Removal of poly- and per-fluoroalkyl substances from aqueous systems by nano-enabled water treatment technologies

<table>
<thead>
<tr>
<th>Journal:</th>
<th><em>Environmental Science: Water Research &amp; Technology</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID</td>
<td>EW-FRO-09-2018-000621.R1</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Frontier</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>08-Dec-2018</td>
</tr>
</tbody>
</table>
| Complete List of Authors: | Saleh, Navid; University of Texas at Austin, Civil, Architectural and Environmental Engineering  
Khalid, Arsalan; University of Massachusetts Lowell, Civil and Environmental Engineering  
Tian, Yuhao; Department of Civil and Environmental Engineering, Washington State University  
Ayres, Craig; University of Texas at Austin, Civil, Architectural and Environmental Engineering  
Sabaraya, Indu; University of Texas at Austin, Civil, Architectural and Environmental Engineering  
Pietari, Jaana; Exponent Inc  
Hanigan, David; University of Nevada, Reno,  
Chowdhury, Indranil; Washington State University, Civil and Environmental Engineering  
Apul, Onur; University of Massachusetts Lowell, Civil and Environmental Engineering; |
**Water Impact Statement**

Inadequate access to clean water and increasing levels of pollution is among the most concerning global problems with an expected increase in severity in coming decades. Therefore, ingenious solutions are needed in engineered water treatment systems to overcome clean water scarcity problem. This article critically reviews recently published nano-enabled strategies focusing on prominent poly- and per-fluoroalkyl substances in aqueous systems.
Removal of poly- and per-fluoroalkyl substances from aqueous systems by nano-enabled water treatment strategies

Navid B. Saleh, Arsalan Khalid, Yuhao Tian, Craig Ayres, Indu V. Sabaraya, Jaana Pietari, David Hanigan, Indranil Chowdhury, Onur G. Apul

1Civil, Architectural and Environmental Engineering, University of Texas at Austin, Austin, TX 78712
2Civil and Environmental Engineering, University of Massachusetts Lowell, Lowell, MA 01854
3Civil and Environmental Engineering, Washington State University, Pullman, WA 99164
4Exponent, Inc., Maynard, MA 01754
5Civil and Environmental Engineering, University of Nevada, Reno, Reno, NV 89557

Prepared for Submission

to

Environmental Science: Water Research and Technology (2018)

*Corresponding author: Onur G. Apul, email: onur_apul@uml.edu, phone: (978) 934-5564
Abstract

Exceptional properties at the nano-scale, if appropriately harnessed, will lead to innovations in water treatment. Nanomaterials can enable treatment processes with accelerated reaction kinetics, self-healing or self-regeneration abilities, and a high degree of selectivity for targeted pollutant removal. These materials can also introduce new pathways for the removal of contaminants that are challenging to degrade employing traditional techniques. One such class of contaminants is poly- and per-fluoroalkyl substances (PFAS), which are widely detected in waterways of the U.S. and drinking water supplies. U.S. Environmental Protection Agency (EPA) has listed two PFAS (i.e., perfluorooctanesulfonic acid or PFOS and perfluorooctanoic acid or PFOA) in the Contaminant Candidate List and recently has revised the lifetime health advisories. PFAS molecules are persistent in the environment over long periods because they are not photolyzed or biodegraded. Current mitigation technologies mostly depend on non-destructive phase transfer processes (e.g., adsorption, filtration, or ion exchange) which results in a concentrated waste stream. Few destructive mitigation methods transform PFAS by cleaving C-C bonds but it is not clear if the transformation products (e.g., shorter chain PFAS) are less toxic or less persistent. Thus, the central challenge for PFAS transformation lies in cleaving the strong C-F bonds. Nanomaterials can enable treatment options by providing high-energy reaction pathways; e.g., electrolysis, thermolysis, or photolysis. This perspective aims to present a critical review on reported PFAS removal/destruction techniques, provide molecular-level insights into possible removal/destruction pathways, and propose potential nano-enabled remediation options for these persistent contaminants.

