. Materials such as Ti_4O_7 exhibit excellent stability in aggressive electrolytes, and large electroactive surface area. However, long-term stability issues may arise due to the presence of Ti^{3+} species, and conductivity decreases for higher values of n in $\text{Ti}_n\text{O}_{2n-1}$ [68].

Examples of active anodes, on the other hand, are platinum, iridium oxide (IrO_2), ruthenium oxide (RuO_2), and carbon-based electrodes.

Electrochemical oxidation offers several advantages over conventional methods. It does not require the addition of chemical reagents, operates at ambient temperature and pressure, and can be easily controlled by adjusting the applied current. However, certain limitations still hinder large-scale implementation. These include high energy consumption, electrode cost, and the potential formation of harmful by-products, such as chlorinated organics when chloride-containing electrolytes are used [64].

Although research on electrochemical PFAS degradation has traditionally focused on anodic materials, cathodic processes can also contribute to PFAS transformation and defluorination, particularly through reductive pathways. At the cathode, the generation of hydrated electrons and other reducing species may promote C–F bond cleavage via reductive mechanisms, complementing anodic oxidation processes. Recent studies have shown that cathodic reactions can enhance overall PFAS degradation efficiency, especially in

paired or integrated electrochemical systems where oxidation and reduction processes occur simultaneously. These findings highlight the importance of considering the synergistic roles of both anode and cathode when evaluating electrochemical remediation strategies [69].

Recent research has focused on improving EO sustainability and efficiency. Hybrid systems that combine EO with other processes, such as photocatalysis, Fenton-based methods, or biological post-treatments, have shown promising results in reducing energy requirements and enhancing mineralization rates. Advances in electrode engineering are also contributing to more efficient and stable EO systems.

Table 2 reports the performances of various electrocatalytic systems investigated for the degradation of PFASs and information on electrolysis chamber configuration (e.g., divided or undivided cells).

Table 2. Performances of various electrocatalytic systems for the degradation of PFASs. C₀, initial PFAS concentration; TOC, Total Organic Carbon; Defl., defluorination efficiency.

Anode	Cathode	Cell type	PFAS	C ₀	Time	Deg. eff.	Mineralization	Ref.
Graphite Intercalated Compound (Ads.+ EO)	Stainless Steel	Divided cells	PFOS PFOA PFBS	100 µg/L 45 µg/L 10 µg/L	5 cycles 3 cycles 5 cycles (1 cycle: 20 min ads + 10 min reaction)	100% 98% 17%	By-products below 100 ng/L (PFOS)	[70]
BDD	Stainless Steel	Single cell	PFOA PFBA GenX 6:2FTCA	20 mg/L	2 h	97.9% 65.6% 84.9% 99.4%	68.6% (Defl.) 60.8% (Defl.) 71.2% (Defl.) 63.1% (Defl.)	[71]
BDD/SnO ₂ -F	Pt sheet	Single cell	F-53B	100 mg/L	0.5 h	95.6%	61.4% (Defl.)	[72]
Ti/Sn-Sb/SnO ₂ -F-Sb multilayer	Ti plate	Single cell	PFOS	100 mg/L	2 h	>99%	87.1% (TOC)	[73]
Ti/SnO ₂ -F	Ti plate	Single cell	PFOA	100 mg/L	0.5 h	99.6%	98.3% (TOC)	[74]
Porous Ti ₄ O ₇ (REM)	Stainless Steel	Single cell	PFOS	2.0 µM	100 min	99.1%	-	[75]
Porous Ti ₄ O ₇	Stainless Steel	Single cell	PFOA PFOS	0.5 mM 0.1 mM	3 h	>99.9% 93.1%	>95% (TOC) 90.3% (TOC)	[76]
Ti ₄ O ₇ doped with amorphous Pd	Ti plate	Single cell	PFOA	0.12 mM	1 h	>90%	99.7% (TOC)	[77]
Si/BDD	Si/BDD	Single cell	Short-chain (C3–C6) and long-chain (C7–C18) PFCAs	200 mg/L	1 h	C10–C18: 95% C6: 70% C5: 66% C4: 41% C3: 39%	PFOA 37% (Defl.) Short chain PFCAs: 45% (Defl.) Long chain PFCAs: 92% (Defl.)	[78]
Ti/SnO ₂ -Sb/PbO ₂	Ti plate	Single cell	PFOA	100 mg/L	1.5 h	91.1%	77.4% (Defl.)	[79]
Ti ₄ O ₇ (REM)	Stainless Steel	Single flow-through cell	PFOA PFOS	4.14 mg/L 5 mg/L	~11 s	PFOA/PFOS: ~5-log removal >99.9%	-	[80]
CeO ₂	AC	Single flow-through cell	PFOA	1 mg/L	12 h	94%	73.0% (Defl.)	[81]
Ti ₄ O ₇	Carbon felt	Single cell	PFOA PFOS	2 mg/L	5 h	92% 100%	-	[82]
BDD (for persulfate activation)	Ti plate	Single cell	PFOA PFOS	50 µM	2 h	100% 100%	60.4% (Defl.) 33.1% (Defl.)	[83]

Non-active anodes are generally preferred for PFAS degradation, as they promote complete mineralization rather than partial transformations [46]. PFASs degradation on BDD electrodes occurs mainly through direct electron transfer (DET) at low current densities, rather than via •OH-mediated oxidation at higher current densities. Barisci et al. (2020) [78] reported that Si/BDD electrodes, consisting of thin film of boron-doped diamond (BDD) deposited on a silicon (Si) substrate, under optimized conditions (applied current

density of 25 mA/cm², pH 5 and 400 mg/L of Na₂SO₄) achieved 74% TOC removal and 37% defluorination for PFOA (10 mg L⁻¹) after a treatment time of 1 h. Ti is most commonly used as a substrate, but Ti/BDD electrodes suffer from relatively short lifetimes [79]. The mechanism was proposed as direct electron transfer, then followed by radical-mediated pathways (Figure 4). In particular, in the first step, PFOA, in its dissociated form, donates an electron to the anode surface, denoted by letter M (1).

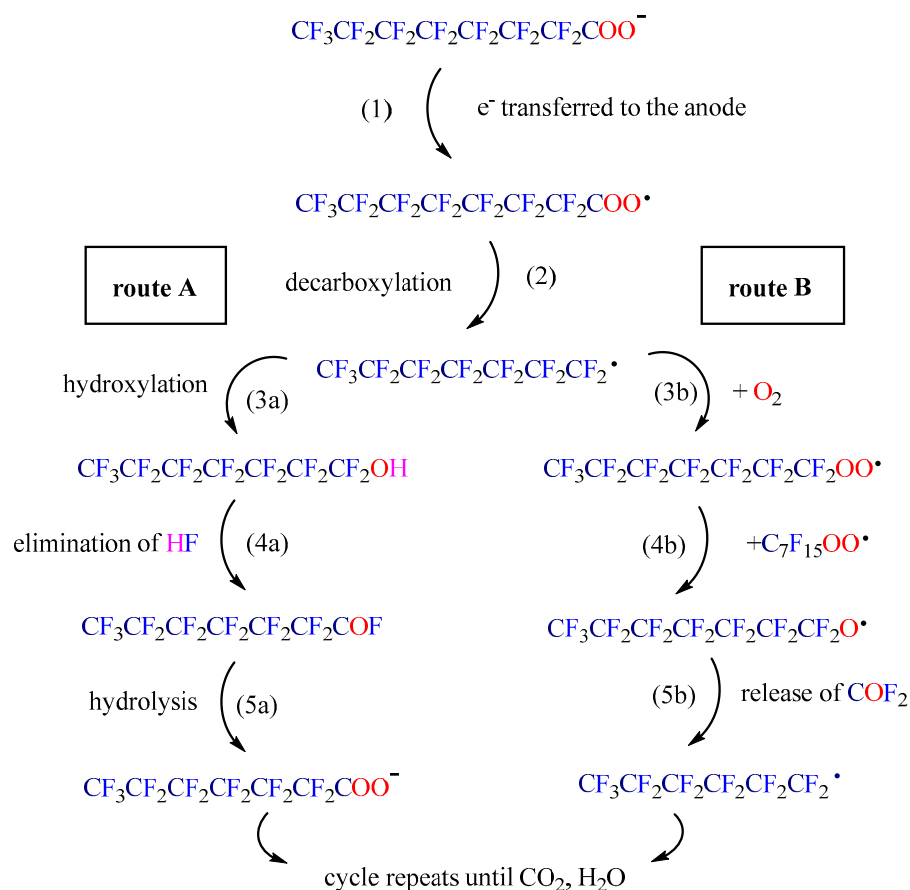
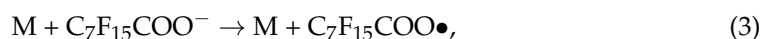


Figure 4. Possible pathways for the degradation of PFOA by Si/BDD electrode [78].

