Light-Induced Advanced Oxidation Processes as PFAS Remediation Methods: A Review

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Abstract: PFAS substances, which have been under investigation in recent years, are certainly some of the most critical emerging contaminants. Their presence in drinking water, correlated with diseases, is consistently being confirmed by scientific studies in the academic and health sectors. With the aim of developing new technologies to mitigate the water contamination problem, research activity based on advanced oxidation processes for PFAS dealkylation and subsequent mineralization is active. While UV radiation could be directly employed for decontamination, there are nevertheless considerable problems regarding its use, even from a large-scale perspective. In contrast, the use of cheap, robust, and green photocatalytic materials active under near UV-visible radiation shows interesting prospects. In this paper we take stock of the health problems related to PFAS, and then provide an update on strategies based on the use of photocatalysts and the latest findings regarding reaction mechanisms. Finally, we detail some brief considerations in relation to the economic aspects of possible solutions.

Keywords: PFAS substances; emerging contaminants; water decontamination; photocatalysts; advanced oxidation processes

1. Introduction

Per- and poly-fluoroalkyl substances (PFASs) are highly fluorinated aliphatic compounds in which the hydrogen atoms are partially or totally replaced by fluorine atoms, resulting in the perfluoroalkyl moiety C_nF_{2n+1} [1]. PFAS compounds are employed worldwide due to their outstanding chemical and physical properties: they are highly stable and show both hydrophobic and lipophobic functionalities. Applications include paintings, clothing, electrical conductors, Teflon® coatings and fluorotelomer production, firefighting foams, paper packaging products, and cookware. Among the most employed PFAS products are perfluorooctanoic (PFOA) and perfluorooctanesulfonic (PFOS) acid [2,3].

Nevertheless, PFASs are also reported to be persistent and bio-accumulative organic pollutants that are extremely toxic to living beings, with continuous exposure increasingly documented as the leading cause of adverse outcomes in humans such as immunotoxicity, hepatotoxicity, and carcinogenicity [4]. Moreover, these substances have been detected in a wide variety of samples including seawater, drinking water, ground water, indoor dust, plants, and the blood of humans and wildlife [5]. Due to the mounting evidence on dangerous effects and the still uncertain efficacy of treatment methods, PFASs are classified as contaminants of emerging concern (CEC), in addition to being

considered as "forever chemicals". Once in the human blood, their elimination can require from months to years [6].

In recent years, different technologies have been developed aiming to purify water contaminated with PFAS compounds. Photolysis has been considered but given the C-F bond strength of around 480 kJ/mol [7], impractical wavelengths shorter than 250 nm are needed to drive efficient cleavage.

Physical adsorption and redox process have been also investigated. Physical adsorption processes using powdered activated carbon (PAC) and granulated activated carbon (GAC) are the most studied and used techniques for PFAS removal from water. These techniques present the limitation of only transferring PFAS molecules from one medium to another, and therefore require further treatments downstream [5].

In this respect, redox processes present potential advantages towards PFAS degradation, enforcing continuous defluorination of the chain and thus featuring degradation to shorter and safer molecules and ultimately to mineralization [1,3,8]. Several efforts to develop cost-effective photocatalytic pathways are currently under investigation, although the overall photocatalytic defluorination and degradation mechanisms are quite complex and still need to be detailed. Novel photocatalytic materials in combination with various illumination sources have been tested for PFAS degradation, with relevant results. High degradation and defluorination efficiencies were achieved in neutral pH conditions, with photocatalyst materials (such as In_2O_3 nanoporous nanospheres [9,10] and Ga_2O_3 needle- and sheaf-like nanostructures [11]) which have drawbacks in terms of biocompatibility, availability, and cost. So far, the most likely solutions rely on the use of either Fe^{2+}/H_2O_2 or TiO_2/O_3 combined with UV light under acidic pH [5].

The challenge here relies on the development of low-toxicity, efficient, and cost-effective materials preferably featuring an optical energy gap compatible with the near UV-visible range (between 350 and 500 nm), therefore providing the possibility of employing lower-cost radiation sources such as artificial visible light illumination, or concentrated sunlight, a clean and renewable resource.

In this review, an analysis of current literature on the applications of advanced oxidation processes for PFAS remediation in water is proposed, focusing on the materials and methods employed with an eye on economic viability. This report starts with a brief overview of PFAS applications and environmental and health concerns, as well as a comparison of conventional vs. emerging treatment methods and related analytical techniques. An extensive review is then presented on light-induced treatment methods (including photolysis), with an update on direct or sacrificial-mediated photocatalysis, materials, methods, and the corresponding reaction mechanisms. Finally, an overview of the employed radiation sources and an economic analysis provides a perspective on possible future outcomes for PFAS treatments as well as costs and efficiencies.

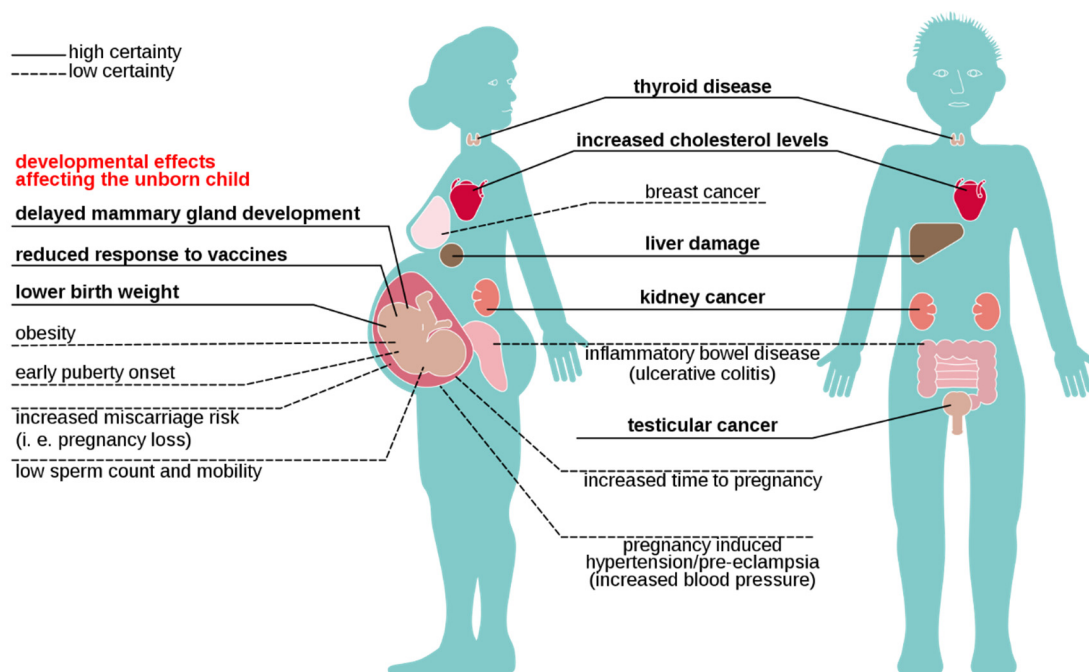## 2. PFAS Applications and Related Concerns

2.1. What Are PFASs Used for?

PFASs can be divided into two main classes: polymers and non-polymers [12]. The most famous example of a non-polymer and one of the most employed PFASs is PFOA, used as a surfactant in the emulsion polymerization of fluoropolymers and as a building block for the synthesis of perfluoroalkyl-substituted compounds, polymers, and polymeric materials, with Teflon® being the most-well known example [13]. Fluorotelomer-based products (non-polymer PFASs) have been shown to degrade to PFOA over periods of decades, and thus they are a huge source of PFOA in the environment [14]. Generally, PFAS release at industrial facilities occurs through wastewater and stormwater discharge, on- and off-site disposal of solid waste, accidental releases through leaks and spills, and stack and fugitive emissions. Stack emissions may result in the aerial deposition of PFAS into soil and surface water (with subsequent

leaching and infiltration to groundwater) related to the facility, as well as short- and long-range air transport of PFAS [3]. In a recent study, more than 200 applications in 64 categories identified nearly 1400 individual types of PFASs supplied by 21 industry branches. Among the use categories, medical instruments, the photographic industry, the semiconductor industry, coatings, paints and varnishes, fire-fighting foams, and printing are the largest employment categories, with more than 100 identified PFASs [15].

2.2. Reasons for Concern

So far, a substantial number of studies have proved many adverse effects of PFASs on human health. PFOS and PFOA, at concentrations of the order of few micrograms per liter in blood, may cause hypercholesterolemia, ulcerative colitis, thyroid disease, cancer, pregnancy-induced hypertension, pre-eclampsia, and liver damage. For each of these outcomes, a molecular mechanism has been tentatively proposed. In this regard, one of the most comprehensive collections of epidemiological studies linking adverse human health effects and many other problems to PFASs (particularly PFOA) is still under investigation and is authored by the C8 Science Panel [4,16]. Figure 1 summarizes the diseases already confirmed to be associated with PFAS substances.

