A Review of Emerging Photo-Induced Degradation Methods for Per- and Polyfluoroalkyl Substances (PFAS) in Water

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Abstract

The remediation of per- and polyfluoroalkyl substances (PFAS) in water continues to garner significant attention due to their environmental persistence and adverse health effects. Among the various PFAS remediation methods, photo-induced approaches have recently emerged as promising techniques for the degradation of these persistent contaminants. However, many questions remain unanswered regarding the detailed mechanisms in these photo-induced methods as well as the best ways to leverage these approaches for PFAS degradation. In this review, we provide an update on recent experimental and theoretical developments in photo-induced PFAS degradation techniques over the past 2 - 5 years. We conclude with a perspective of promising research directions in this vibrant area and give recommendations on future experimental and computational approaches needed to further advance these photo-induced remediation capabilities.

Introduction

Per- and polyfluoroalkyl substances (PFAS) are artificially-made compounds composed of strong carbon-fluorine (C–F) bonds that endow them with exceptional chemical and thermal stability. Because of their intrinsic stability, PFAS have been used in various applications, including packaging materials,[1] fire-fighting foams,[2-4] non-stick cookware,[5-6] and surfactants.[7-8] Due to their widespread use, PFAS have been detected in drinking water sources and various consumer products, which has raised significant concern since exposure to these contaminants is associated with various adverse health effects.[9-12] Because of their environmental persistence and negative human/ecological impacts, finding efficient approaches to eliminating PFAS is timely and essential.

Among the various PFAS remediation methods, photo-induced approaches have recently emerged as promising techniques for the degradation of these contaminants.[13-17] However, due to the inherent complexity of these processes, many questions remain unanswered regarding the detailed mechanisms in these emerging methods as well as the best ways to leverage these approaches for PFAS degradation. In contrast to the numerous PFAS degradation studies focusing on chemical reactions on the electronic *ground state*, there has been comparably little work on understanding the *electronic excited-state* mechanisms that actually drive the initial excitations and influence the entire degradation dynamics. Our capability to fully harness these photo-induced processes has tremendous potential to grow further as we build our understanding of these excited-state dynamical processes. The purpose of this short review is to provide an update on recent developments in photo-induced PFAS degradation techniques over the past 2 - 5 years and give a perspective of promising research directions (both experimental and theoretical) in this vibrant area.