Then, the decarboxylation leads to the perfluoroheptyl radical $C_7F_{15}\bullet$ (2), which then can follow two different pathways. The first one involves the hydroxylation of this intermediate by the formed $OH\bullet$ (3a) and the subsequent elimination of HF (4a). The hydrolysis of the formed $C_6F_{13}COF$ generated $C_6F_{13}COO^-$ (5a). Afterwards, the cycle is initiated again by one electron transfer from the anode surface until the formation of CF_3COO^- . This pathway was observed multiple times by other researchers [74,79]. In the second pathway proposed, perfluoroheptyl radical $C_7F_{15}\bullet$ reacts with O_2 to form perfluoroheptylperoxy radical $C_7F_{15}OO\bullet$ (3b), which combines with another $C_7F_{15}OO\bullet$ to generate $C_7F_{15}O\bullet$ (4b). Afterwards, the releasing of COF_2 leads to $C_6F_{13}\bullet$ (5b). Carbonyl fluoride (COF_2) is included in the mechanistic scheme as a plausible transient intermediate during PFAS defluorination. However, its direct detection in aqueous electrochemical degradation experiments has not been widely reported in the literature. COF_2 undergoes rapid hydrolysis in the presence of water, a reaction that has been explored through ab initio studies demonstrating the importance of water coordination in facilitating the breakdown of COF_2 into HF and carbonyl-containing species [84]. This rapid hydrolysis is consistent

with general observations that acyl fluorides are highly susceptible to nucleophilic attack by water, leading to fast conversion to fluoride-containing products [84]. As a result, COF_2 is typically considered a short-lived intermediate, inferred indirectly through fluoride release and CO_2 evolution rather than observed experimentally under aqueous conditions.

As mentioned, high cost and difficulties in producing BDD electrodes with complex geometries limit large-scale deployment. Moreover, it has been reported that the surface fluorination of BDD due to bonding with F^- ions in the solution can hinder electrocatalytic activity [46].

Metal oxide anodes, particularly SnO_2 and PbO_2 , have been investigated as lower-cost alternatives to BDD for PFASs degradation, often requiring doping to enhance conductivity and stability [74,85]. Sb-doped and F-doped SnO_2 are among the most studied modifications: Sb improves conductivity but raises concerns of toxicity, while F-doping increases stability and durability. For instance, $\text{Ti}/\text{SnO}_2\text{-F}$ electrodes achieved >99% PFOA removal in 30 min at $20 \text{ mA}/\text{cm}^2$. Fluoride is considered an ideal dopant because its ionic radius (0.133 nm) closely matches that of O^{2-} (0.132 nm), favouring coherent crystal growth [74]. $\text{Ti}/\text{SnO}_2\text{-Sb}$ electrodes also demonstrated high efficiency, with 90.3% PFOA removal in 90 min [79]. Additionally, Ti_4O_7 electrodes loaded with amorphous Pd clusters ($\text{Ti}_4\text{O}_7/\text{Pd-A}$) effectively degraded PFOA, outperforming bare or crystalline Pd-loaded Ti_4O_7 . In this case, surface fluorination was found to inhibit $\bullet\text{OH}$ formation [77]. Therefore, an oxidation mechanism totally electrocatalytically driven was proposed (Figure 5). According to Huang et al. (2020) [77], after the usual formation of $\text{C}_6\text{F}_{13}\bullet$, this radical is anodically oxidized to $\text{C}_6\text{F}_{13}\text{C}^{(+)}\text{F}_2$ (2), which is unstable for the high electronegativity of F, and so rapidly binds to H_2O to form perfluoroheptyl alcohol $\text{C}_6\text{F}_{13}\text{OH}$ (3). The $-\text{OH}$ group reacts with the anode, transferring an electron to it for the formation of $\text{C}_6\text{F}_{13}\text{COF}$ (4).

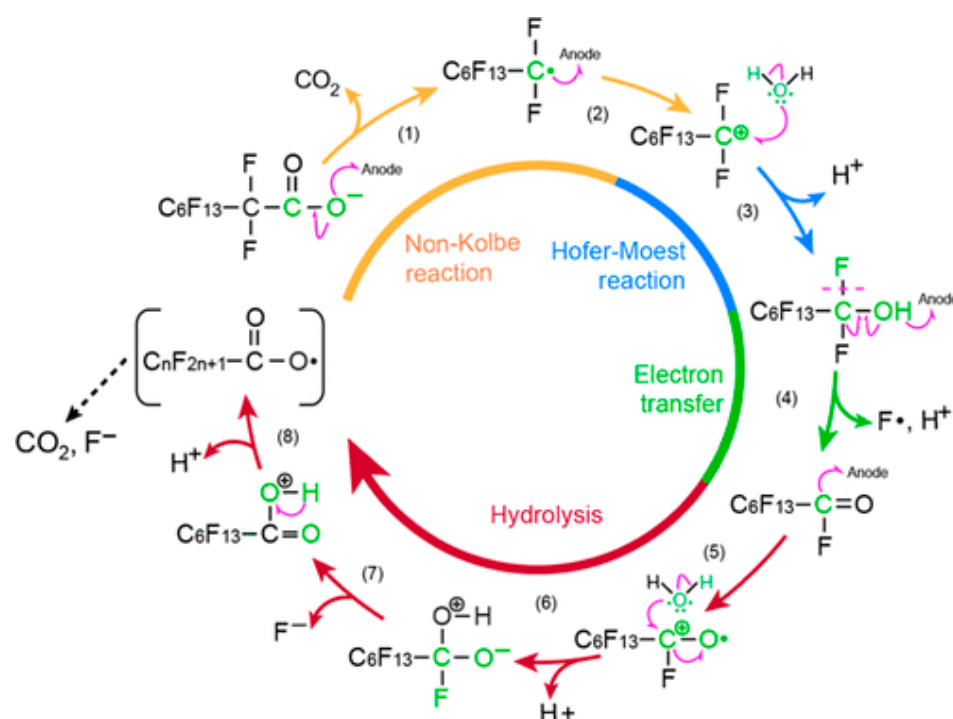


Figure 5. Possible pathway for the degradation of PFOA by Pd-loaded Ti_4O_7 electrode. Reprinted with permission from [77] Copyright @ 2020 American Chemical Society.

Again, the intermediate $\text{C}_6\text{F}_{13}\text{C}^+\text{FO}\bullet$ participates in an electron-transfer step: the strong polarization of the carbonyl makes the carbon centre strongly electrophilic (5), promoting nucleophilic attack by H_2O , which donates electron density and forms a short-

lived C–O–bound intermediate (6). At the same time, the hydrogen atom transfers its electron to the oxygen bearing the unpaired electron (7). This negatively charged oxygen subsequently restores the C=O bond, while the C–F bond electrons shift to fluorine, which is released as F[−] (8). A final deprotonation step yields the short-chain perfluorinated carboxyl radical C₆F₁₃COO• (9).