Figure 1. Effects of exposure to PFASs on human health. Some have confirmed certainty (continuous line), while others are still under study (dotted line) [17–22]. (From: https://www.eea.europa.eu/publications/emerging-chemical-risks-in-europe/emerging-chemical-risks-in-europe (accessed on 31 March 2021)).

PFOA and PFOS are long-chain acids, meaning that the fluoroalkyl moiety $(-CF_2-)_n$ with $n \geq 6$ presents a higher potential for adsorption than short-chain ones, leading to greater bioaccumulation and hence toxicity [3,5]. The serum half-life of perfluorobutanesulfonic acid (PFBS) ($n = 4$) was found to be approximately 44 days, whereas for PFOA it was reported to be 21 months, and for PFOS 35 months. Consequently, the persistence of such compounds leads to increased damage to human health [6]. Moreover, the half-lives of PFOS and PFOA has been compared with those of other substances under different follow-up times, and the results evidenced that the elimination levels for PFOA were slower after the range of 12 and 24 months, meaning that the average half-life can be as long as 48 months [6]. In addition, PFOA strongly bioaccumulates in the environment as compared to PFBS, with partition coefficient

logarithms of 4.59 and 2.73, respectively [23]. Given the chemical structure of PFOA and PFBS, chains presenting the $(-CF_2-)_n$ monomers with $n \leq 5$ are identified to be "safer" than longer chains. Further investigations are needed to better understand the behavior of short PFASs compounds and their effects on health.

A threshold of tolerable weekly intake (TWI) of 4.4 nanograms per kilogram of body weight per week is part of a scientific opinion on the risks to people's health deriving from the presence of these substances in food [24]. However, in contaminated drinking water, PFASs are sufficiently "abundant" that the TWI is easily overpassed just by drinking 2 L of water per day since the monitoring system of many PWSs (Public Water Systems) already report concentrations far above the actual limit of 0.5 µg/L of PFAS [3,25].

2.3. Physical Separation vs. Advanced Oxidation Processes

Physical separation methods remain the most common treatments for PFAS-contaminated liquids. Although such methods do not degrade PFAS, these processes are considered as a rapid solution involving only the mass transfer of PFAS from one media to another. These approaches can process extremely large volumes of liquid possessing low PFAS concentrations (levels of ppt to ppb), with the drawback of demanding consequent disposal, generally by incineration in furnaces [26].

Among physical separation technologies, the most employed techniques are procedures such as sorption on granulars of different particles, nanotubes of activated carbon (AC), biomaterials, molecularly imprinted polymers (resins), and mineral composites (e.g., zeolites). As mentioned, all these processes require further, generally off-site, treatment steps [27].

In the case of AC, the main issues are related to the poor removal of short-chained PFAS, difficulties in disposal, and eventually in the reactivation of carbon and the corresponding need for regeneration. These steps are necessary due to the reduction in removal efficiency with use. If frequent replacement of the material is ensured, AC can achieve 10–97% removal of PFAS [28].

The application of ion exchange resins provides up to 90–99% efficiency for some PFASs, although poor removal for selected PFAS is an unsolved problem, along with the potential complications related to the incineration and disposal of the adsorbents [29].

High-pressure filtration membranes are generally related to elevated capital and operation costs, uncertain corrosion control, lack of options for concentrate stream treatment or disposal, and finally membrane fouling. Furthermore, in this case, despite several disadvantages such as those mentioned above, the reported levels of PFAS removal from water range between 93% and 99% [30].

Emerging treatment methods are based on a series of chemical reactions which eventually result in PFAS degradation directly in water streams. Among these techniques, electrochemical oxidation, photocatalysis, photolysis, reduction processes using for example customized iodide or dithionite and sulfites, high-voltage electric discharges, bioremediation using microbial and fungal treatment, sonochemical degradation, ozonation under alkaline conditions, permanganate oxidation, sub or supercritical treatment, and microwave-hydrothermal treatments have been applied to PFAS degradation, with varying degrees of effectiveness [31]. Electrochemical oxidation, plasma, sonolysis, and hydrothermal/supercritical oxidation are some emerging technologies that are in the process of transitioning from laboratory-scale research to field-scale testing [32]. While promising, these technologies need extreme operating conditions, centralized laboratory equipment, and/or high chemical and energy requirements [30].

A combination of different approaches (perhaps using in situ and ex situ approaches) may be needed at a given site to cost-effectively address other areas with different water settings, orders of magnitude in concentration, co-contaminants, and remedial objectives. Selecting the most appropriate remedial strategy for PFAS is challenging. In this review paper we indicate the most promising technologies.

2.4. Analytical Techniques for PFAS Detection in Water

Qualitative and quantitative analysis of PFAS in water systems is extremely important, not only to assess the scale of contamination but also to inform and direct the development of remediation methods. Recent discussions [33] in the field of PFAS analysis highlighted the need to reach a consensus on standard methods for several analytes (short-chain PFAS in particular) and to validate methodologies beyond those for potable water. These objectives will require efforts regarding multi-laboratory validation for analytical methods.

Indeed, numerous analytical techniques for PFAS have been developed over time, in line with the observation of emerging contamination [33]. The most used methods in water systems to date are presented here.

2.4.1. Chromatographic Techniques

Several chromatography analysis techniques have been reported since the early 2000s, including gas chromatography (GC), high-performance liquid chromatography (HPLC), ultra-high-performance liquid chromatography (UHPLC), and capillary liquid chromatography (CLC). HPLC is in regular use for ionic PFASs such as perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs), while GC is mostly employed for more volatile compounds such as fluorotelomer alcohols and perfluorinated sulfonamide ethanols [34]. Capillary electrophoresis has been investigated as an alternative for ionic and polar PFAS determination, but sensitivities and detection limits are lower than those of HPLC [31]. Specifically, the required detection limits for aqueous matrices can be in the range of parts-per-billion or even parts-per-trillion due to the health risks associated. For example, an analysis of groundwater contamination by recently identified PFAS compounds was conducted with a large-volume injection high-performance liquid chromatography (LVI-HPLC) procedure with a detection range of 0.71–67 ng/L (ppt) [35].

PFAS precursors varying in chain length (short or ultra-short chain) and moieties (anionic, cationic, or zwitterionic), have been detected in both tap and bottled water [36]. For ultra-short-chain PFAS, methods coupling LC to a quadrupole time-of-flight mass spectrometer (MS) as well as ultra-performance (UP) convergence chromatography coupled to MS were also reported [37,38]. The detection of 11 PFCAs and 4 PFSAs and short-chain PFCAs (C2–C8) at levels ranging from 70 to 200 ng/L in surface and ground waters was performed using HPLC-MS/MS [39,40], and an analysis of 19 PFAS in potable water was performed using UPLC-MS/MS [41].

HPLC coupled to ultra-high resolution orbitrap mass spectrometry (HPLC-uHRMS) for PFAS (C5–C17) monitoring showed to be advantageous in longer chain monitoring, with detection limits estimated at 0.005–0.2 ng/mL [42].

2.4.2. Sensing Systems for PFAS Detection

Since 2010, nanoscale materials have emerged as possible approaches for the monitoring of PFAS contaminants. Sensing nanomaterials present advantages due to the possibility of exploiting the unique physico-chemical properties of the nanometric size, such as aggregation, disaggregation, adsorption and desorption, potentially unparalleled sensitivity, and tunability. For example, chitosan-coated magnetite nanoparticles (Fe_3O_4-C18-chitosan-MNPs) were employed for the extraction of several PFAS compounds from both rainwater and tap water [43].

Gold nanoparticles (AuNP) are among the most studied nanosensors in general and for PFAS sensing. A significant improvement in this kind of sensing platform was obtained by employing peroxisome proliferator-activated receptor α (PPARα)-responsive elements (PPRE) to modify AuNP sensors for the qualitative and quantitative analysis of PFAS in freshwater. This method was capable of detection at the ppt (2.5 ng/L) level [44]. Further efforts employing AuNPs were also reported using thiol-terminated-polystyrene,

polyethylene glycol and perfluorinated thiols, polydopamine-polyvinylidene fluoro-membrane, and polydopamine [45–47].

The high sensitivity offered by surface-enhanced Raman scattering (SERS) was exploited to detect fluorosurfactants (FS) in groundwater using silver nanoparticles (AgNPs) for Raman enhancement. Immiscible ion pairs were formed between cationic dyes (methylene blue or ethyl violet) and anionic FSs. In addition, graphene oxide (GO) was used to enhance the loading of FSs [48].