Keywords: PFAS, PFOA nanomaterials, advanced oxidation, adsorption, photolysis, electrochemistry, thermolysis, water treatment
1. Introduction

Poly- and per-fluoroalkyl substances (PFAS) are a diverse class of over 3,000 anthropogenic compounds, which are produced for their unique amphiphilic properties and are used in applications ranging from stain and water repellents to fire suppressants\[1, 2\]. Their production in the United States began in 1949\[3, 4\], and the total global production is estimated to be in the tens of thousands of metric tonnes, and has been decreasing as some major manufacturers ceased production\[3, 5, 6\]. PFAS enter aquatic environments during use and post-application and cause reproductive, liver, and adverse immunological effects in animals, and immunotoxicological and neuro-developmental issues in children. PFAS are detectable at 1-10 ng/L in surface waters with >100 ng/L present at or near point sources\[7, 8\] or in densely populated urban areas\[9, 10\]. Some PFAS species were detected in 194 of the 4,864 public water supplies that serve more than 10,000 individuals (U.S. Environmental Protection Agency’s 3rd Unregulated Contaminant Monitoring Rule, UCMR 3)\[11\]. These persistent and toxic compounds and their degradation products are ubiquitous in biota and human domains\[3, 11-17\] thus necessitate the development of effective remediation approaches. Based on their environmental persistence and potential health risks, it necessary to develop novel and effective mitigation strategies.

Research related to mitigation over the past two decades has attempted to remove PFAS from water with conventional physicochemical treatment processes, which produce a PFAS-laden waste stream\[18-20\]. Achieving destructive C-F bond cleavage has been somewhat successful with various metal catalysts, sulfate radicals, and/or by substantial heating\[21, 22\]. There are some recent effort that focuses on developing nano-enabled PFAS remediation techniques; examples include high surface area sorbents (e.g., carbonaceous nanomaterials)\[23\], photocatalysts that result in hydrodefluorination (e.g., SiC and graphene as catalyst)\[24\] or utilize oxygen vacancies in the nanocrystals (e.g., In₂O₃), and advanced oxidants (e.g., ultrananocrystalline boron-doped conductive diamond mediated electro-oxidation)\[25, 26\]. However, research gaps in nano-remediation include limitations regarding regeneration and sorbate selectivity, overcoming thermodynamic limitations for C-F bond (with the bond strength of 544 kJ/mol) cleavage, and integrating nanomaterials into treatment devices that are safe and energy efficient. This frontiers review aims to (i) summarize non-destructive and destructive PFAS removal routes from water and provide molecular-level insights, (ii) review recent literature on reported nano-enabled techniques for PFAS removal, (iii) discuss potential nano-enabled PFAS remediation routes, which may be more effective.

2. Critical summary of PFAS removal techniques from aquatic systems

Non-Destructive Removal: Remediation of PFAS contaminated water is generally achieved by physical removal processes of adsorption and membrane filtration\[27-31\]. Regarding adsorption, the polar and apolar sorbent functional groups adsorb PFAS molecules through electrochemical interactions with the charged PFAS functional group, and hydrophobic interactions with the non-polar tail, respectively\[32-39\]. These mechanisms either in isolation or in concert are the dominant
removal mechanisms for conventional sorbents and exchange resins including activated carbon, anion exchange, and non-ionic resins, biosorbents, mineral sorbents,[40-43] modified, hierarchical designed, and hybrid mineral materials[44] e.g., mesoporous Fe₃O₄@SiO₂@CTAB–SiO₂ magnetic microspheres with a core/shell structure[33, 45-48]. Advancements in sorbents thus are necessitated, where novel adsorbents with molecular specificity, remarkable affinity for PFAS with a wide range of chemical composition, surface regenerability, and robustness against background water chemistry are realized. Membrane-based treatment techniques (e.g., nanofiltration and reverse osmosis) rely on removing PFAS by charge and size exclusion, or by sorption onto the membrane polymer. Membranes have high PFAS rejection (>99% in some cases)[28], but are constrained by energy demand and lack of molecular selectivity[49]. Both membrane rejection and sorption result in a waste stream that must be further processed.

**Destructive Removal:** Degrading PFAS is more challenging in practice but is desirable as long as the daughter products do not present higher risks than the reactants. It is generally targeted by reactive radicals (produced via photo-, electro-, sono-lysis)[50-52]. Thermal degradation can also achieve PFAS degradation at elevated temperatures (i.e., > 900 °C)[53], where bulk solution would not be in liquid phase. Furthermore, microbial-mediated routes to cleave the C-F bonds have been mostly unsuccessful with a few exceptions: anaerobic biodegradation and fungal degradation options[54].