Photo-induced PFAS degradation approaches generally fall into two broad categories: advanced oxidation processes (AOPs)[18-19] and advanced reduction processes (ARPs),[20-21] both of which are briefly reviewed below. In AOPs, light (typically in the ultraviolet (UV) range) is harnessed to generate oxidizing agents such as superoxide radicals to decompose chemical contaminants.[22] In contrast, ARPs utilize electromagnetic radiation to generate strongly reducing species (hydrated electrons (e_{aq}^-), hydrogen radicals (·H), or radicals from the catalyst itself) to induce PFAS degradation.[23-24] Despite their differences, the basic mechanism of the initial photo-induced process is similar from the viewpoint of electronic excited-state dynamics. **Figure 1** depicts a simplified schematic of the various excited-state processes in photo-induced PFAS degradation, expressed in terms of ground- and excited-state potential surfaces: **(1)** light absorption initiates a charge separation in the system (such as the photocatalytic material, the surrounding solvent, or PFAS itself), leading to **(2)** recombination/relaxation back to the initial reactant or subsequent generation of the desired oxidation/reduction products. The most salient point of **Figure 1** is that the photo-induced degradation process occurs on *different* excited-state potential surfaces and, therefore, *cannot* be fully described from the viewpoint of ground-state concepts. In other words, familiar constructs such as chemical reactivity and transition states on the electronic ground state cannot be used to describe excited-state dynamics, which is crucial for understanding these photo-induced PFAS degradation processes. Ongoing research efforts have only begun to scratch the surface of this evolving topic, and we briefly describe selected recent experimental and theoretical studies in these emerging approaches.
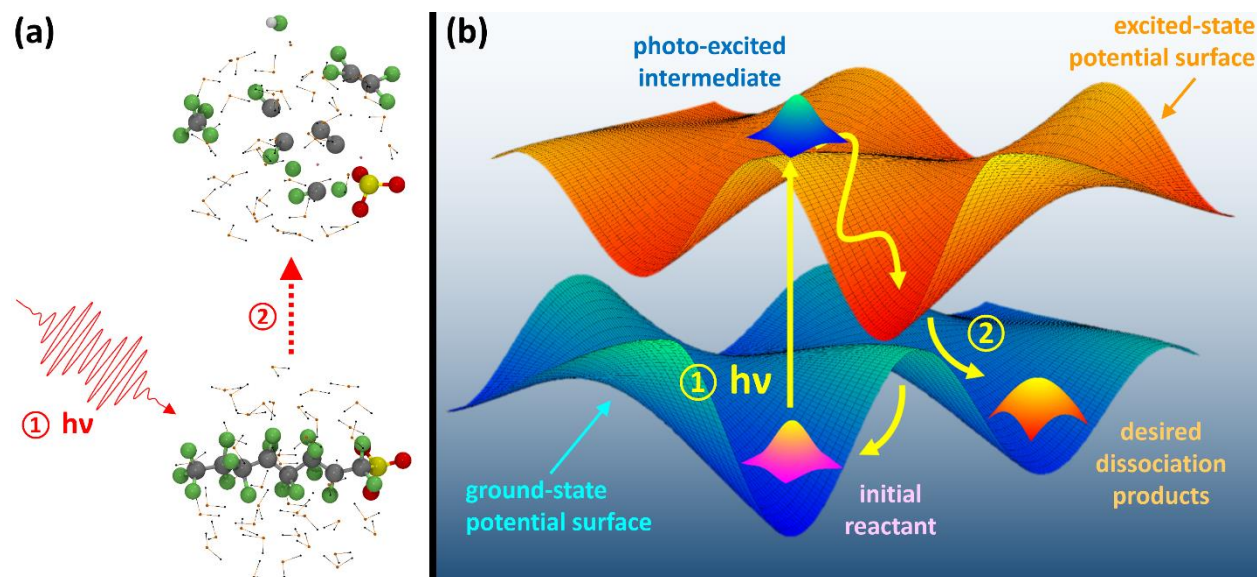
Figure 1. (a) Simplified schematic of excited-state electronic processes occurring in photo-induced PFAS degradation: **(1)** light absorption initiates a charge separation in the system, leading to **(2)** recombination/relaxation back to the initial reactant or subsequent generation of the desired oxidation/reduction products. **(b)** Same schematic as the mechanisms depicted in the left panel but expressed in terms of ground- and excited-state potential energy surfaces.

Photo-Induced AOP methods

Recent work by the Wong group at Rice University used photocatalytic BN/TiO_2 composite materials (**Figure 2(a)**) to target PFAS degradation.[25] In their photo-induced AOP experiments, the Wong group showed that BN/TiO_2 exhibited better photocatalytic activity compared to either BN or TiO_2 separately. Specifically, in the presence of UV-C (254 nm) light, BN/TiO_2 was able to degrade PFOA into shorter-chain perfluoroalkyl carboxylic acid (PFCA) intermediates (to a non-detectable PFOA concentration level of 2.4 μM) after 30 min., whereas BN required 45 min (**Figure 2(b)**). Furthermore, one hour of UV-C irradiation of BN/TiO_2 resulted in more than 50% defluorination, whereas BN and TiO_2 only resulted in 29% and 7% defluorination, respectively. Under UV-A (365 nm) light, BN/TiO_2 accelerated PFOA degradation nearly 15 times faster than TiO_2, whereas BN remained inactive. Electron paramagnetic resonance spectroscopic experiments by the Wong group showed a net charge separation across the BN/TiO_2