2.4.3. Total Fluorine Analysis (TF)

Typical methods for organic and inorganic TF determination include particle-induced gamma-ray emission (PIGE), absorbable organic fluorine (AOF), and combustion ion chromatography (CIC). Recently, fluorine-19 nuclear magnetic resonance spectroscopy (19F-NMR), inductively coupled plasma-mass spectrometry (ICP-MS/MS), and X-ray photoelectron spectroscopy (XPS) were also reported on for fluorine detection [49–51].

3. Advanced Oxidation Processes (AOPs) for PFAS

3.1. Heterogeneous Photocatalysis Materials

Heterogeneous photocatalysis involving semiconductor catalysts provides one of the best remediation techniques for PFAS remediation by involving UV-Vis light and sometimes oxidation reactants [52–55]. The most important advantage of using photocatalysis is that both photo-oxidation and photoreduction pathways operate in tandem to effectively decompose PFAS to shorter-chain perfluoro carboxylic acid (PFCA) by the stepwise elimination of CF_2 groups. Finally, these PFCA intermediates completely mineralize to CO_2 and fluoride ions through repeating similar steps. The photocatalytic material, along with appropriate opto-electronic features, must also be chemically stable, recyclable, non-toxic, and available with a low price tag. Based on these requirements, Ti, Ga, In, and Bi-based compound photocatalysts have been primarily implemented in the literature to remove PFAS from wastewater (Table 1).
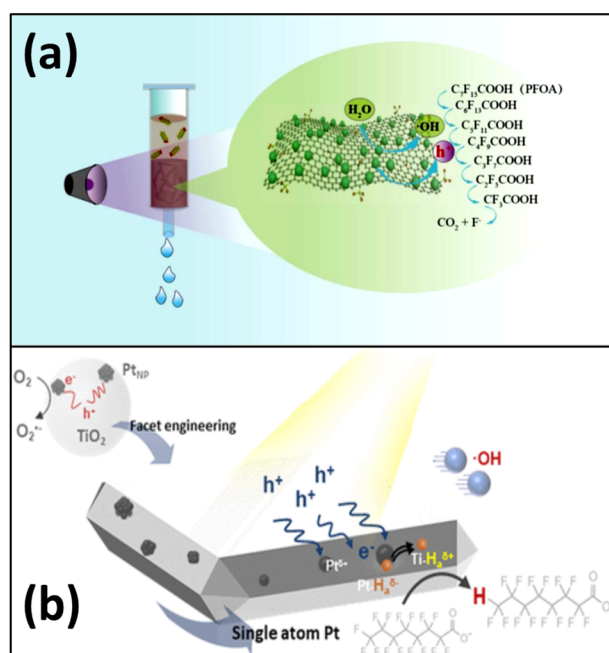
3.1.1. Metal Oxides

TiO_2 was the first photocatalyst investigated for the removal of PFOA in water bodies [56] due to its well-known high activity towards the degradation of pollutants. However, TiO_2 showed a very low reaction rate constant (~0.0001 min^{-1}), and high half-life (~6931 min) for PFOA degradation [57]. Similar problems were observed in the presence of titanate nanotubes (TNTs) synthesized by hydrothermal methods to improve the surface area, which were even less effective in removing PFAS under UV light [58]. This inefficiency of Ti-based photocatalysts was attributed to the strong repulsion of anionic PFAS molecules from the negatively charged surface of TNT. Commercial P25 TiO_2, a benchmark in the field, was able to complete the degradation reaction of PFOA within 4 h under illumination with 254 nm UV light [59]. However, under higher wavelength light (315–400 nm), the degradation of PFOA decreased drastically. The photocatalytic ability of TiO_2 to degrade organic pollutants mainly relies on the formation of $HO^{\bullet}$ and $O_2^{-\bullet}$ radicals by oxidation of water and reduction of O_2 through photogenerated holes and electrons, respectively. Nevertheless, both these reactive oxidation species (ROS) are less active for the decomposition of PFOA. Thus, in the case of TiO_2, photogenerated h$^+$ and e$^-$ directly initiate the decarboxylation of PFAS to mineralize them to CO_2 and fluoride ions in a stepwise manner. For this phenomenon to occur, the absorption of PFAS molecule on TiO_2 surface becomes a necessary condition. This can be achieved by spreading positive surface charges on the TiO_2 by carrying out the photocatalytic reaction of PFAS in acidic conditions. Panchangan et al. [56] showed that in the presence of 0.15 M perchloric acid, the rate constant of PFOA degradation increased by ~46 times with respect to that performed in the absence of acid. Following this work, most of the research for TiO_2-based

photocatalytic degradation of PFAS was performed at a pH below 4. Acids such as oxalic acid increase the photoreduction capability of TiO_2 to degrade PFAS. Wang et al. [60] demonstrated that adding oxalic acid leads to the formation of carboxyl anion radicals ($CO_2^{-\bullet}$) by photogenerated holes that have a higher reduction potential (−1.85 V) than that of photogenerated electrons. The same work also reported that oxalic acid is ~11.6 times more effective in PFOA decomposition than perchloric acid under the equivalent pH of the reaction. TiO_2 nanoparticles in the presence of oxalic acid effectively degrade 86.7% of PFOA in 180 min under N_2 bubbling.

TiO_2 supported on carbon allotropes such as MWCNT [61], graphene [62], and reduced-graphene oxide (rGO) [63] also increased the direct interaction between PFOA and TiO_2 photocatalysis owing to the high adsorption capacity of the carbon-based material provided by the high surface area and surface functional group. Carbon can also trap the photogenerated electrons of TiO_2 and reduce the electron–hole recombination process during the photocatalytic reaction. TiO_2-MWCNT and TiO_2-rGO were able to degrade ~100% of PFOA under UV irradiation in 8 h and 12 h, respectively. Recently, Shen et al. [64] fabricated TiO_2 quantum dots of 2–5 nm in size on sulfonated graphene nanosheets using sodium dodecyl sulfate as a surfactant (Figure 2a). Due to the hydrophobic nature of sulfonate graphene and highly dispersed TiO_2 quantum dots, PFOA pollutants could instantaneously be adsorbed on the surface, followed by fast decomposition by eliminating CF_2 species. Apart from carbon, molecule-imprinted polymer (MIS)-modified TiO_2 nanotubes also boosted contact between PFOA and TiO_2 and reduced the recombination of h^+ and e^- pairs by capturing photogenerated electrons [65].

Noble metal nanoparticles deposited on TiO_2 can also act as an electron sink to increase the lifetime of photogenerated h^+ and e^- pairs. Among Pt, Pd, and Ag nanoparticles deposited by TiO_2, Pt-TiO_2 showed a considerable improvement (~12.5 times) in the photocatalytic performance of PFOA removal as compared to pure TiO_2 [66]. With the highest work function, Pt can attract more electrons from TiO_2 to form a strong Schottky barrier at the interface, which improves h^+/e^- separation during irradiation. Weon et al. [67] successfully loaded Pt nanoparticles on the reductive sites of the TiO_2 facet to precisely capture photoinduced electrons (Figure 2b). This charge separation led to an increase in the number of holes on TiO_2 sites which participate in PFOA degradation. At the same time, electrons on the Pt atom produced hydrogen atoms and led to hydrogen spillover onto the TiO_2 surface. The Ti-H bond formed on the surface facilitates hydrodefluorination of PFOA through the cleavage of the C-F bond. In addition to reducing recombination, doping with transition metals like Cu, Fe, and Pb also increased visible light absorption by lowering the band gap of TiO_2, leading to superior photocatalytic degradation of PFAS [57,68]. Combining different strategies can lead to significant advancements in photocatalytic performance by creating a synergetic effect. Fe-deposited titanate nanotubes (TNT) supported on activated carbon (AC) (Fe/TNTs@AC) demonstrated highly efficient photodegradation of PFOA (~90%) in 4 h under UV light irradiation with 62% of the defluorination reaction [69]. In Fe/TNTs@AC, the nanotube architecture and AC provided a high surface area, while α-Fe_2O_3 particles and AC considerably boosted PFOA adsorption on the surface and separation of the h^+/e^- pair by acting as the electron acceptor. Fe/TNTs@AC was recycled without significant loss in adsorption and degradation capacity of the photocatalyst. Similarly, Ga/TNTs@AC showed faster adsorption kinetics and degraded ~75.0% while mineralizing 66.2% of PFOS after 4 h of UV irradiation [70]. This type of study opens an avenue towards developing more such TiO_2-based photocatalysts by integrating different strategies, with each modification step playing a specific role.