3. Evaluation of Energy Efficiency Across Photocatalytic and Electrochemical Treatments

To enable a consistent comparison of the energetic performance of the different systems reported in the literature, the electric energy consumption associated with the photodegradation of PFOA was evaluated. Specifically, the energy demand (E_{EO}) required to achieve 90% removal of the contaminant in a unit volume m³ of water was estimated using the correlation proposed by Bolton et al. [86], which allows normalization of experimental data obtained under diverse operational conditions. This parameter provides a useful metric for assessing the efficiency of electric energy-driven degradation processes, facilitating a more objective evaluation of their practical feasibility and sustainability. The following section applies this approach to analyze and compare the energetic requirements reported across selected studies.

$$E_{EO} = \frac{Pt_{90\%} \cdot 1000}{V \cdot 60 \cdot \ln \frac{C(t_0)}{C(t)}}, \quad (4)$$

In this equation, *P* indicates the nominal power applied by the system (kW), *t*_{90%} corresponds to the irradiation time necessary to reach 90% degradation of the contaminant (min), *V* refers to the total volume of solution treated (L), *C*(*t*₀) is the initial concentration of the pollutant (ppm), and *C*(*t*) represents the concentration measured after irradiation time *t*.

The calculated E_{EO} values for UV-irradiated systems are summarized in Table 3. It should be noted that, although some studies report irradiance values (e.g., mW·cm^{−2}), the effective radiation reaching the reaction medium strongly depends on reactor configuration, optical path length, lamp positioning, and solution properties. Therefore, in order to ensure consistency and comparability across different studies, the calculation of energy consumption in this review is based on the nominal electrical power of the light source, following the standard E_{EO} methodology.

Table 3. Energy efficiency of various UV-light-driven photocatalytic systems for PFOA degradation.

Photocatalyst	Electrical Power [W]	Volume [L]	<i>t</i> _{90%} [min]	E _{EO} [kWh m ^{−3}]
BiOCl	32	0.05	24.8	114.7
In ₂ O ₃ microspheres	15	0.1	17.4	18.9
Indium-modified Ga ₂ O ₃	200	0.03	55.7	2688.2
MnOx-modified In ₂ O ₃	500	0.05	5.9	426.0
(2%)Pb-TiO ₂	400	1.1	40	105.3
needle-like Ga ₂ O ₃	14	0.15	60.6	40.9

In₂O₃ microspheres exhibit the lowest E_{EO} (18.9 kWh m^{−3}), confirming the excellent energy efficiency of indium oxide-based photocatalysts for PFOA degradation under UV irradiation. In the related study, this high photocatalytic activity was achieved using

a low-pressure mercury lamp (15 W) emitting at 254 nm, positioned at the centre of a tubular quartz reactor [42]. Similarly, needle-like Ga_2O_3 , tested with a 14 W lamp, showed a competitive E_{EO} of 40.9 kWh m^{-3} . The authors compared two lamps with identical electrical power: one emitting only 254 nm UV light and the other combining 254 nm UV and 185 nm vacuum UV (VUV) irradiation. The system exposed to VUV light achieved a higher decomposition rate, attributed to the enhanced generation of reactive species from direct water photolysis [52]. The Pb– TiO_2 system, employing a 400 W UV lamp (254 nm), treats the largest volume (1.1 L) while retaining a satisfactory E_{EO} (105.3 kWh m^{-3}). However, the presence of Pb element in the catalyst composition raises environmental concerns regarding its potential secondary toxicity [49]. The MnO_x – In_2O_3 composite achieved the shortest irradiation time reported in the literature (at pH 3), but, given the small treated volume and high lamp power (500 W), its E_{EO} is comparatively higher (426.0 kWh m^{-3}) [48]. However, the application of solar irradiation represents a key step toward more sustainable photocatalytic processes. The lower photon flux and broader spectral distribution of sunlight typically lead to higher E_{EO} values compared to UV-driven systems.

The calculated E_{EO} values for solar systems are summarized in Table 4.

Table 4. Energy efficiency of various simulated solar light-driven photocatalytic systems for PFOA degradation.

Photocatalyst	Electrical Power [W]	Volume [L]	$t_{90\%}$ [min]	E_{EO} [kWh m^{-3}]
MnO _x -Modified In ₂ O ₃	500	0.05	97.4	7052.2
Bismuth oxyiodide	700	0.01	81.3	41,176.5
BiOI/ZnO 4:1	500	0.1	20	723.8
Fe-BTC/BiOCl	5	0.05	15.9	11.5

The data in Table 4 reveal that Bi-based photocatalysts perform particularly well under solar irradiation, with respect to other photocatalysts, due to their suitable bandgap alignment with the visible range. In particular, Fe-BTC/BiOCl, a bifunctional heterogeneous photocatalyst combining an iron-based metal–organic framework (MOF) with bismuth oxychloride, demonstrates a noteworthy energy efficiency value ($E_{\text{EO}} = 11.5 \text{ kWh m}^{-3}$). This material is designed to integrate reductive and oxidative mechanisms: Fe-BTC enhances electron transfer and pollutant adsorption, while BiOCl facilitates visible-light absorption and charge carrier separation. Upon irradiation, CB electrons from BiOCl generate hydrated electrons (e_{aq}^-) and hydrogen atoms ($\text{H}\bullet$), both strong reducing species capable of initiating defluorination by C–F bond scission. Simultaneously, VB holes and reduced oxygen species ($\bullet\text{O}_2^-$, $\bullet\text{OH}$) promote oxidation and mineralization of the degradation intermediates [60]. Moreover, MnO_x – In_2O_3 catalyst previously tested under UV was also evaluated under simulated sunlight using a lamp of the same nominal power (500 W). In this case, the E_{EO} increased from 426.0 to 7052.2 kWh m^{-3} , corresponding to a 16.6-fold rise in energy demand. This result highlights how differences in spectral distribution and photon flux density can dramatically influence energetic efficiency, even when electrical power remains constant [48].

The energy efficiency of electro-oxidation processes strongly depends on the anodic material and the reactor configuration. Most of the studies reported electric current density or potential as the main parameter related to energy consumption; therefore, the most promising systems are compared on this basis in Table 5. Moreover, charge demand per degraded mole of PFAS amount (F mol^{-1} PFAS) was included as an additional comparative

parameter. Estimated values were derived from reported current density, electrode area, treatment time and degradation efficiencies, when sufficient information was available.

Table 5. Electric current density of various electrochemical systems for PFASs degradation.

Anode	Pollutant	Current Density or Applied Potential	Time	Deg. Eff.	Charge [F mol ⁻¹ PFAS]	Ref.
Graphite Intercalated Compound (Ads. + EO)	PFOS PFOA PFBS	28 mA/cm ² 25 mA/cm ² 43 mA/cm ²		100% 98% 17%	-	[70]
BDD	PFOA PFBA GenX 6:2 FTCA	10 mA·cm ⁻²	2 h	97.9% 65.6% 84.9% 99.4%	1042 803.5 1007 1061	[71]
BDD/SnO ₂ -F	F-53B	30 mA/cm ²		95.6%	150.3	[72]
Ti/Sn-Sb/SnO ₂ -F-Sb multilayer	PFOS	20 mA/cm ²		>99%	37.40	[73]
Ti/SnO ₂ -F	PFOA	20 mA·cm ⁻²	0.5 h	99.6%	7.760	[74]
Porous tubular Ti ₄ O ₇ (REM)	PFOS	4 mA·cm ⁻²	100 min	99.1%	31,790	[75]
Porous Ti ₄ O ₇	PFOA/PFOS	5 mA·cm ⁻²	3 h	>99.9% 93.1%	280.2 1503	[76]
Ti ₄ O ₇ doped with amorphous Pd	PFOA	10 mA/cm ²		>90%	2861	[77]
Si/BDD	Short-chain (C3-C6) and long-chain (C7-C18) PFCA _s	25 mA·cm ⁻²	1 h	Long-chain (C10-C18): 95% C3: 39% C4: 41% C5: 66% C6: 70%	-	[78]
Ti/SnO ₂ -Sb/PbO ₂	PFOA	10 mA·cm ⁻²	1.5 h	91.1%	1526	[79]
Ti ₄ O ₇ (REM)	PFOA PFOS	3.3 V 3.6 V		PFOA/PFOS: ~5-log removal >99.9%	-	[80]
CeO ₂	PFOA	1.4 V		94%	-	[81]
Ti ₄ O ₇	PFOA PFOS	13 mA·cm ⁻²		92% 100%	81,865 90,970	[82]
BDD (for persulfate activation)	PFOA PFOS	40 mA·cm ⁻²		100% 100%	7165 7166	[83]