interface, which enables the migration of holes from TiO_2 to BN. Similar trends were also observed with UV-C light with the exception that BN can also be excited in this energy range, resulting in holes and electrons migrating toward BN and TiO_2, respectively. Based on their findings, the Wong group proposed that PFOA and short-chain PFCAs adsorb on the BN surface, react with the photogenerated holes to form perfluoroalkyl radical, and undergo a final oxidation process that leads to the shortening of the PFCA chains. Although the proposed mechanism for PFAS degradation requires further analysis, the photodegradation capabilities of composite materials, nevertheless, showed promising results.
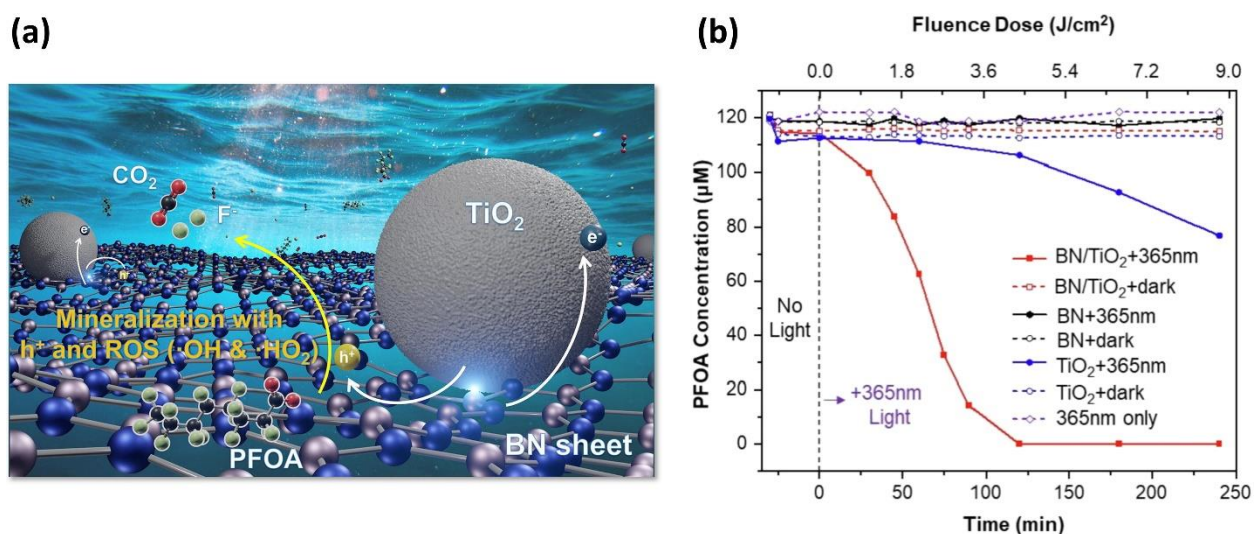
Figure 2. (a) Schematic of AOP approaches using BN/TiO_2 as the catalyst and **(b)** PFOA concentration–time profiles with and without UV-A (365-nm) irradiation using BN, TiO_2, and BN/TiO_2. After UV illumination, the photoexcited holes and generated reactive oxygen species (ROS) contributed to PFOA oxidation. The specific ROS species produced were hydroperoxyl and hydroxyl radicals. Adapted from Ref. 25.

In other AOP experiments on PFOA defluorination, the efficacy of hydroxyl radicals ($\cdot$OH) with iron-based materials has generated mixed results in UV-Fenton and UV-Fe(III) experiments.[26] To shed additional insight into this general area, the Alvarez group at Rice

University conducted experiments in the presence and absence of hydrogen peroxide (H_2O_2) and compared PFOA degradation between UV-C (254 nm) photolysis and UV-C with H_2O_2. The latter produces $\cdot OH$, which indicates that H_2O_2 hinders PFOA photolysis by absorbing UV irradiation.[27] The Alvarez group carried out irradiation experiments ranging from 1-3 days with H_2O_2 concentrations of 0.5 - 5 g/L, which broadly covers the typical concentrations used by many researchers. Further analysis of their experiments showed that a 5 g/L concentration resulted in the highest $\cdot OH$ production. In addition, the Alvarez group found that after one day of UV-C irradiation, PFOA degradation in the presence and absence of H_2O_2 was 19.7% and 21.1%, respectively, which indicates direct photolysis as the main degradation mechanism. Their defluorination results showed a similar trend, with a defluorination efficiency of 9.5% for UV/photolysis versus 6.8% for UV-C with H_2O_2. In the presence of H_2O_2, two pathways for enhancing PFOA degradation were proposed: (1) $\cdot OH$ initiates decarboxylation or (2) $\cdot OH$ accelerates the conversion of perfluorinated organic radicals to perfluorinated alcohols during intermediate steps. The present study found that $\cdot OH$ played a very minor role compared to effects from the UV-C irradiation on its own. Since optimal results were not obtained from AOP experiments using UV-C with H_2O_2, the underlying chemical mechanisms of these processes are still not well understood and additional studies are needed. Taking these techniques further, recent studies have explored applying AOP techniques to degrade complex water pollutants. For example, a study on landfill leachate degradation found that the $UV/Fe^{2+}/H_2O_2$ and $UV/Fe^{2+}/S_2O_8^{2-}$ processes achieved significant removal efficiencies for Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), and color index.[28] These recent findings underscore the potential of AOP techniques, such as $UV/Fe^{2+}/H_2O_2$ and UV/Fenton, for treating diverse water pollutants, including landfill leachate and cyanobacterial toxins.