Figure 2. PFOA degradation using (**a**) TiO₂ quantum dots supported on sulfonated graphene nanosheets (reprinted from [64], copyright (2020) with permission from Elsevier) and (**b**) single Pt atoms loaded on the reductive sites of the TiO₂ facet (reprinted from [67], copyright (2021) with permission from ACS Publications).

Along with TiO_2, ZnO was also studied for remediating wastewater from PFAS but with limited success [71]. Although heterojunction between ZnO/rGO did degrade 90.9% of PFOA [72], no other work on ZnO has been reported.
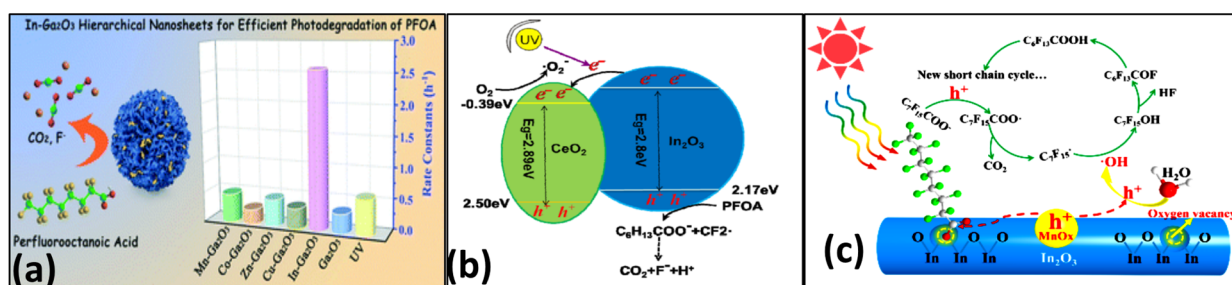
With a more negative conduction band edge and a wider band gap (4.8 eV) than TiO_2, gallium oxide (Ga_2O_3) displayed a better capability for removing PFAS than TiO_2. In contrast to TiO_2, the scavenging experiment proved that the breaking down of PFOA proceeds via a reduction reaction in Ga_2O_3 involving photogenerated electrons to produce a rate constant ~19 times higher than that of TiO_2 [73]. Nanostructured Ga_2O_3 in nanoneedle [74], sheaf-like [75], and nanorod [76] forms with improved surface area presented escalation in the demolition of PFOA from wastewater. Among them, the sheaf-like nanostructure assembled with nanoplates of an average width of 100 nm and thickness of 10 nm exhibited the highest reaction rate constant (4.85 h⁻¹). Compared to commercial Ga_2O_3 and TiO_2 powder, this value was ~16 and ~44 times higher, respectively. Nevertheless, the mechanism involved in all the nanostructures remained same where photoinduced electrons were used for the decarbonization of PFOA followed by HF elimination. To improve photocatalytic activity towards PFOA degradation, Huang and coworkers [77] modified Ga_2O_3 hierarchical nanosheets by doping a series of transition metals (Mn, Co, Zn, Cu, Ti, and In). Indium doping in the Ga_2O_3 hierarchical composite resulted best, completely degrading PFOA within 1 h with degradation kinetics ~7.8 times higher than those of pristine Ga_2O_3 (Figure 3a).

By investigating the reaction mechanism, this considerable improvement was attributed to not only enhanced light absorption and charge separation but also to the activated surface that provided conducive conditions for better adsorption of PFOA.

In_2O_3 is highly active in removing PFAS, and it follows a similar photo-oxidation pathway as TiO_2, but with significantly higher photocatalytic performance with a reaction rate approximately ~59 times higher than that of TiO_2 [10]. As In_2O_3 provides the surface with better adsorption capacity for PFOA, photogenerated holes directly attack the carboxyl group of PFOA rather than forming the $HO^•$ radical as in TiO_2. Since the surface plays the prime role in In_2O_3, substantial work on In_2O_3 was dedicated to refining the surface area by fabricating different nano morphologies like nanospheres, nanoplates,

microspheres, and nanocubes [9,78–79]. Among them, nanoplates showed the highest surface area of 156.9 m^2/g, exposing many active sites and leading to the highest photocatalytic performance in the degradation of PFOA [79]. In recent work, In$_2$O$_3$ nanospheres derived from MOF offered a surface of a super-hydrophilic nature to facilitate the adsorption and tight attachment of PFOA [80]. This behavior results in complete decomposition and mineralization of PFOA in 3 h and 6 h, respectively. Oxygen vacancies also play a vital role in these nanostructured In$_2$O$_3$ photocatalysts by acting as the adsorption sites for PFOA on the In$_2$O$_3$ surface. Higher photocatalytic activity has been recorded for nanostructures possessing greater amounts of oxygen vacancies. In addition to the adsorption of reactants, photogenerated charge separation is also essential for enhancing the photocatalytic reaction rate. As in other semiconductors, a strategy of heterojunction was also adopted for In$_2$O$_3$ to avoid the recombination process. Composites of In$_2$O$_3$/graphene [81], In$_2$O$_3$/Ce$_2$O$_3$ (Figure 3b) [82], and In$_2$O$_3$/MnO$_x$ (Figure 3c) [83], synthesized by cost-effective techniques, formed a heterojunction at the interface due to the difference in the energy levels, which drives the photogenerated h$^+$ and e$^-$ to spatially separated from each other. The synergic role played by both materials also escalated the adsorption of PFOA and the harvesting of visible light in the composite. All these promotive effects caused the complete decomposition of PFOA in 3 h for In$_2$O$_3$/graphene and In$_2$O$_3$/MnO$_x$, and in 1 h for In$_2$O$_3$/Ce$_2$O$_3$ under UV light irradiation (254 nm), but with a higher intensity used in the case of In$_2$O$_3$/Ce$_2$O$_3$ composites. Oxy/hydroxide forms of In (InOOH) degrade PFOA, with a rate constant ~27.6 times higher than that of the commercial P25 photocatalyst [84]. Enhanced adsorption of PFOA on the surface of InOOH is the prime factor responsible for higher photocatalyst performance compared to P25 under UV light irradiation.

Figure 3. (**a**) Effect of transition metal doping in Ga$_2$O$_3$ hierarchical composites on PFOA degradation (reprinted from [77], copyright (2020) with permission from RSC Publishing). Photogenerated charge separation across the heterojunction of a (**b**) In$_2$O$_3$/Ce$_2$O$_3$ (reprinted from [82], copyright (2016) with permission from RSC Publishing) and (**c**) In$_2$O$_3$/MnO$_x$ composite (reprinted from [83], copyright (2019) with permission from John Wiley and Sons).

Mixed metal oxides possess multifunctionality qualities owing to the combined effect generated by different metals, where one metal will act as the active site, whereas the other metal modulates the electronic and structural configuration. Nadagauda and coworkers [85] synthesized the nanocrystalline ferrite catalyst Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ using a sol–gel autocombustion method for the degradation of PFOA in the presence of oxalic acid. Under UV light irradiation, Zn$_x$Cu$_{1-x}$Fe$_2$O$_4$ produces large quantities of ROS in aid of oxalic acid, as detected from intermediate products using liquid chromatography.

3.1.2. Other Photocatalysts

Bismuth oxyhalide (BiOX: where X = F, Cl, Br, and I) photocatalysts are effective for the degradation of PFAS under light irradiation. Different bandgap and energy levels can be obtained for different X combinations, with BiOF, BiOCl, BiOBr, and BiOI showing bandgaps of 3.99, 3.22, 2.64, and 1.77 eV, respectively [86]. The optical and electronic properties can be further tuned using two different combinations of X in the compounds. Thus, these compounds provide the advantage of harvesting visible light for