However, several studies reported the E_{EO} parameter across different electrochemical oxidation systems. Among the systems, reactive electrochemical membranes (REMs) based on Magnéli-phase titanium suboxides consistently demonstrate the lowest specific energy consumption. For instance, the Ti₄O₇ REM anode achieved E_{EO} values of 5.1 and 6.7 kWh m⁻³ for the removal of PFOA and PFOS, respectively [80]. Moreover, Zeidabadi et al. (2024) [71] reported an E_{EO} of 20.1 kWh m⁻³ for degradation of PFOA by using a commercial boron-doped diamond (BDD) anode [71], while in pilot-scale BDD systems treating real contaminated matrices exhibited energy consumptions of 160 kWh m⁻³ in groundwater and 240 kWh m⁻³ in landfill leachate [87]. The difference in energy efficiency can be attributed to the simplified composition of most laboratory-scale solutions, where the absence of competing species often leads to an overestimation of treatment efficiency. In contrast, natural organic matter, scavenging compounds, and inorganic salts contained in real matrices can quench reactive species. As a consequence, achieving comparable degradation levels in such complex systems requires a higher total energy density, obtained by increasing either current intensity or treatment duration. These results still demonstrate the practical robustness of BDD in complex matrices [87].

When different anodic materials were compared in simulating slow-flow aquifer systems, the Magnéli-phase $\text{Ti}_n\text{O}_{2n-1}$ anode again showed superior energetic performance, with an E_{EO} of 4000 kWh m^{-3} , compared to 4500 kWh m^{-3} for mixed $\text{IrO}_2\text{--Ta}_2\text{O}_5$ oxides and 9600 kWh m^{-3} for ultrananocrystalline BDD. These values, two orders of magnitude higher than those obtained in high-flow electrochemical reactors, underscore the strong influence of mass-transfer kinetics [88]. Other electrode materials, such as PbO_2 or SnO_2 -based anodes, exhibited moderate energy requirements: 53.6 kWh m^{-3} and 71.6 kWh m^{-3} , respectively, when tested for the degradation of perfluorononanoic acid (PFNA); 76.6 kWh m^{-3} and 105.5 kWh m^{-3} when tested for perfluorodecanoic acid (PFDA). Moreover, to assess the safety of the treated effluents after 3 h of electrolysis, the concentration of potentially toxic metal ions released from the electrodes was compared with drinking water quality standards. For the PbO_2 anode, the dissolved Pb concentrations after the treatment of PFNA and PFDA were 0.005 and 0.004 mg L^{-1} , respectively (below the U.S. EPA drinking water limit of 0.01 mg L^{-1}). In the case of the SnO_2 electrode, the concentrations of dissolved Sn ions were 0.59 and 0.43 mg L^{-1} , levels considered non-toxic due to the low inherent toxicity of inorganic tin. However, the release of Sb ions (0.09 and 0.07 mg L^{-1} for PFNA and PFDA) suggests potential concerns, as antimony is more toxic and may pose a risk to water quality if leaching is not controlled [89].

4. Concluding Remarks

The persistence, bioaccumulation, and toxicity of per- and polyfluoroalkyl substances (PFASs) make their removal from aquatic environments one of the most critical environmental issues of contemporary water research. Conventional physical and biological treatments remain largely ineffective in achieving full mineralisation of these compounds, highlighting the need for advanced, energy-efficient, and environmentally sustainable degradation strategies.

Among these, advanced oxidation processes (AOPs) have shown the greatest promise, particularly those based on heterogeneous photocatalysis and electrochemical oxidation, which represent the most actively explored technologies for PFAS destruction. Photocatalytic systems based on In_2O_3 , Bi-based oxyhalides, and Ga_2O_3 achieve outstanding degradation efficiencies under UV irradiation while maintaining relatively low energy demand in optimized systems. Nevertheless, their photocatalytic activity under solar irradiation remains limited due to the lower photon flux and inadequate bandgap alignment with visible light, which lead to increased energy consumption. Recent developments in heterojunction and metal–organic framework (MOF)-based photocatalysts, such as Fe-BTC/ BiOCl , demonstrate that integrating oxidative and reductive reaction pathways can significantly improve both defluorination and mineralisation, paving the way for efficient solar-driven systems.

Electrochemical oxidation has also emerged as a powerful and comparatively energy-efficient process, with Ti_4O_7 -based reactive electrochemical membranes exhibiting remarkably low specific energy consumption (E_{EO} values as low as $5\text{--}7 \text{ kWh}\cdot\text{m}^{-3}$). Boron-doped diamond (BDD) anodes, while offering excellent stability and strong mineralisation capabilities, are still constrained by their high manufacturing cost and increased energy demand when treating complex real-world matrices. The overall energy efficiency of electrochemical systems is style strongly dependent on reactor configuration and key operational parameters, including current density, electrolyte composition, and pH. Optimal performance for both photocatalytic and electrochemical processes is often achieved under mildly acidic conditions, which enhance radical generation and pollutant adsorption. However, most laboratory-scale investigations employ simplified synthetic matrices containing PFOA at concentrations far higher than those encountered in real waters. In

natural systems, the presence of dissolved organic matter and inorganic ions can act as radical scavengers, hinder PFAS adsorption onto catalyst surfaces, and thereby reduce overall degradation efficiency. Consequently, future research should expand towards more representative studies involving complex environmental matrices and different PFAS subclasses, including short- and ultra-short-chain compounds such as PFBA, which are more persistent and widespread. Moreover, the identification and toxicity assessment of degradation intermediates, particularly fluoride ions, must be prioritized to ensure safe and complete remediation.

Future efforts should focus on the design of photocatalysts with enhanced durability, recoverability, and scalability; for example, through immobilization on macroscopic supports that facilitate reuse and integration into continuous-flow systems. In parallel, advances in anode engineering are essential to maximize the generation of reactive oxygen species (ROS) and improve charge and mass transfer efficiency. The integration of photocatalysis with electrochemical oxidation, or their coupling with adsorption-based pre-concentration steps, can further lower energy consumption and enhance process selectivity.

Ultimately, systematic assessments on real wastewater samples are required to evaluate the true sustainability and scalability of PFAS degradation technologies. Comprehensive analyses of energy balance, electrode and catalyst stability, and the potential formation of toxic by-products are essential to guide the transition from laboratory-scale studies to full-scale, field-applicable remediation systems.

In this context, despite the significant progress achieved in PFAS degradation, a substantial number of studies still focus primarily on pollutant conversion, without fully elucidating the final fate of fluorine atoms. This represents a critical knowledge gap, as conversion alone does not necessarily imply detoxification. A thorough characterization of degradation products is therefore crucial to properly assess environmental risks, particularly with respect to transient but potentially hazardous intermediates.