Photo-Induced ARP Methods

While the previous studies leveraged AOP processes, there have also been complementary ARP studies to probe time-resolved excited-state dynamics in these systems. Recent work by the Hoffman group from the Linde-Robinson Laboratories at the California Institute of Technology conducted ARP experiments using humic acid (HA) as a photocatalyst.[29] By irradiating iodide with UV-C (254 nm) light, the Hoffman group showed that the presence of HA significantly increases the defluorination of PFOA. Under anaerobic conditions at 25 °C and pH = 10, their experiments showed that 1.5 hours of UV-C irradiation of iodide and HA increased PFOA decomposition and defluorination ratios to 67.5% and 23.5%, respectively. In contrast, decomposition and defluorination with only UV-C and iodide resulted in 8.7% decomposition and 3.3% defluorination ratios. To understand these effects, the Hoffman group carried out fluorescence spectroscopic studies, which allowed them to propose that the aromatic ring of HA binds with I_2 to form π-complexes, which effectively prevents I_2 molecules from quenching the hydrated electrons. In addition, their findings suggested that phenolic and quinone functional groups give rise to electron-donating and electron-transfer effects, respectively, resulting in an improved decomposition and defluorination of PFOA. After subsequent oxidation of phenolic hydroxyl groups by I_2 within the π-complexes, I^- was subsequently regenerated, which allowed for the continuous photo-production of e_{aq}^-. The quinone moieties led to an accelerated reduction of I_2 back to $2I^-$, which resulted in an accelerated decomposition of the PFOAs. In line with advancing PFAS degradation, a recent study investigated using sulfite and iodide in a UV-activated system to destroy PFAS in water.[30] This innovative approach achieved significant degradation and defluorination efficiencies for various PFAS compounds, underscoring ongoing

efforts to develop effective methods for tackling PFAS contamination. Advancements in UV/sulfite/iodide processes hold promise for PFAS treatment and expand the range of effective techniques for more comprehensive PFAS degradation solutions.
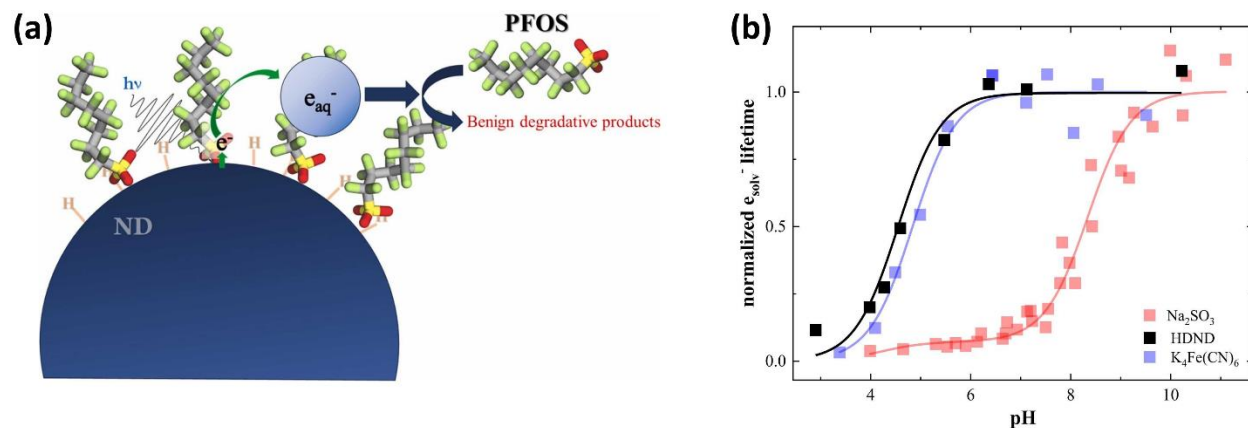
Figure 3: **(a)** Schematic of ARP approaches using HND as the catalyst, and **(b)** the hydrated electrons lifetime dependence is plotted with respect to the pH level in solutions of ferrocyanide (blue squares), sulfite (red squares), and HND (black squares). The solid lines represent a regression of data to their respective solutions. Adapted from Ref. 31.