photocatalytic reactions. Most importantly, the formation energy for oxygen vacancies (OVs) of BiOX is very low, generating an abundant quantity of OVs on the surface. This feature further modulates the bandgap, providing sites for electron capture to delay the recombination of photogenerated charge carriers. The oxygen-deficient sites further participate in binding PFAS pollutants, with optimum interactions as compared to metal oxide. The layered structure of BiOX also offers a large surface-to-volume ratio with extensive exposure of active facets like (001). Because of these merits, BiOX showed an exceptional capability towards the photodegradation of PFOA, as reported first by Song et al. [87] for BiOCl. In their subsequent work [88], the same group systematically performed experiments to prove the linear relationship between the OVs and the photodegradation of PFOA. Doubling the OVs in BiOCl led to a four-fold increase in efficiency of defluorination in PFOA. The wide-bandgap BiOF photocatalyst can be modified by inducting OVs, which introduce the intermediate band in the forbidden gap to lower the energy required to excite the electrons by irradiation [89]. A study conducted by Zu and coworkers [89] demonstrated that OVs could be tuned on exposed (001) facets of BiOF by adjusting the concentration of ethylene glycol during synthesis. The BiOF (001) produced by using 50% ethylene glycol could completely decompose PFOA within 6 h based on developed OVs. BiOI material, even with the smallest bandgap of ~1.8 eV, was not conducive to the photocatalytic removal of PFAS, mainly owing to the lower valence band edge than that of the redox potential of ($HO^-/HO^\bullet$) [90]. However, $BiOI_{0.95}Br_{0.05}$ displayed considerably high photocatalytic activity, requiring only 2 h to decompose 96% and 3 h to mineralize 65% of PFOA, thus showing the significance of the small amount of Br doping [90]. Here, rather than ROS, the holes and electrons played a more dominant role in the photocatalytic process. Doping of Br led to a reduction in bandgap for enhanced light harvesting and increased exposure of the (001) facet to elevate the separation of h^+/e^- pairs. This promoting characteristic of $BiOI_{0.95}Br_{0.05}$ produced a degradation rate constant ~4.3 times higher than that of BiOI. A similar boost in photocatalytic performance was observed when BiOI was mixed with BiOF and loaded with Bi nanoparticles to provide $Bi/BiOI_{1-x}F_x$ [91]. Integrating both these bismuth oxyhalides further reduced the bandgap to increase the visible light absorption and elevated the surface area by two times due to the formation of hollow flower-like microspheres. On the other hand, Bi nanoparticles on the surface give rise to a surface plasma resonance effect to favor photogenerated charge separation by generating an electric field near the junction. Because of these properties, the $Bi/BiOI_{0.8}F_{0.2}$ composite presented the best activity for the decomposition of PFOA (40 mg/L) in just 2 h of illumination of simulated solar light with a ~10 times higher degradation rate than that of pure BiOF and BiOI. As per the results of the EPR spectra and scavenging experiment, superoxide radicals ($O_2^{-\bullet}$) are dominant species for dissociating the bonds of PFOA. The p-n heterojunction of $BiOI@Bi_5O_7I$ (Figure 4a) was formed to improve charge separation by the facile heat treatment of BiOI in the air at a moderate temperature of 390 °C [92].

The resulting p-n heterojunction causes photogenerated electrons to be immediately driven to the conduction band of Bi_5O_7I while leaving the holes in the valence band of BiOI, thereby spatially separating h^+/e^- pair. This heterojunction is efficient in degrading 80% of PFOA in 6 h under irradiation with visible light, with the $HO^\bullet$ radical as the oxidizing agent. Similar charge separation was observed in the case of the Bi_5O_7I/ZnO n-n heterojunction microsphere, but here photogenerated holes were found to be responsible for attacking carboxylic groups of PFOA [93].

A novel $Bi_3O(OH)(PO_4)_2$ (BOHP) compound, despite having a larger bandgap and lower surface area than $BiPO_4$ and β-Ga_2O_3, showed ~15 times higher photocatalytic activity towards the degradation of PFOA [94]. The highly positive surface charge of BOHP induces an incremental rise in the adsorption behavior of PFOA on the surface. Along with this, the favorable redox potential of the BOHP also participates in enhancing PFOA mineralization. The performance of BOHP was amplified by Xu et al. [95], forming composites with carbon spheres (CS) and upgrading the stability of BOHP by suppressing

the photo corrosion of the composites via acting as an electron sink. The adsorption capacity of PFOA was also improved through CS, which contributes to the adsorption of PFOA. Carbon spheres were also found to be beneficial for an iron (hydro)oxide photocatalyst (FeO), where a 1:1 composite of FeO/CS was developed by the same research group that presented the BOHP/CS composites (Figure 4b) [96]. Here, CS aids in forming ferrihydride on the surface, which improves the adsorption of PFOA via binuclear and bidentate complexation and increases direct electron extraction from PFOA under stimulated solar light. FeO/CS was able to photodegrade 95.2% of PFOA, with 57.2% defluorination in 4 h in neutral pH.

Figure 4. Charge separation and PFOA degradation (**a**) at the p-n heterojunction of BiOI@Bi_5O_7I (reprinted from [92], copyright (2020) with permission from Elsevier) and (**b**) in BOHP/CS composites (reprinted from [95], copyright (2020) with permission from Elsevier).

The wide-bandgap semiconductor boron nitride (BN) was also reported for photocatalytic degradation of PFOA under UV light (Figure 5a) [97]. Boron nitride followed a similar photo-oxidation pathway as TiO_2, mainly involving holes to bifurcate PFOA but with rate twice that of TiO_2. The exfoliation of BN layers through ball milling further improved the degradation rate. Tungstic heteropoly acid ($H_3PW_{12}O_{40}$) supported on high-surface-area bimodal mesoporous silica (BMS) displayed an enhanced defluorination rate of PFOA compared to direct photolysis under vacuum UV light irradiation with a wavelength of 185 nm [98]. Recently, a Z-scheme-based heterojunction was discovered to be highly effective in photocatalytic applications, considering its ability to cause charge separation at the junction to increase the lifetime of photogenerated charges. Tang et al. [99] fabricated a Z-scheme heterojunction of core–shell CeO_2@NiAl-LDHs (Figure 5b) to proficiently remove PFOA from wastewater. A built-in electric field in the Z-scheme heterojunction causes instantaneous separation of photogenerated charges to record photodegradation of 90.2% of PFOA under stimulated solar light. Although implementing various photocatalytic materials and their different forms and compounds provides the solution for adequate removal of PFAS, maintaining a conducive environment during the photocatalytic reaction is equally vital. Factors such as aerobic or anaerobic conditions, type of light used, pH and temperature of the solution, and the presence of other impurities are crucial in deciding the photocatalytic degradation rate of PFAS. The effect of these factors is covered in other review articles [100–103], and is out of scope for the present report.

Figure 5. PFOA degradation mechanism over (**a**) boron nitride (reprinted from [97], copyright (2020) with permission from ACS publications) and (**b**) the z-scheme based heterojunction of core–shell CeO₂@NiAl-LDHs (reprinted from [99], copyright (2021) with permission from Elsevier).

Table 1. Heterogeneous photocatalysis applied to PFAS decontamination.

Photocatalytic Performance					Photocatalytic Reaction Condition				Ref
Photocatalyst	Reaction Time (h)	Rate Constant (min⁻¹)	% Degradation	% Defluorination	Concentration of PFOA/PFOS	Catalyst Dosage (g/L)	pH of Solution	Light Source	
TiO_2	12	0.0001	15%	---	50 mg/L	0.5	5	254 nm and 400 W	[57]
Titanate nanotubes	24	---	59%	---	120.8 μM	0.125	4	254 nm and 400 W	[58]
P25 TiO_2	3	0.0005	30%	----	12 mM	0.66	3	310–400 nm and 75 W/m²	[59]
TiO_2-HClO₄	7	0.0047	97%	38%	120 μM	0.66	2.47	254 nm and 16 W	[56]
TiO_2-Oxalic acid	3	---	86.7%	16.5%	24 μM	0.5	2.47	254 nm and 23 W	[60]
TiO_2-MWCNT	8	---	100%	----	72.5 μM	0.4	5	365 nm and 300 W	[61]
TiO_2-rGO	12	0.0027	93 ± 7%	20%	240 μM	0.1	3.8	254 nm and 150 W	[63]
TiO_2-MIP	10	0.0044	81%	30.2%	72.5 μM	--	5	254 nm and 23 W	[65]

Material	Time	k	Degradation %	Mineralization %	Concentration	Loading	pH	Light source	Ref.
TiO_2 QD/Graphene	10	0.0098	~90%	----	300 μM	0.02	5	UV light 150 W	[64]
TiO_2-Pt		0.0121	100	34.8	144.9 μM	0.5	3	365 nm and 135 W	[66]
TiO_2-Pd	7	0.0073	94.2	25.9					
TiO_2-Ag		0.0021	57.7	8.1					
TiO_2-Cu	12	0.0031	91	19	121 μM	0.5	5	254 nm and 400 W	[57]
TiO_2-Fe	4	0.0015	60	--					
TiO_2-Pb	4.5	0.0086	99	22.4	121 μM	0.5	5	254 nm and 400 W	[68]
TiO_2-Pt single atom	2		40	35	100 μM	0.25	7	254 nm and 7.87 mW/cm²	[67]
Fe/TNT@AC	4	0.0153	90	62	100 μM	1	7	254 nm and 21 mW/cm²	[69]
Ga/TNT@AC	4		75	66.2	0.1 mg/L	3	7	254 nm and 210 W/m²	[70]
ZnO	3 days	---	95	---	25.5 μM	1	6.5–7.0	365 nm and 13 W/m²	[71]
Ga_2O_3	3	0.0020	36	15	0.5 mg/L	0.5	--	254 nm and 14 W	[73]
Ga_2O_3 needle-like	40 min	0.0380	100	58	0.5 mg/L	0.5	--	254 nm and 14 W	[74]
Ga_2O_3 sheaf-like	45 min	0.0240	100	60	0.5 mg/L	0.5	---	254 nm and 14 W	[75]
β-Ga_2O_3 nanorods	1.5	0.0425	98.8	56.2	10 mg/L	0.5	3	254 nm and 50 W	[76]
In-doped Ga_2O_3 nanosheets	1	0.0416	100	--	20 mg/L	0.5	--	Hg lamp	[77]
In_2O_3	4	0.006	75	33	40 mg/L	3.4	5	254 nm and 23 W	[10]
In_2O_3 microspheres	17 min	0.130	100	--	30 mg/L	0.5	3	254 nm and 15 W	[78]
In_2O_3 nanocubes	2	0.030	100	--					
In_2O_3 nanoplates	42 min	0.073	100	--					
In_2O_3 nanoporous nanospheres	30 min	0.100	100	71	30 mg/L	0.5	3.9	254 nm and 23 W	[9]
In_2O_3 porous nanoplates	30 min	0.158	100	---	30 mg/L	0.5	---	254 nm and 15 W	[79]