Although fluoride release is widely used as an indicator of defluorination, it provides only partial information on transformation pathways and intermediate species. In this regard, advanced analytical techniques such as ^{19}F nuclear magnetic resonance (^{19}F NMR) have recently demonstrated strong potential for tracking fluorine-containing intermediates and end products in complex systems, as highlighted by recent high-impact studies [90,91]. The broader application of such techniques to catalytic PFAS degradation systems would substantially enhance mechanistic understanding and enable a more reliable evaluation of process safety and long-term sustainability.

Author Contributions: Conceptualization, A.M., O.S. and V.V. (Vincenzo Vaiano); resources, V.V. (Vincenzo Vaiano); writing—original draft preparation, V.V. (Vincenzo Vietri); writing—review and editing, A.M., O.S. and V.V. (Vincenzo Vaiano); visualization, A.M. and V.V. (Vincenzo Vietri); supervision, V.V. (Vincenzo Vaiano). All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Acknowledgments: During the preparation of this manuscript, the authors used ChatGPT 5.1 for English language editing. The authors have reviewed and edited the output and take full responsibility for the content of this publication.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

PFAS	Per and polyalkyl substances
WWTP	Wastewater treatment plants
PFOS	Perfluorooctanesulfonic acid
PFOA	Perfluorooctanoic acid
TFA	Trifluoroacetic acid
PFBS	Perfluorobutanesulfonic acid
EPA	Environmental Protection Agency
MCL	Maximum Contaminants Levels
PFNA	Perfluoronanoic acid
PFHxS	Perfluorohexane sulfonic acid
PFHxA	Perfluorohexanoic acid
HFPO-DA	Hexafluoropropylene Oxide Dimer Acid
POP	Persistent Organic Pollutants
AOP	Advanced Oxidation Processes
NF	Nanofiltration
RO	Reverse Osmosis
VB	Valence band
CB	Conduction band
rGO	Reduced Graphene Oxide
TNT	Titanium Nanotubes
MOF	Metal–Organic Framework
TOC	Total Organic Carbon
EO	Electro-Oxidation
BDD	Boron-Doped Diamond
FTCA	Fluorotelomer Carboxylic Acids
REM	Reactive Electrochemical Membrane

References

1. Sunderland, E.M.; Hu, X.C.; Dassuncao, C.; Tokranov, A.K.; Wagner, C.C.; Allen, J.G. A review of the pathways of human exposure to poly-and perfluoroalkyl substances (PFASs) and present understanding of health effects. *J. Expo. Sci. Environ. Epidemiol.* **2019**, *29*, 131–147. [[CrossRef](#)] [[PubMed](#)]
2. Dong, C.; Huang, F.; Deng, H.; Schaffrath, C.; Spencer, J.B.; O'hagan, D.; Naismith, J.H. Crystal structure and mechanism of a bacterial fluorinating enzyme. *Nature* **2004**, *427*, 561–565. [[CrossRef](#)]
3. Kurwadkar, S.; Dane, J.; Kanel, S.R.; Nadagouda, M.N.; Cawdrey, R.W.; Ambade, B.; Struckhoff, G.C.; Wilkin, R. Per-and polyfluoroalkyl substances in water and wastewater: A critical review of their global occurrence and distribution. *Sci. Total Environ.* **2022**, *809*, 151003.
4. Verma, S.; Mezgebe, B.; Hejase, C.A.; Sahle-Demessie, E.; Nadagouda, M.N. Photodegradation and photocatalysis of per-and polyfluoroalkyl substances (PFAS): A review of recent progress. *Next Mater.* **2024**, *2*, 100077.
5. Glüge, J.; Scheringer, M.; Cousins, I.T.; DeWitt, J.C.; Goldenman, G.; Herzke, D.; Lohmann, R.; Ng, C.A.; Trier, X.; Wang, Z. An overview of the uses of per-and polyfluoroalkyl substances (PFAS). *Environ. Sci. Process. Impacts* **2020**, *22*, 2345–2373.
6. Xu, B.; Ahmed, M.B.; Zhou, J.L.; Altaee, A.; Wu, M.; Xu, G. Photocatalytic removal of perfluoroalkyl substances from water and wastewater: Mechanism, kinetics and controlling factors. *Chemosphere* **2017**, *189*, 717–729. [[CrossRef](#)]
7. Lenka, S.P.; Kah, M.; Padhye, L.P. A review of the occurrence, transformation, and removal of poly-and perfluoroalkyl substances (PFAS) in wastewater treatment plants. *Water Res.* **2021**, *199*, 117187.
8. Wang, X.; Halsall, C.; Codling, G.; Xie, Z.; Xu, B.; Zhao, Z.; Xue, Y.; Ebinghaus, R.; Jones, K.C. Accumulation of perfluoroalkyl compounds in tibetan mountain snow: Temporal patterns from 1980 to 2010. *Environ. Sci. Technol.* **2014**, *48*, 173–181. [[CrossRef](#)]
9. Young, C.J.; Furdui, V.I.; Franklin, J.; Koerner, R.M.; Muir, D.C.; Mabury, S.A. Perfluorinated acids in arctic snow: New evidence for atmospheric formation. *Environ. Sci. Technol.* **2007**, *41*, 3455–3461. [[CrossRef](#)] [[PubMed](#)]
10. Banks, D.; Jun, B.-M.; Heo, J.; Her, N.; Park, C.M.; Yoon, Y. Selected advanced water treatment technologies for perfluoroalkyl and polyfluoroalkyl substances: A review. *Sep. Purif. Technol.* **2020**, *231*, 115929. [[CrossRef](#)]