Photolytic, sonochemical electrochemical, and photo-assisted Fenton-like reagents produce hydroxyl radicals (OH•) to break C-F bonds in PFAS in a limited capacity. Examples include zero-valent iron supported on clay and bismuth oxyhydroxyphosphate that are irradiated with UV to degrade PFOA[52, 55, 56]. Similarly, electrochemically produced OH• can react with PFAS molecules, produce perfluoro radicals on the anodes, which then undergo cascading reactions in multiple cycles to decompose short-chain PFAS molecules[50]. Electrochemical degradation has limited efficiency in generating perfluoro radicals on the anode surfaces. Materials engineering to improve anodic performance is necessary[30, 50, 57-62].

OH• have a strong electron withdrawing capability when abstractable H-atoms are available, resulting in formation of H₂O ($E^0=2.7$V). However, perfluorinated compounds (e.g., PFOA, PFOS) do not contain abstractable H atoms and thus the radical must react through direct electron transfer to form hydroxide ions, a less thermodynamically favorable reaction ($E^0=1.9$V), which results in negligible mineralization.[63-68] Synergistically coupling OH• with other radicals may result in favorable decomposition, (e.g., aqueous electrons ($e_{\text{aq}}^{-}$), which forms perfluoroalkyl radicals with $e_{\text{aq}}^{-}$, followed by an OH• addition reaction, and subsequent HF elimination).[69] Photolytic persulfate oxidation may be another decomposition method[67]; however, photoreactions are limited by the weak electro-magnetic absorbance of PFOA and PFOS[69]. Heat-activated (via Xenon-lamp irradiation) persulfate oxidation can be utilized for oxidation of PFOA to form perfluorocarboxylic acid (PFCA) under acidic conditions (pH < 3) [70, 71], potentially generating concerning by-products such as HF (pKₐ = 3.2) and ClO₃⁻[72]. On the contrary, PFOS and PFHxS was reported inert under all heat activated persulfate oxidation.
conditions tested\textsuperscript{[72]}.

In addition, Fenton reagents and sulfate radicals, high pressure and temperature requirements are some of the materials and energy limitations for practical adoption of this technology\textsuperscript{[55]}.

As an alternative to chemical oxidation, thermolysis is known to degrade PFOA and PFOS\textsuperscript{[67]} in controlled conditions. Cleavage of C\textsubscript{7}-C\textsubscript{8} bonds in PFOA at temperatures less than 1000 °C is reported\textsuperscript{[53]}; this process is found to be thermodynamically more favorable than defluorination, which can lead to the formation of shorter chain soluble byproducts. Similarly, complete degradation of PFOS with final reaction products of SO\textsubscript{2}, short-chain fluoroalkanes (e.g., CHF\textsubscript{3}, CF\textsubscript{4}, C\textsubscript{2}F\textsubscript{6}), fluorobenzene, and 1,1-difluoroethene, have been observed during lab-scale gasification (4000 °C) and incineration (900 °C)\textsuperscript{[73]}. Further investigation to gain insights into thermal degradation mechanisms can lead to approaches that can achieve complete degradation of aqueous PFAS.

Biological alternatives have mostly investigated fluorotelomer alcohols as the substrate, which yield PFOA or other shorter chain PFAS molecules. PFOA is inert under methanogenic, nitrate, sulfate and iron reducing conditions, and under aerobic respiration over a 110-day incubation period or per catabolism modeling efforts\textsuperscript{[74-77]}. \textit{P. chrysosporiium} was reported to partially degrade polyfluorinated compounds but was not able to convert perfluoroalkyl substances\textsuperscript{[54]}. A few fungal isolates related to \textit{Geomyces} mineralizes some PFAS, possibly via hemicellulose activity\textsuperscript{[54]}. Further investigation is required to identify the strains that can biodegrade PFAS. Currently, biodegradation of fluorotelomer alcohols are shown to be degraded to shorter PFAS; however, achieving further degradation is being debated.