MOF-derived In_2O_3 nanospheres	3	---	100	50	10 mg/L	0.2	---	254 nm and 32 W	[80]
In_2O_3/graphene	3	0.008	100	60.9	30 mg/L	0.5	3	254 nm and 15 W	[81]
In_2O_3/Ce_2O_3	1	0.063	100	53.3	100 mg/L	0.4	--	254 nm and 500 W	[82]
In_2O_3/MnO_x	3	0.301	100	17.4	50 mg/L	0.5	3.8	Xenon lamp and 500 W	[83]
InOOH	3	0.008	83.4	---	20 mg/L	0.25		254 nm and 18 W	[84]
BiOCl	12	---	100	59.3	20 μM	0.5	4.8	254 nm and 10 W	[87]
BiOCl with OV	8.5	---	68.8	12.86	50 μM	1	2	Xenon lamp and 300 W	[88]
BiOF	6	0.006	100	56.8	15 mg/L		3–5	UV light	[89]
BiOI	2	0.0048	66	37% in 3h	20 mg/L	0.4	--	Hg lamp and 300 W	[90]
$BiOI_{0.95}Br_{0.05}$	2	0.0205	100	65% in 3h	20 mg/L	0.4	--	Hg lamp and 300 W	[90]
Bi/$BiOI_{1-x}F_x$	2	0.0375	100	10	40 mg/L	0.4	3–5	Xenon lamp and 800 W	[91]
BiOI@Bi_5O_7I	6	0.0041	81	60	15 mg/L	0.5	3	Xenon lamp and 800 W	[92]
BiOI/ZnO	6	0.0002	91	52.2	1 mg/L	0.5	4	Xenon lamp and 500 W	[93]
BOHP	1	0.1000	100	60	0.13 mM	1.8	4	254 nm and 18 W	[94]
BOHP/CS	4	---	100	32.5	0.2 mg/L	1.0	7	254 nm and 18 W	[95]
FeO/CS	1	---	95.2	57.2	0.2 mg/L	1.0	7	Stimulated solar light	[96]
Boron nitride	4		100	52	0.12 mM	2.5	6.5	254 nm and	[97]

H$_3$PW$_{12}$O$_{40}$/bimodal mesoporous silica	4	0.0018	50	10 mg/L	0.2	4	24 W 254 nm and 8 W	[98]

3.1.3. Reaction Mechanisms

The mineralization of PFOA in water can be summarized as in Equation (1)

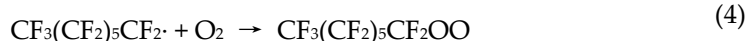$$CF_3(CF_2)_6COOH + 7/2\ O_2 + 7\ H_2O \rightarrow 8\ CO_2 + 15\ HF \tag{1}$$

The reaction has been investigated in irradiated aqueous suspensions of TiO$_2$, one of the most extensively investigated photocatalysts, and the commonly accepted mechanism is the result of a photo-redox and β-scission pathway [104]

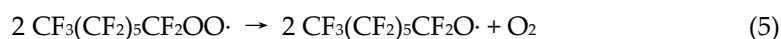Upon irradiation of suitable energy, electrons (e$^-_{CB}$) and holes (h$^+_{VB}$) are localized respectively within the conduction and valence band of TiO$_2$ [105], according to Equation (2).

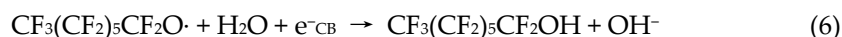$$TiO_2 + h\nu \rightarrow TiO_2\ (e^-_{CB};\ h^+_{VB}) \tag{2}$$

It is worth noting that PFOA exists mainly in its deprotonated form under natural pH conditions. Deprotonated PFOA undergoes hole-induced Kolbe decarboxylation [60,106,107], giving rise to the C7 radical intermediate (Equation (3)), which in turn reacts with molecular oxygen, producing a peroxy-radical [108] (Equation (4))
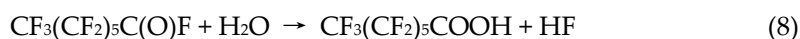
$$CF_3(CF_2)_6\ COO^- + h^+_{VB} \rightarrow CF_3(CF_2)_5CF_2\cdot + CO_2 \tag{3}$$

$$CF_3(CF_2)_5CF_2\cdot + O_2 \rightarrow CF_3(CF_2)_5CF_2OO \tag{4}$$

The coupling of two peroxyradicals forms molecular oxygen and two oxyradicals (Equation (5)).

$$2\ CF_3(CF_2)_5CF_2OO\cdot \rightarrow 2\ CF_3(CF_2)_5CF_2O\cdot + O_2 \tag{5}$$

The oxyradical undergoes electron-coupled hydrogen abstraction from water and evolves to an unstable primary perfluorinated alcohol [109] (Equation (6)), which eventually leads to acylfluoride and hydrogen fluoride [110] (Equation (7))

$$CF_3(CF_2)_5CF_2O\cdot + H_2O + e^-_{CB} \rightarrow CF_3(CF_2)_5CF_2OH + OH^- \tag{6}$$

$$CF_3(CF_2)_5CF_2OH \rightarrow CF_3(CF_2)_5C(O)F + HF \tag{7}$$

Finally, the acyl fluoride undergoes hydrolysis to the C6 carboxylic acid (Equation (8))

$$CF_3(CF_2)_5C(O)F + H_2O \rightarrow CF_3(CF_2)_5COOH + HF \tag{8}$$

This in turn can undergo the same photo-redox mechanism several times until the chain length is reduced step by step [111].

Another pathway relies on the capability of the oxyradical C7 generated in Equation (5) to undergo monomolecular β-scission by eliminating fluorofosgene (COF$_2$) and giving rise to a C6 perfluoroalkyl radical [112–114] (Equation (9)).

$$CF_3(CF_2)_5CF_2O\cdot \rightarrow COF_2 + CF_3(CF_2)_4CF_2 \tag{9}$$

Fluorofosgene is easily hydrolyzed to HF and CO$_2$ (Equation (10))

$$COF_2 + H_2O \rightarrow CO_2 + 2\ HF \tag{10}$$

The perfluoroalkyl radical can undergo the reaction steps as described above, starting from Equation (4). The mechanism described above is schematically represented in Figure 6.
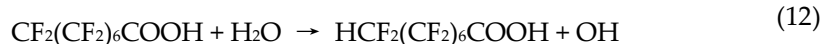
Figure 6. A hypothesized degradation mechanism of PFOA. Dashed lines indicate that the Cn product undergoes the same path, reducing the number of carbon atoms step by step.

Notably, the β-scission mechanism (Equations (9) and (10)) induces the decomposition of PFOA without forming carboxylic intermediates, which instead are produced when the photoredox mechanism (Equations (3)–(8)) occurs. Therefore, the concentration of shorter-chain perfluorinated acids should increase proportionally to fluoride formation if the photoredox mechanism preferentially occurs. Gatto et al. [104] observed that the shorter-chain carboxylic acids slowly started to form after switching on the lamp, but during the first hours of reaction, a direct correlation between PFOA mineralization and fluoride formation was evident. This suggests that the reaction takes place initially through the predominant β-scission mechanism, which efficiently competes with the photo-redox one. The authors also observed a slight loss of fluoride ions of ca. 3% in the aqueous phase, possibly due to fluorination of the surface of TiO_2.