Current state-of-the-art UV-sulfite ARP techniques are susceptible to solutions with a pH below 9, at which point bisulfite inhibits the PFOS reduction.[32] Recently, the Epshteyn group at the Naval Research Laboratory carried out UV-C (25 4nm) ARP experiments with suspended hydrogen-terminated detonation nanodiamond (HND) at varying pH levels as a source of hydrated electrons (**Figure 3(a)**).[31] Their findings showed that the lifetime of hydrated electrons in the HND solution remains constant down to ~pH = 6 but decreases at pH < 6, which resembles another common e_{aq}^- source, UV-C/ferrocyanide, shown in **Figure 3(b)**. At pH = 10, almost 85% of the initial PFOS degraded after 5 hours of irradiation in the HND solution, whereas nearly 100% of the PFOS degraded after irradiation of sulfite. On the other hand, at pH = 7, about 50% of PFOS degraded after 5 hours in the HND solution, while showing further PFOS degradation at longer

times. Solutions containing sulfite reached nearly 30% PFOS degradation after 10 mins, with no changes up to 5 hours, which is consistent with previous studies.[33] Un-buffered HND solutions were also irradiated, which resulted in 100% PFOS degradation was observed after 6 hours. From their observed reaction products, the overall PFOS degradation involved H/F exchange and chain shortening via C–C bond cleavage reactions. One such proposed H/F exchange was suggested by Bentel et al.[34] by means of a similar mechanism with both perfluorinated carboxylates and sulfonates, where the reductive defluorination of PFOS by e_{aq}^- is followed by proton abstraction from neighboring water molecules. Finally, it was reported that surface interactions contributed to a greater efficiency in the photoelectron generation, but it is still not clear whether this surface interaction either contributes to or facilitates PFOS degradation. These studies shed insight into the treatment and management of PFAS, but ongoing research efforts continue to advance these techniques and explore their applicability in different scenarios. The investigation of central composite design (CCD) and other emerging techniques continues to uncover the effects and interactions of operational parameters, enhancing our understanding of PFAS remediation.[35] Furthermore, the promising results of dry pyrolysis provide a foundation for continued exploration and optimization while efforts are underway to address residual PFAS and transformation reactions.[36-37] These ongoing experiments and proposed methods hold promise for developing more efficient and comprehensive approaches to address PFAS contamination in the environment.

PFAS degradation can be achieved through various techniques. Photolysis, involving UV light irradiation, has been explored as a simple method. More recent research has focused on UVC light and chlorine to degrade PFOA into shorter-chain PFASs, showing removal rates of 12% within 30 minutes.[38] Photolysis mechanisms involving stepwise removal of CF_2 moieties, known as the DHEH (decarboxylation − hydroxylation − elimination − hydrolysis) mechanism, have been

proposed.[39-40] However, direct photolysis without mediators is inefficient and energy intensive. To address these limitations, researchers have shifted towards photocatalysis to enhance degradation while reducing energy consumption. It is important to note that photolysis typically generates shorter-chain alkyl substances that may require further degradation.

While there have been several experimental photocatalytic and spectroscopic studies on PFAS degradation, computational/theoretical studies on time-resolved dynamics of photo-induced degradation are scarce. This disparity arises from the difficulty and complexity of calculating excited-state quantum dynamics of large chemical systems. To further understand these processes, our group recently carried out the first real-time time-dependent density functional theory (RT-TDDFT) study of electronic-excited state PFAS dynamics in the presence of external electromagnetic fields.[41] It is important to point out that most density functional theory (DFT) studies on PFAS have focused on ground-state reactions[42-43] (i.e., "after the fact" when the light-induced process has already transpired). While conventional DFT approaches can probe reaction rates and transition states in ground-state systems, they cannot describe excited-state electron dynamics (i.e., photo-induced reactions involving chemical species and adsorbates), which is crucial for describing photo-catalytic processes in PFAS. In contrast, the RT-TDDFT formalism[44] can describe electronic excited-state dynamics beyond conventional ground-state DFT to explore photo-induced mechanisms and bring a fundamental understanding of these degradation processes.

To shed mechanistic insight into these photo-induced processes, we carried out large-scale RT-TDDFT calculations to probe PFAS/PFOS degradation surrounded by 43 explicit water molecules in the presence of an external electromagnetic pulse. In a computational *tour de force*, the time-dependent Kohn-Sham equations were propagated to probe the photo-induced, excited-state dynamics responsible for initiating the defluorination process. **Figure 4** depicts the irradiated