11. Kunacheva, C.; Fujii, S.; Tanaka, S.; Seneviratne, S.; Lien, N.P.H.; Nozoe, M.; Kimura, K.; Shivakoti, B.R.; Harada, H. Worldwide surveys of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in water environment in recent years. *Water Sci. Technol.* **2012**, *66*, 2764–2771. [CrossRef]
12. McLachlan, M.S.; Holmström, K.E.; Reth, M.; Berger, U. Riverine discharge of perfluorinated carboxylates from the European continent. *Environ. Sci. Technol.* **2007**, *41*, 7260–7265. [CrossRef]
13. Domingo, J.L.; Nadal, M. Human exposure to per-and polyfluoroalkyl substances (PFAS) through drinking water: A review of the recent scientific literature. *Environ. Res.* **2019**, *177*, 108648. [PubMed]
14. Castiglioni, S.; Valsecchi, S.; Polesello, S.; Rusconi, M.; Melis, M.; Palmiotto, M.; Manenti, A.; Davoli, E.; Zuccato, E. Sources and fate of perfluorinated compounds in the aqueous environment and in drinking water of a highly urbanized and industrialized area in Italy. *J. Hazard. Mater.* **2015**, *282*, 51–60. [CrossRef]
15. Italia, G. Acque Senza Veleni. Available online: https://www.greenpeace.org/static/planet4-italy-stateless/2025/01/4bbb41f2-report_def_a_s_v_2025-1.pdf (accessed on 28 November 2025).
16. Italy, G. Investigation of Per- and Polyfluorinated Alkyl Substances (PFAS), Especially Tetrafluoroacetate (TFA) in Italian Bottled Mineral Water. Available online: https://www.greenpeace.org/static/planet4-italy-stateless/2025/10/1517fe65-20250805_gpitt_bottledwater_en_final_a_2.pdf (accessed on 28 November 2025).
17. Paul Guin, J.; Sullivan, J.A.; Thampi, K.R. Challenges facing sustainable visible light induced degradation of poly-and perfluoroalkyls (PFA) in water: A critical review. *ACS Eng. Au* **2022**, *2*, 134–150.
18. Cao, C.-S.; Wang, J.; Yang, L.; Wang, J.; Zhang, Y.; Zhu, L. A review on the advancement in photocatalytic degradation of poly/perfluoroalkyl substances in water: Insights into the mechanisms and structure-function relationship. *Sci. Total Environ.* **2024**, *946*, 174137.
19. Ahrens, L. Polyfluoroalkyl compounds in the aquatic environment: A review of their occurrence and fate. *J. Environ. Monit.* **2011**, *13*, 20–31. [CrossRef] [PubMed]
20. Leonello, D.; Fendrich, M.A.; Parrino, F.; Patel, N.; Orlandi, M.; Miotello, A. Light-induced advanced oxidation processes as pfas remediation methods: A review. *Appl. Sci.* **2021**, *11*, 8458. [CrossRef]
21. Meegoda, J.N.; Bezerra de Souza, B.; Casarini, M.M.; Kewalramani, J.A. A review of PFAS destruction technologies. *Int. J. Environ. Res. Public Health* **2022**, *19*, 16397. [CrossRef]
22. Matesun, J.; Petrik, L.; Musvoto, E.; Ayinde, W.; Ikumi, D. Limitations of wastewater treatment plants in removing trace anthropogenic biomarkers and future directions: A review. *Ecotoxicol. Environ. Saf.* **2024**, *281*, 116610. [CrossRef]
23. Ata, R.; Merdan, G.F.; Töre, G.Y. Activated sludge process for refractory pollutants removal. In *Removal of Refractory Pollutants from Wastewater Treatment Plants*; CRC Press: Boca Raton, FL, USA, 2021; pp. 137–184.
24. Łukasiewicz, E. Coagulation–Sedimentation in Water and Wastewater Treatment: Removal of Pesticides, Pharmaceuticals, PFAS, Microplastics, and Natural Organic Matter. *Water* **2025**, *17*, 3048. [CrossRef]
25. Ogbey, G.O.; Ogunlela, A.O.; Akinbile, C.O.; Iwar, R.T. Adsorption of organic micropollutants in water: A review of advances in modelling, mechanisms, adsorbents, and their characteristics. *Environ. Eng. Res.* **2025**, *30*, 230733.
26. De Almeida, R.; Porto, R.F.; Quintaes, B.R.; Bila, D.M.; Lavagnolo, M.C.; Campos, J.C. A review on membrane concentrate management from landfill leachate treatment plants: The relevance of resource recovery to close the leachate treatment loop. *Waste Manag. Res.* **2023**, *41*, 264–284. [CrossRef] [PubMed]
27. Chen, X.; Yuan, T.; Yang, X.; Ding, S.; Ma, M. Insights into photo/electrocatalysts for the degradation of per-and polyfluoroalkyl substances (PFAS) by advanced oxidation processes. *Catalysts* **2023**, *13*, 1308.
28. Cardoso, I.M.; Pinto da Silva, L.; Esteves da Silva, J.C. Nanomaterial-based advanced oxidation/reduction processes for the degradation of PFAS. *Nanomaterials* **2023**, *13*, 1668.
29. Rajesh Banu, J.; Merrylin, J.; Kavitha, S.; Yukesh Kannah, R.; Selvakumar, P.; Gopikumar, S.; Sivashanmugam, P.; Do, K.-U.; Kumar, G. Trends in biological nutrient removal for the treatment of low strength organic wastewaters. *Curr. Pollut. Rep.* **2021**, *7*, 1–30. [CrossRef]
30. Raj, C.C.; Quen, H.L. Advanced oxidation processes for wastewater treatment: Optimization of UV/H₂O₂ process through a statistical technique. *Chem. Eng. Sci.* **2005**, *60*, 5305–5311.
31. Rodríguez, J.; Mutis, A.; Yeber, M.; Freer, J.; Baeza, J.; Mansilla, H. Chemical degradation of EDTA and DTPA in a totally chlorine free (TCF) effluent. *Water Sci. Technol.* **1999**, *40*, 267–272.
32. Wang, B.; Yang, C.; Zhong, J.; Li, J.; Zhu, Y.; Miao, J. Photocatalytic properties of visible light-responsive rGO/BiOCl photocatalysts benefited from enriched oxygen vacancies. *Solid State Sci.* **2023**, *138*, 107155.
33. Gulumian, M.; Andraos, C.; Afantitis, A.; Puzyn, T.; Coville, N.J. Importance of surface topography in both biological activity and catalysis of nanomaterials: Can catalysis by design guide safe by design? *Int. J. Mol. Sci.* **2021**, *22*, 8347. [CrossRef]
34. Narayanan, R.; El-Sayed, M.A. Shape-dependent catalytic activity of platinum nanoparticles in colloidal solution. *Nano Lett.* **2004**, *4*, 1343–1348. [CrossRef]