3. Nano-enabled strategies for PFAS removal from natural waters

\textit{Nano-Enabled Non-Destructive Removal:} Nano-environmental literature has reported passive or non-destructive approaches for removal of PFAS from water over the past decade\textsuperscript{[23, 78-82]}. These approaches primarily focus on partitioning onto suspended sorbents. Though PFAS removal with nano-enabled membrane processes (or by attached sorbents) can be effective, our field has not made this a priority yet. Figure 1a shows the distribution of the PFAS and types of nano-sorbents that have been studied for sorption in single-solute systems. Also to be noted that PFOS and PFOA are the most studied compounds and there have been limited efforts directed towards other PFAS molecules\textsuperscript{[23, 79, 81]}. Particularly, there is a paucity of studies on sorptive removal of perfluorononanoic acid (PFNA) and perfluorohexanoic acid (PFHpA), despite these being part of EPA’s UCMR 3\textsuperscript{[83]}. Among the reported nano-sorbents, carbon-based nanomaterials tend to dominate; e.g., pristine and oxidized multiwalled carbon nanotubes (MWNTs) and graphene-like materials\textsuperscript{[32]}. Inorganic oxides (e.g., iron, silicon, titanium, and aluminum oxides)\textsuperscript{[39, 40, 42, 79]} have been studied as sorbents in selected studies (Figure 1b). Finally, sorption is dependent on sorbate concentration, and nearly all published literature assess adsorption performance of PFOA and PFOS at concentrations much higher than levels expected in the environment thus limiting their relevance (Figure 1c-d).
Strategies for enhanced removal with carbonaceous nanomaterials: The choice of hydrophobic carbonaceous nanomaterials as PFAS sorbents is not surprising, primarily because of the physicochemical properties of these lyophilic particulates\cite{23, 80, 81, 84, 85}. Figure 2a-b present the pseudo-equilibrium adsorption capacities of the tubular carbon allotropes, i.e., that of single-walled nanotubes (SWNTs), MWNTs, and oxidized MWNTs (O-MWNTs). PFOS is more hydrophobic than PFOA (Table 1), and thus is removed more effectively by carbonaceous nano-sorbents. Specifically, the sorption capacity for PFOS is between 85 to 260 mg/g and that for PFOA is between 1 to 72 mg/g (Figure 2). Adsorption capacity appeared to be dependent on surface area rather than on morphology (e.g., SWNTs with higher surface area adsorb greater PFOS than MWNTs with reported sorption capacity of 167 to 663 and 52 to 563 m²/g, respectively as seen in Figure 2). O-MWNTs have higher adsorption capacity compared to pristine MWNTs for both PFOS and PFOA (refer to Figure 2). This was attributed to improved wettability and dispersion with greater sorbate penetration and pore accessibility. Furthermore, the extent of hydration of the oxygen-containing moieties on the O-MWNTs may allow for preferable association of these surface groups with electron deficient atoms of the PFAS molecules via induced polarization\cite{32, 86}. Tuning surface chemistry of high surface area nano-adsorbents (e.g., SWNT) and controlling pore structure i.e., interstitial channels formed during aggregation of carbon nano-adsorbents or sheet-like graphene structures could favor selective removal of target PFAS species\cite{87}, suppress natural organic matter competition, and improve multiple-point attachment onto the ultimate sorption sites\cite{81}.

Equilibrium sorption capacity enhancement by hybridization: Mass and surface area based PFOS equilibrium adsorption capacities of carbonaceous and inorganic oxide nanoparticles are compared in Figure 2c and d, respectively. Nano-scale inorganic oxide surfaces have considerably lower sorption capacities (ranging between 0.05 and 2 mg/g) compared to carbonaceous nanomaterials (ranging between 4 and 73 mg/g). A recent study hybridized CNTs with copper oxide (6 wt.%), zinc oxide (12 wt.%) and iron oxide (12 wt.%) and showed an increase in adsorption of PFOA compared to pristine MWNTs\cite{88}. PFOS sorption on various inorganic oxides was reported to result from outer-sphere surface complexation and from hydrogen bonding between hydroxyl groups on the surfaces of the nanoparticles and the PFOS molecules\cite{79}. PFOA sorption, on the other hand, was reported to have occurred from inner-sphere surface complexation as shown with water-soluble starch-modified nano-iron oxides (n-Fe₂O₃)\cite{42}. Thus, sorbent surfaces can be tuned to selectively sorb target PFAS molecules.

Electrically augmented adsorption: Electrically augmented PFAS adsorption has also been reported as an effective but low-energy alternative for PFAS removal\cite{78}. A remarkable removal of PFOS/PFOA was observed (94 and 150 folds for PFOS and PFOA, respectively, compared to MWNT control case) when 0.6 V potential was applied\cite{78}. Similarly, CNT-graphene composite electrodes have reported adsorption capacity of 556 and 492 mg/g for PFOS and PFOA, respectively (at an applied potential of 1.5 V).\cite{89} Adsorption of charged PFAS species can be facilitated by applying a potential in the system, which induces mobility of charged species.
toward the electrode. Such charging process is non-Faradaic, i.e., electrical double layer modulated rather than Faradaic current driven. The classical electro-adsorption process for ions results in low capacity, which demands for high surface area materials to improve their performance.\textsuperscript{[90]} Nano-scale materials are ideal to fulfil such demands. We believe, nano-enabled electrode design and exploitation of the generous electron budget of graphene-based nanomaterials are also some of the most unexplored and potentially valuable nano-based PFAS remediation technologies.