On the other hand, for longer reaction times the mineralization of PFOA nearly stopped, and an enhanced formation of shorter chain carboxylic acids was observed, with a concentration trend following the molecular weight of the intermediates. This indicates the preferential occurrence of the photo-redox mechanism with longer reaction times.

Another mechanism proposed in literature relies on the initial one-electron reduction of PFOA by photogenerated electrons, which results in the defluorination of the terminal perfluorinated carbon atom and the consequent formation of the corresponding perfluoroalkyl radical (Equation (11)). The latter in turn abstracts a hydrogen atom from the water, forming an OH radical and a monohydrogenated intermediate (Equation (12)). Repeating the same pathway results in the progressive hydrogenation of the alkyl chain, eventually leading to mineralization [54].

$$CF_3(CF_2)_6COOH + e^-_{CB} \rightarrow CF_2(CF_2)_6COOH + F^- \tag{11}$$

$$CF_2(CF_2)_6COOH + H_2O \rightarrow HCF_2(CF_2)_6COOH + OH \tag{12}$$
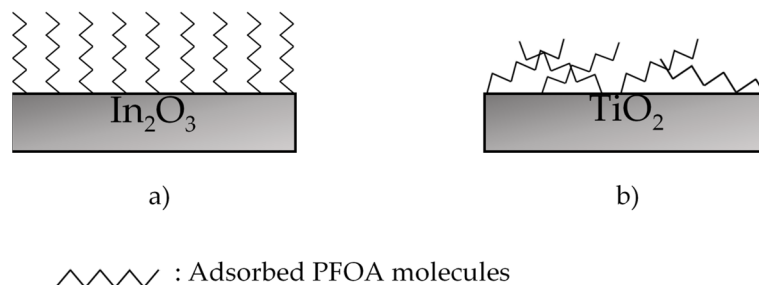
This pathway seems less probable compared to the other above-mentioned pathways considering the reduction of oxygen, which should preferentially occur.

Finally, it is worth noting that direct photolysis of PFOA could take place only under irradiation shorter than 220 nm, which corresponds to the bond dissociation energy of the C-F bond, i.e., ca. 544 kJ/mol [102,115].

Only ca. 10% of degradation was observed through photolysis at 254 nm [116, 117].

It is worth noting that PFOA is almost inert towards the OH radicals produced in the presence of irradiated TiO_2 ($k_{OH+PFOA} \leq 10^5$ M^{-1} s^{-1}) [118], due to the absence of hydrogen atoms prone to OH radical abstraction in the PFOA structure. Moreover, the initial decarboxylation (Equation (3)) is not likely to be induced by OH radical attack. In fact, the perfluorination of the alkyl chain reduces the electronic density of the carboxylic moiety, making the OH radical-mediated electron transfer unfavorable. Therefore, TiO_2, generally very active for the degradation of a wide range of organic substrates, is rather poorly efficient in the degradation of PFOA. Its activity is slightly enhanced only under highly acidic pH conditions ($HClO_4$, pH < 2) [56, 119] where the pH-dependent potential of the photogenerated holes is higher. An analogous situation is observed for the TiO_2-induced degradation of trichloroacetate, which does not possess any hydrogen atoms [120]. Therefore, the lower the efficiency of hole-induced water oxidation to OH radicals, the better the efficacy obtained in terms of PFOA degradation. Accordingly, other semiconductors with a poor ability to produce OH radicals are instead more active in PFOA degradation. For instance, Li et al. [10] found that the apparent rate constant for the degradation of PFOA was 8.4 times higher in the presence of In_2O_3 than in the presence of TiO_2. This result was justified by considering the peculiar adsorption mode of PFOA onto the In_2O_3 surface and the higher hole availability for PFOA oxidation with respect to TiO_2, where water oxidation preferentially occurs. PFOA is bound to In_2O_3 in a bidentate or bridging configuration, resulting in a vertical and ordered arrangement of chains (Figure 7a). On the TiO_2 surface, PFOA instead binds in a monodentate way (Figure 7b) which results in a tilted configuration of the chains.

a)　　　　　　　　　　　　　　　　　　　　　　　b)

$\wedge\wedge\wedge\vee$: Adsorbed PFOA molecules

Figure 7. Adsorption modes of PFOA onto In_2O_3 (**a**) and TiO_2 (**b**).

Consequently, some of the inner CF_2 groups of PFOA can interact with the TiO_2 surface through hydrogen bonding. The ordered and tight configuration of the PFOA chains onto the In_2O_3 surface favors direct hole oxidation with respect to water oxidation to hydroxyl radicals, and consequently the PFOA degradation occurs more efficiently on the surface of irradiated In_2O_3 than of TiO_2. Moreover, OH radical-trapping experiments through electron paramagnetic resonance spectroscopy showed that the photogenerated holes are easily transformed into OH radicals on the TiO_2 surface and only slowly react with adsorbed water or hydroxyl groups on the surface of In_2O_3. The addition of PFOA enhances the amount of OH radicals produced in the presence of TiO_2 due to the electron-withdrawing ability of fluorine atoms reported elsewhere [121]. This does not help PFOA degradation, as OH radicals are not effective to this end [122], and holes are preferentially consumed to oxidize water. On the other hand, the already-small amount of OH radicals generated in the presence of In_2O_3 further decreases in the presence of PFOA. This indicates the favored direct hole oxidation of PFOA at the surface of In_2O_3.

Of several attempts to enhance the PFOA degradation rate in the presence of TiO_2 under UV irradiation, Pb^{2+} modification showed the most promising results, providing a
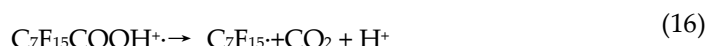
degradation rate 32.5 times higher with respect to the bare material [68]. Authors attributed the enhanced activity to the capability of Pb for acting as an electron trap, thus increasing the availability of holes for the degradation of PFOA.

Persulfate ($S_2O_8^{2-}$) has also been used as a promising alternative for the degradation of PFOA. The preliminary activation of persulfate is required to generate sulfate radicals (Equation (13)), which in turn may directly induce oxidation or react with water, producing OH radicals (Equation (14)) [123]. This reaction is slow at room temperature ($k = 2 \times 10^{-3}$ s^{-1}) but quickly proceeds at higher temperatures [124].

$$S_2O_8^{2-} \rightarrow 2SO_4^{-} \tag{13}$$

$$SO_4^{-} \cdot + H_2O \rightarrow SO_4^{2-} + \cdot OH + H^+ \tag{14}$$

The activation of persulfate can be performed through thermal energy. For instance, complete defluorination of PFOA (0.1 mM) was observed after 18 h at 70 °C [125]. Several other methods to activate persulfate have been proposed to degrade PFAS, including ultraviolet, microwave, Fe^{2+}, and ultrasound approaches. However, the highest defluorination efficiency was achieved by heat activation [126].

Sulfate radicals induce PFOA degradation but with a much lower defluorination ratio, indicating an insufficient degree of mineralization. Several short-chain perfluoroalkyl carboxylates (C2-C6) have been identified [127, 128]. The proposed reaction mechanism proceeds with a sequential elimination of CF_2 groups [129]. Decarboxylation of PFOA is induced by sulfate radical attack through the formation of a radical cation intermediate (Equations (15) and (16)).

$$SO_4^{-} \cdot + C_7F_{15}COOH \rightarrow SO_4^{2-} + C_7F_{15}COOH^+ \tag{15}$$

$$C_7F_{15}COOH^+ \cdot \rightarrow C_7F_{15} \cdot + CO_2 + H^+ \tag{16}$$

The resulting radical couples with an OH radical, producing the unstable alcohol intermediate which eventually evolves according to Equations (7)–(10).

4. Direct Photolysis

Given that PFAS does not absorb visible light and absorption is generally limited to the UVC region [130], the use of solar irradiation is not possible and artificial sources are required. In fact, the dissociation energy for C-F bonds can be up to 544 kJ/mol [102], corresponding to photons of 220 nm. UV light sources of wavelength < 220 nm and high power are somewhat less common than their UV-A or B counterparts. They have generally lower lifetime, require more specialized equipment and safety precautions, and as such the associated costs are higher. This is reflected by the scarcity of reports focusing on this approach present in literature. Nevertheless, important results can be found either in dedicated reports or extracted from photocatalysis papers where they appear as baseline or control experiments. Some results are collected in the Table 2 below:

Table 2. Direct photolysis of PFAS compounds in water.