35. Chen, A.; Ji, H.; Xu, Z.; Wang, Z.; Xie, H.; Zhang, L. Unique S-scheme structures in electrostatic self-assembled ReS₂-TiO₂ for high-efficiency perfluorooctanoic acid removal. *J. Colloid Interface Sci.* **2025**, *681*, 63–70. [\[CrossRef\]](#)
36. Do, H.T.; Phan Thi, L.A.; Dao Nguyen, N.H.; Huang, C.W.; Le, Q.V.; Nguyen, V.H. Tailoring photocatalysts and elucidating mechanisms of photocatalytic degradation of perfluorocarboxylic acids (PFCAs) in water: A comparative overview. *J. Chem. Technol. Biotechnol.* **2020**, *95*, 2569–2578. [\[CrossRef\]](#)
37. Hojamberdiev, M.; Larralde, A.L.; Vargas, R.; Madriz, L.; Yubuta, K.; Sannegowda, L.K.; Sadok, I.; Krzyszczyk-Turczyn, A.; Oleszczuk, P.; Czech, B. Unlocking the effect of Zn²⁺ on crystal structure, optical properties, and photocatalytic degradation of perfluoroalkyl substances (PFAS) of Bi₂WO₆. *Environ. Sci. Water Res. Technol.* **2023**, *9*, 2866–2879.
38. Qanbarzadeh, M.; Wang, D.; Ateia, M.; Sahu, S.P.; Cates, E.L. Impacts of reactor configuration, degradation mechanisms, and water matrices on perfluorocarboxylic acid treatment efficiency by the UV/Bi₃O(OH)(PO₄)₂ photocatalytic process. *ACS EST Eng.* **2020**, *1*, 239–248. [\[CrossRef\]](#)
39. Nabi, I.; Fu, Z.; Li, K.; Cheng, H.; Zhang, L. A comparative study of bismuth-based photocatalysts with titanium dioxide for perfluorooctanoic acid degradation. *Chin. Chem. Lett.* **2019**, *30*, 2225–2230. [\[CrossRef\]](#)
40. Xu, T.; Ji, H.; Gu, Y.; Tong, T.; Xia, Y.; Zhang, L.; Zhao, D. Enhanced adsorption and photocatalytic degradation of perfluorooctanoic acid in water using iron (hydr) oxides/carbon sphere composite. *Chem. Eng. J.* **2020**, *388*, 124230.
41. Li, T.; Wang, C.; Wang, T.; Zhu, L. Highly efficient photocatalytic degradation toward perfluorooctanoic acid by bromine doped BiOI with high exposure of (001) facet. *Appl. Catal. B Environ.* **2020**, *268*, 118442.
42. Li, Z.; Zhang, P.; Shao, T.; Wang, J.; Jin, L.; Li, X. Different nanostructured In₂O₃ for photocatalytic decomposition of perfluorooctanoic acid (PFOA). *J. Hazard. Mater.* **2013**, *260*, 40–46. [\[CrossRef\]](#)
43. Tan, X.; Chen, G.; Xing, D.; Ding, W.; Liu, H.; Li, T.; Huang, Y. Indium-modified Ga₂O₃ hierarchical nanosheets as efficient photocatalysts for the degradation of perfluorooctanoic acid. *Environ. Sci. Nano* **2020**, *7*, 2229–2239. [\[CrossRef\]](#)
44. Xia, C.; Lim, X.; Yang, H.; Goodson, B.M.; Liu, J. Degradation of per- and polyfluoroalkyl substances (PFAS) in wastewater effluents by photocatalysis for water reuse. *J. Water Process Eng.* **2022**, *46*, 102556.
45. Wang, L.; Sun, L.; Yu, Z.; Hou, Y.; Peng, Z.; Yang, F.; Chen, Y.; Huang, J. Synergetic decomposition performance and mechanism of perfluorooctanoic acid in dielectric barrier discharge plasma system with Fe₃O₄@SiO₂-BiOBr magnetic photocatalyst. *Mol. Catal.* **2017**, *441*, 179–189.
46. Wang, J.; Cao, C.-S.; Wang, J.; Zhang, Y.; Zhu, L. Insights into highly efficient photodegradation of poly/perfluoroalkyl substances by In-MOF/BiOF heterojunctions: Built-in electric field and strong surface adsorption. *Appl. Catal. B Environ.* **2022**, *304*, 121013.
47. Xu, C.; Qiu, P.; Chen, H.; Jiang, F. Platinum modified indium oxide nanorods with enhanced photocatalytic activity on degradation of perfluorooctanoic acid (PFOA). *J. Taiwan Inst. Chem. Eng.* **2017**, *80*, 761–768. [\[CrossRef\]](#)
48. Wu, Y.; Li, Y.; Fang, C.; Li, C. Highly efficient degradation of perfluorooctanoic acid over a MnOx-modified oxygen-vacancy-rich In₂O₃ photocatalyst. *ChemCatChem* **2019**, *11*, 2297–2303.
49. Chen, M.-J.; Lo, S.-L.; Lee, Y.-C.; Kuo, J.; Wu, C.-H. Decomposition of perfluorooctanoic acid by ultraviolet light irradiation with Pb-modified titanium dioxide. *J. Hazard. Mater.* **2016**, *303*, 111–118. [\[CrossRef\]](#) [\[PubMed\]](#)
50. Ong, C.B.; Mohammad, A.W.; Ng, L.Y.; Mahmoudi, E.; Azizkhani, S.; Hairom, N.H.H. Solar photocatalytic and surface enhancement of ZnO/rGO nanocomposite: Degradation of perfluorooctanoic acid and dye. *Process Saf. Environ. Prot.* **2017**, *112*, 298–307.
51. Guin, J.P.; Sullivan, J.A.; Muldoon, J.; Thampi, K.R. Visible light induced degradation of perfluorooctanoic acid using iodine deficient bismuth oxyiodide photocatalyst. *J. Hazard. Mater.* **2023**, *458*, 131897. [\[CrossRef\]](#)
52. Shao, T.; Zhang, P.; Li, Z.; Jin, L. Photocatalytic decomposition of perfluorooctanoic acid in pure water and wastewater by needle-like nanostructured gallium oxide. *Chin. J. Catal.* **2013**, *34*, 1551–1559. [\[CrossRef\]](#)
53. Wu, J.; Si, C.; Zhong, L.; Duan, X.; Zhang, D.; Xu, W. Enhanced photocatalytic degradation of perfluorooctanoic acid using BiOCl@PMoV-X heterojunction photocatalyst coupled with persulfate activation. *J. Water Process Eng.* **2025**, *69*, 106791.
54. Wang, Z.; Li, M.; Cao, W.; Liu, Z.; Kong, D.; Jiang, W. Efficient photocatalytic degradation of perfluorooctanoic acid by bismuth nanoparticle modified titanium dioxide. *Sci. Total Environ.* **2024**, *927*, 172028.
55. Zhang, K.; Li, C.; Xu, L.; He, Z.; Zhang, Z.; Ghumro, J.A.; Dong, K. MXene and its composites combined with photocatalytic degradation of Perfluorooctanoic acid: Efficiency and active species study. *Environ. Res.* **2025**, *278*, 121690. [\[CrossRef\]](#)
56. Barnor, B.; Eshun, A.; Prabakaran, E.; Adeiga, O.I.; Curtis, C.; Pillay, K. The investigations of photocatalytic degradation and defluorination of perfluorooctanoic acid using palm kernel shell activated carbon and Fe-Sn binary oxides nanocomposite under visible light irradiation. *Results Chem.* **2025**, *17*, 102607. [\[CrossRef\]](#)
57. Duan, L.; Gu, M.; Wang, M.; Liu, L.; Cheng, X.; Huang, J. Mechanism of Z-scheme BN/BiOI heterojunction for efficient photodegradation of perfluorooctane sulfonate (PFOS). *Sep. Purif. Technol.* **2025**, *360*, 131229.
58. Mazen, K.; Venkatesh, G.; Samara, F.; Kanan, S. ZnO/BiOI heterojunction catalyst: Efficient photocatalytic decomposition of perfluorooctanoic acid (PFOA) and mixed dye pollutants in wastewater. *Sep. Purif. Technol.* **2025**, *376*, 133953. [\[CrossRef\]](#)