PFOA molecule and selected snapshots of various C–F bonds as a function of time obtained from the RT-TDDFT calculations. Upon irradiation, most of the bonds in the PFOA molecule oscillate, and a few of the C–F bonds began to subsequently dissociate after 20 fs. To further understand the electronic mechanisms enabling this process, we analyzed the time-dependent Kohn-Sham orbitals, which showed that the highest occupied molecular orbital (HOMO) is almost entirely localized on the surrounding water molecules. As time progresses, the HOMO starts to delocalize onto the PFOA molecule during 8-16 fs, and a charge transfer occurs from the water to PFOA. This excess charge occupies the previously empty $3s_F$ and $2p_C$ atomic orbitals on PFOA, which possesses a strong σ* anti-bonding character. Once these empty orbitals become occupied, the C–F bond to elongate and destabilize (since the HOMO now has an anti-bonding character) until it irreversibly dissociates. It is worth mentioning that these excited-state RT-TDDFT calculations are significantly more expensive than conventional ground-state DFT calculations. In particular, these massive calculations used over 570,000 high-performance computing (HPC) hours,[45] which was recently recognized by an HPCWire 2022 Editors' Choice Award for "Best Use of HPC in Response to Societal Plights."[46]

$$i\hbar \frac{\partial \psi_n(\mathbf{r}, t)}{\partial t} = \left[\hat{\mathbf{H}}(\mathbf{r}, t) + V_{ext}(\mathbf{r}, t)\right]\psi_n(\mathbf{r}, t)$$

Time (fs)
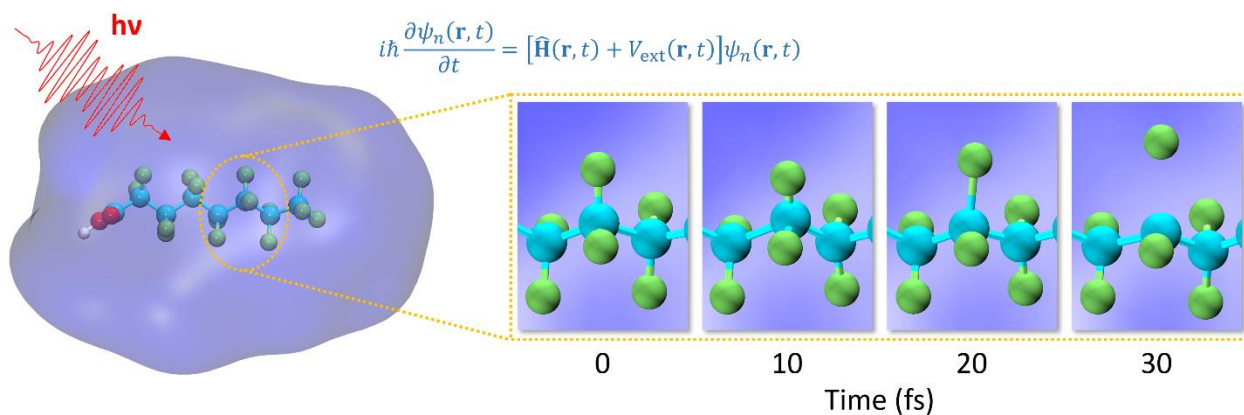
Figure 4. (a) PFOA molecule (explicit solvent not shown for clarity) with an applied optical pulse. (b) Dissociation of a C–F bond as a function of time obtained from propagation of the time-dependent Kohn-Sham equations. Adapted from Ref. 41.

Conclusion and Future Outlook

In conclusion, we have provided a brief overview of recent developments in photo-induced PFAS degradation techniques (both experimental and theoretical) in this rapidly emerging area. Compared to the numerous PFAS degradation studies of chemical reactivity on the electronic ground-state, excited-state photo-initiated processes in PFAS (*which drive the actual chemistry*) have received significantly less attention. However, recent experimental and theoretical efforts in photo-induced PFAS degradation (such as the studies examined in this review) have started to set the stage for probing these excited-state processes and providing a fundamental understanding of these degradation processes.

Nevertheless, further studies and advancements in experimental and computational approaches are still needed to push these capabilities even further. On the experimental side, several questions remain unanswered on detailed mechanisms of photo-generated holes/electrons, their reaction with water/surfaces, and/or the generation of highly reactive radicals to induce PFAS degradation. We believe that future efforts using ultrafast spectroscopic methods could shed critical insight in probing the true time-resolved nature of these complex dynamic processes. Similarly, on the theoretical side, additional work (beyond the level of conventional ground-state DFT) is needed to probe the time-resolved photo-induced dynamics of PFAS degradation. More specifically, larger quantum dynamics simulations (such as excited-state semi-empirical methods[47-50]) that can handle photocatalytic surfaces, explicit solvent, and PFAS contaminants could be a viable solution to understand time-resolved photo-induced PFAS degradation efforts in this exciting area.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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