Irradiation Wavelength (nm)	Power (Electrical, W)	Substrates	Reaction Time	Degradation/Defluorination Yield (%)	Ref.
254	200	PFOA 1.35 mM	72 h.	89/33	[116]
254	15	PFOA 0.025 mM	6 h.	13/2	[131]
185 (prevalent)	20	PFOA 0.12–2.42 µM	3 h.	87/21	[132]
254 (prevalent)				31/0.5	
185	15	PFOA 60 µM	2 h.	62/17	[133]
220–460	200	perfluoropropionic acid, perfluorobutyric acid, perfluoropentanoic acid	24 h.	16–24/9–12	[134]
254	36	PFOA 0.024 mM	8 h.	20/9	[135]

| 254 | 24 | PFOA 1 mg/L | 24 h. | 21/9 | [136] |

Although direct photolysis seems to be moderately effective for initiating degradation, the reported defluorination yields are quite low, indicating that complex mechanisms are taking place rather than simple photoinduced bond dissociation. Along with the problems related to equipment, the difficulties presented by the direct photolysis approach provide the motivation to investigate other methodologies, for example where light absorption is performed by a photocatalyst (as described in the previous section).

5. Methods Based on a Sacrificial Radical Source

A different approach involves the presence of a sacrificial agent in the solution, enabling pathways based on the generation of radical species. Among these latter, it is worth mentioning the use of aqueous electrons to perform reductive defluorination, as explored by Qu et al. [131]. These authors employed potassium iodide to generate hydrated electrons from a water–iodide complex under 254 nm wavelength irradiation from a 15 W lamp. A combination of photolysis and reduction by electrons then yielded a 96% defluorination for 0.025 mM PFOA in a 12 h experiment. Another report along the same lines is that by Zhang et al. [137], though in this case aqueous electrons, along with hydroxyl and other radicals, were generated by the more exotic approach of irradiating water with γ-rays. In addition to mineralization of around 86% and nearly 100% defluorination for 20 mg/L PFOA in a 22 h experiment, the report highlights the synergistic effect of hydroxyl radicals and aqueous electrons, which are both necessary to achieve efficient removal. Indeed, hydroxyl radical-based processes such as Fenton, photo-Fenton, and hydrogen peroxide activation are ineffective due to the inactivity of $OH°$, as also recently clarified by Javed et al. [136], who found no significant difference in PFOA degradation under UV irradiation and UV/H_2O_2. In contrast, several processes based on sulfate radicals ($SO_4^{•-}$), obtained by persulfate activation, have been reported to be effective, though defluorination efficiencies remain low. Hori et al. used a 200 W Xe-Hg UV-visible lamp to activate persulfate (50 mM) for treating 1.35 mM PFOA in a 4 h experiment, observing an 11-fold increase in decomposition with respect to direct photolysis [138]. Similarly, Chen and Zhang used UV-activated persulfate on PFOA, reporting that while using 185 nm irradiation, decomposition was proceeded by both direct photolysis and sulfate radicals, under 254 nm light the latter was the prevalent mechanism [139]. A step forward was made by introducing ferrous iron as a persulfate activator in the system, enabling a low activation energy pathway for the decomposition of persulfate to sulfate radicals [140]. Using this approach, Tran et al. recently reported 64% degradation of PFOA (initial concentration: 1.64 µM) in a 4 h anoxic experiment [141]. However, the role of light was not clarified and defluorination not discussed, leaving room for further investigations. A further effort in this direction was made by Xu et al. [11], who combined a Ga_2O_3 photocatalyst with peroxymonosulfate as a sulfate radical sacrificial source. Under illumination from either a 32 W 185 nm light or a 32 W 254 nm light, complete degradation of a PFOA solution in the 50 ng/L to 50 mg/L range was claimed, although defluorination was not quantified. A more detailed examination of persulfate-based methods (out of the scope of this work) is being currently studied, and can be found in a recent article by Yang et al. [142]. Overall, methods based on sacrificial radical sources look promising in terms of yields, but may have similar drawbacks to direct photolysis because radical generation is often performed by activation with the same artificial UVC light sources, with all its related problems. Furthermore, the sacrificial nature of the reagents used to generate the radicals implies extra costs with respect to direct photolysis or photocatalysis. In this respect, further work is needed not only to clarify the reaction mechanisms and improve efficiency but also to evaluate the economic viability and industrial scalability of this approach with respect to current methods or other methods under study.

6. Light Sources

To date, the application of photocatalysis to PFAS compounds has mostly been performed by means of the use of artificial light sources of varying wavelengths of ultraviolet A (UVA 315–400 nm) using lamps with a light emission peak at 365 nm, and ultraviolet C (UVC 100–280 nm) using lamps with peaks at 254 and 185 nm [54]. The wavelength of 185 nm itself can degrade PFAS, since the absorption of PFOA has been confirmed for this wavelength. However, this range of wavelength at the industrial level, because of the high costs, represents a market block for AOP as a possible approach for PFAS-contaminated wastewater [133].

The employment of UVA lamps with a peak at the wavelength of 365 nm has mostly been used in systems of power ranging from 125 to 300 W in TiO_2-based photocatalysts with Pt, Pd, and Ag nanoparticles or in the presence of multi-wall carbon nanotubes (MWCNTs) [57,66]. For UVC (254 nm), studies report emission powers from 16 to 500 W for pure TiO_2, TiO_2 doped with Cu, Fe, and Pb ions, and composites with molecularly imprinted polymers. Studies have also been reported using In_2O_3 and Ga_2O_3 in sheaf, needle, microsphere, nanotube, and nanoparticle forms, as well doping with nitrogen and with CeO_2 [78,82]. Applications using ZnO have been also reported [143].

Given the present situation, an advantage could be to move towards possible photocatalysts that can absorb in the near-UV range. Indeed, by using solar concentrators, the near-UV part of the solar spectrum is reflected and focused, thus permitting its utilization with photocatalysts. Anodized aluminum mirrors with special acrylic resin coatings are interesting examples for exploiting the near-UV part of the solar spectrum [144].

7. Economic Aspects

As the applications of the advanced oxidation process seem to be in an early stage in the field of PFAS remediation, to the best of our knowledge, an in-depth analysis regarding the costs of such methodologies has not yet been published.

State agency studies report an average cost of USD 2.00/gallon for PFAS treatment when considering the combined activity of GAC and AIX (anion exchange resins)) for infrastructure capacities from 2 to 50 million gallons per day (MGD) and with an initial investment from USD 3 to 120 million [145].

For budgeting PFAS management, the United States Environmental Protection Agency proposed a sequence of several necessary activities in the following order: Baseline monitoring > Public engagement > Regulatory engagement > Bench or pilot testing > Capital investment in full-scale treatment > Operation and maintenance costs of full-scale treatment > Long-term monitoring [146].

The same institution has a "Drinking water treatment technology unit cost model" and emphasizes the need for updating the model to be capable of addressing PFAS issues. The updating appears necessary because of the lack of consensus throughout the world regarding the acceptable levels of the diverse PFASs present in drinking water.

Olatunde et al. [147] undertook an economical evaluation on the applications of AOPs for degradation of PFAS substances, taking into consideration the stage of development of the technology, energy consumption, the time required to achieve 90% degradation of the substance, and the total volume of contaminated solution. Table 3 summarizes the results obtained with initial budgeting costs. The reported data show still an advantage in costs related to the use of direct photolysis, with the highest costs attributed to photocatalysis. However, the need to use radiation at a 185 nm wavelength imposes limitations to such applications in terms of lamp durability and safety. In the other hand, investments in photocatalysis research could lead to materials capable of efficiently degrading PFAS compounds with the positive feature of working under near UV-visible light.

Table 3. Relative cost comparisons between the most successful employed techniques employed for PFAS degradation (adapted from [147]).

Technology	Stage of Development	Energy (KWh/m³)	Relative Cost (USD)	Removal Efficiency (%)	Time to 90% Degradation (min)
Photolysis (185 nm)	Emerging	99	14	82	216
Photochemicals (persulfates)	Research	864	121	99	460
Photocatalysis (indium oxides + 254 nm)	Emerging	2106	295	89	705

8. Conclusions

The degradation of PFAS substances that contaminate water represents a strong challenge for the scientific, industrial, and regulation sectors. Great efforts to develop new photocatalysts able to efficiently degrade PFAS substances have been made. However, advances are still necessary to permit the full transfer of laboratory results to field applications in wastewater treatment plants. For example, photocatalysts based on indium or gallium have scarce prospects at a large scale, while some others need to be illuminated by high-power UV emission lamps that involve large costs and a limited lifetime. However, efforts have been made to develop environmentally friendly semiconductors such as zinc and titanium-based materials that, with appropriate doping or in composites, may be activated by near UV-visible radiation, thus making use of sunlight.

A shared study that highlights the sources of PFAS pollution and their evolution, while establishing intervention strategies for the further development of efficient and low-cost photocatalysts for large-scale production that favor the use of solar radiation, will allow us to effectively provide a solution for the PFAS contamination problem. The objective of this review paper is precisely to aid in this direction.

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