59. Jiang, T.; Pervez, M.N.; Ilango, A.K.; Liang, Y. Enhanced removal and destruction of per- and polyfluoroalkyl substances (PFAS) mixtures by coupling magnetic modified clay and photoreductive degradation. *J. Water Process Eng.* **2025**, *69*, 106733.
60. Yan, C.; Zhong, Z.; Wang, J.; Feng, K.; Xing, D. Enhanced photocatalytic defluorination of perfluorooctanoic acid through integrated hydrogen atoms/electrons reduction and ROS oxidation with metal–organic framework heterogeneous catalysts. *Chem. Eng. J.* **2025**, *513*, 163058.
61. Hu, Z.; Li, H.; Yu, H. Study on the performance and mechanism of ap–n type $\text{In}_2\text{O}_3/\text{BiOCl}$ heterojunction prepared using a sacrificial MOF framework for the degradation of PFOA. *RSC Adv.* **2025**, *15*, 15029–15051. [[CrossRef](#)]
62. Li, X.; Zhang, P.; Jin, L.; Shao, T.; Li, Z.; Cao, J. Efficient photocatalytic decomposition of perfluorooctanoic acid by indium oxide and its mechanism. *Environ. Sci. Technol.* **2012**, *46*, 5528–5534. [[CrossRef](#)]
63. Castillo-Cabrera, G.X.; Espinoza-Montero, P.J.; Alulema-Pullupaxi, P.; Mora, J.R.; Villacís-García, M.H. Bismuth oxyhalide-based materials (BiOX : $\text{X} = \text{Cl}, \text{Br}, \text{I}$) and their application in photoelectrocatalytic degradation of organic pollutants in water: A review. *Front. Chem.* **2022**, *10*, 900622.
64. Martínez-Huitle, C.A.; Ferro, S. Electrochemical oxidation of organic pollutants for the wastewater treatment: Direct and indirect processes. *Chem. Soc. Rev.* **2006**, *35*, 1324–1340. [[CrossRef](#)]
65. Hossain, M.S.; Mollah, M.Y.A.; Susan, M.A.B.H.; Islam, M.M. Role of in situ electrogenerated reactive oxygen species towards degradation of organic dye in aqueous solution. *Electrochim. Acta* **2020**, *344*, 136146.
66. Moreira, F.C.; Boaventura, R.A.; Brillas, E.; Vilar, V.J. Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters. *Appl. Catal. B Environ.* **2017**, *202*, 217–261.
67. Chaplin, B.P. Critical review of electrochemical advanced oxidation processes for water treatment applications. *Environ. Sci. Process. Impacts* **2014**, *16*, 1182–1203. [[CrossRef](#)]
68. Wu, X.; Wang, H.; Wang, Y. A review: Synthesis and applications of titanium sub-oxides. *Materials* **2023**, *16*, 6874. [[CrossRef](#)]
69. Yang, Y.; Guan, Y.; Jain, A.; Meese, A.; Yan, Y.; Xu, X.; Kim, J.; Muhich, C. Photo-Electrochemical Reduction of PFAS in Complex Water Matrices. *Res. Sq.* **2025**. [[CrossRef](#)]
70. Trzcinski, A.P.; Harada, K.H. Comparison of perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and perfluorobutane sulfonate (PFBS) removal in a combined adsorption and electrochemical oxidation process. *Sci. Total Environ.* **2024**, *927*, 172184. [[PubMed](#)]
71. Zeidabadi, F.A.; Esfahani, E.B.; Moreira, R.; McBeath, S.T.; Foster, J.; Mohseni, M. Structural dependence of PFAS oxidation in a boron doped diamond-electrochemical system. *Environ. Res.* **2024**, *246*, 118103. [[CrossRef](#)] [[PubMed](#)]
72. Zhuo, Q.; Wang, J.; Niu, J.; Yang, B.; Yang, Y. Electrochemical oxidation of perfluorooctane sulfonate (PFOS) substitute by modified boron doped diamond (BDD) anodes. *Chem. Eng. J.* **2020**, *379*, 122280. [[CrossRef](#)]
73. Yang, B.; Wang, J.; Jiang, C.; Li, J.; Yu, G.; Deng, S.; Lu, S.; Zhang, P.; Zhu, C.; Zhuo, Q. Electrochemical mineralization of perfluorooctane sulfonate by novel F and Sb co-doped Ti/SnO_2 electrode containing Sn-Sb interlayer. *Chem. Eng. J.* **2017**, *316*, 296–304.
74. Yang, B.; Jiang, C.; Yu, G.; Zhuo, Q.; Deng, S.; Wu, J.; Zhang, H. Highly efficient electrochemical degradation of perfluorooctanoic acid (PFOA) by F-doped Ti/SnO_2 electrode. *J. Hazard. Mater.* **2015**, *299*, 417–424. [[CrossRef](#)]
75. Shi, H.; Wang, Y.; Li, C.; Pierce, R.; Gao, S.; Huang, Q. Degradation of perfluorooctanesulfonate by reactive electrochemical membrane composed of magneli phase titanium suboxide. *Environ. Sci. Technol.* **2019**, *53*, 14528–14537. [[CrossRef](#)]
76. Lin, H.; Niu, J.; Liang, S.; Wang, C.; Wang, Y.; Jin, F.; Luo, Q.; Huang, Q. Development of macroporous Magnéli phase Ti_4O_7 ceramic materials: As an efficient anode for mineralization of poly- and perfluoroalkyl substances. *Chem. Eng. J.* **2018**, *354*, 1058–1067. [[CrossRef](#)]
77. Huang, D.; Wang, K.; Niu, J.; Chu, C.; Weon, S.; Zhu, Q.; Lu, J.; Stavitski, E.; Kim, J.-H. Amorphous Pd-loaded Ti_4O_7 electrode for direct anodic destruction of perfluorooctanoic acid. *Environ. Sci. Technol.* **2020**, *54*, 10954–10963. [[CrossRef](#)] [[PubMed](#)]
78. Barisci, S.; Suri, R. Electrooxidation of short and long chain perfluorocarboxylic acids using boron doped diamond electrodes. *Chemosphere* **2020**, *243*, 125349. [[CrossRef](#)]
79. Lin, H.; Niu, J.; Ding, S.; Zhang, L. Electrochemical degradation of perfluorooctanoic acid (PFOA) by $\text{Ti}/\text{SnO}_2\text{--Sb}$, $\text{Ti}/\text{SnO}_2\text{--Sb}/\text{PbO}_2$ and $\text{Ti}/\text{SnO}_2\text{--Sb}/\text{MnO}_2$ anodes. *Water Res.* **2012**, *46*, 2281–2289. [[CrossRef](#)]
80. Le, T.X.H.; Haflich, H.; Shah, A.D.; Chaplin, B.P. Energy-efficient electrochemical oxidation of perfluoroalkyl substances using a Ti_4O_7 reactive electrochemical membrane anode. *Environ. Sci. Technol. Lett.* **2019**, *6*, 504–510. [[CrossRef](#)]
81. Liu, X.; Shu, Y.; Pan, Y.; Zeng, G.; Zhang, M.; Zhu, C.; Xu, Y.; Wan, A.; Wang, M.; Han, Q. Electrochemical destruction of PFAS at low oxidation potential enabled by CeO_2 electrodes utilizing adsorption and activation strategies. *J. Hazard. Mater.* **2025**, *486*, 137043. [[CrossRef](#)]
82. Gomri, C.; Makhoul, E.; Koundia, F.N.; Petit, E.; Raffy, S.; Bechelany, M.; Semsarilar, M.; Cretin, M. Electrochemical advanced oxidation combined to electro-Fenton for effective treatment of perfluoroalkyl substances “PFAS” in water using a Magnéli phase-based anode. *Nanoscale Adv.* **2025**, *7*, 261–268. [[CrossRef](#)] [[PubMed](#)]

83. Zhao, L.; Pu, R.; Deng, S.; Lin, L.; Mantzavinos, D.; Naidu, R.; Fang, C.; Lei, Y. Enhanced electrochemical degradation of per- and polyfluoroalkyl substances (PFAS) by activating persulfate on boron-doped diamond (BDD) anode. *Sep. Purif. Technol.* **2025**, *359*, 130459. [\[CrossRef\]](#)
84. Uchimaru, T.; Tsuzuki, S.; Sugie, M.; Tokuhashi, K.; Sekiya, A. Ab initio study of the hydrolysis of carbonyl difluoride (CF₂O): Importance of an additional water molecule. *Chem. Phys. Lett.* **2004**, *396*, 110–116. [\[CrossRef\]](#)
85. Li, G.; Peng, M.; Huang, Q.; Huang, C.-H.; Chen, Y.; Hawkins, G.; Li, K. A review on the recent mechanisms investigation of PFAS electrochemical oxidation degradation: Mechanisms, DFT calculation, and pathways. *Front. Environ. Eng.* **2025**, *4*, 1568542. [\[CrossRef\]](#)
86. Bolton, J.R.; Bircher, K.G.; Tumas, W.; Tolman, C.A. Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems (IUPAC Technical Report). *Pure Appl. Chem.* **2001**, *73*, 627–637. [\[CrossRef\]](#)
87. Smith, S.J.; Lauria, M.; Ahrens, L.; McCleaf, P.; Hollman, P.; Bjälkefur Seroka, S.; Hamers, T.; Arp, H.P.H.; Wiberg, K. Electrochemical oxidation for treatment of PFAS in contaminated water and fractionated foam—A pilot-scale study. *ACS Est Water* **2023**, *3*, 1201–1211.
88. Fenti, A.; Jin, Y.; Rhoades, A.J.H.; Dooley, G.P.; Iovino, P.; Salvestrini, S.; Musmarra, D.; Mahendra, S.; Peaslee, G.F.; Blotvogel, J. Performance testing of mesh anodes for in situ electrochemical oxidation of PFAS. *Chem. Eng. J. Adv.* **2022**, *9*, 100205. [\[CrossRef\]](#)
89. Lin, H.; Niu, J.; Xu, J.; Huang, H.; Li, D.; Yue, Z.; Feng, C. Highly efficient and mild electrochemical mineralization of long-chain perfluorocarboxylic acids (C₉–C₁₀) by Ti/SnO₂–Sb–Ce, Ti/SnO₂–Sb/Ce–PbO₂, and Ti/BDD electrodes. *Environ. Sci. Technol.* **2013**, *47*, 13039–13046.
90. Trang, B.; Li, Y.; Xue, X.-S.; Ateia, M.; Houk, K.; Dichtel, W.R. Low-temperature mineralization of perfluorocarboxylic acids. *Science* **2022**, *377*, 839–845. [\[CrossRef\]](#)
91. Yang, L.; Chen, Z.; Goult, C.A.; Schlatzer, T.; Paton, R.S.; Gouverneur, V. Phosphate-enabled mechanochemical PFAS destruction for fluoride reuse. *Nature* **2025**, *640*, 100–106. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.