\textit{Nano-enabled destructive removal—Synergistic multi-agent delivery at the C-F bonds:} Nanomaterials should be utilized in treatment or remediation applications, not to extract incremental benefits, but rather to address environmental challenges that are insurmountable to traditional approaches. Table 2 summarizes nano-enabled approaches reported in the literature. The strength of the C-F bonds necessitates novel material and/or strategy development that can allow for delivery of reactive species or directing energy (electrical or thermal) to the C-F locus, and thereby facilitate bond cleavage.

One nano-enabled strategy to attack these bonds is to synergistically combine multiple mechanisms. Effective delivery of more than one degradation agent (e.g., reactive chemicals and thermal or electrical energy) at the C-F locus may be achieved by combining localization of PFAS molecules on a surface (i.e., utilizing adsorption) with targeted delivery of the agents at that surface. For example, carbon nanotube sponges used as anodes can effectively adsorb PFAS. Upon sorption (or concentration of PFAS molecules at the anodes) electrolysis can be performed (over 180 minutes at 3.5 V) to decompose PFOA\textsuperscript{[91]}. The underlying PFOA degradation pathway is decarboxylation, as a single electron transfers from the carboxyl group of PFOA to the electrode. This electron transfer generates perfluoroheptyl radical, which is further hydrolyzed and subsequently oxidized producing fluoride ion and perfluorocarboxylic acid with one less CF$_2$ than PFOA. This CF$_2$ unzipping cycle occurs repetitively\textsuperscript{[91]}. We believe that electron delivery with nano-carbon is a promising but undervalued technology for PFAS remediation.

\textit{Utilizing inherent electronic and band properties of nano-photocatalysts:} Nano-scale photocatalysts (i.e., TiO$_2$ nanoparticles, nanostructured In$_2$O$_3$) are commonly used for degrading synthetic organic compounds\textsuperscript{[92-95]}. The material band gap (i.e., the difference between the energetic states of electronic conduction and valence bands) depends on composition, nanoparticle size, nanostructure, and surface ligands\textsuperscript{[56, 96, 97]}, and is utilized to excite electrons to the conduction band that generates holes in the valence band; both the electrons and the holes are known to generate reactive oxygen species (ROS), such as hydroxyl radical and superoxides\textsuperscript{[92-94]}. To improve the PFAS decomposition performance, various TiO$_2$ modification techniques have been developed and investigated. For example, molecularly imprinted polymers and silver nanoparticle-modified TiO$_2$ nanotubes have been developed\textsuperscript{[98]}, which enhance decomposition of PFOA by generating electron traps in Ag nanoparticles.
Band gap modulation and electron-hole pair separation are also effective approaches for improving photocatalyst performance\[^{92,99}\]. Using alternate nanostructured metal oxides with lower band gap (e.g., In\(_2\)O\(_3\) with 2.9-3.0 eV) and greater accessible surface area (e.g., porous microspheres, nanoplates and nanocubes) improvement in photocatalytic performance can be achieved\[^{99}\]. Such performances can also be increased by introducing a foreign metal that enhances electron-hole separation\[^{99}\]. For example, Pt, Pd, or Ag are used as electron acceptors in TiO\(_2\) crystals, which lead to uncombined holes that result in enhanced ROS generation\[^{92}\]. The PFOA degradation rate for Pt, Pd, Ag modified TiO\(_2\) were 12.5, 7.5 and 2.2 times higher than that for pristine TiO\(_2\), respectively\[^{92}\].

Improving electron transport can also improve degradation. TiO\(_2\) hybridized MWNT nanocomposite had much higher photocatalytic activity (PFOA degradation in 8-h increased from 19 to 89\%), likely due to the PFOA adsorption ability of the MWNTs (thereby bringing the contaminant molecules to the catalyst surface) and subsequent use of electron transport capacity of the MWNTs, which enhanced photocatalytic activity under UV irradiation\[^{100}\].

Another approach in the literature has been to take advantage of the properties of different photocatalytic nanomaterials by preparing composite structures, which resulted in improved removal performance\[^{94,95,99,101}\]. For example, ZnO/reduced-GO nanocomposites improved PFOA removal substantially (56.6\% for ZnO vs. 90.9\% for ZnO/rGO nanocomposites)\[^{102}\]. The likely mechanism was identified as the presence of heterojunctions between ZnO and reduced-GO in the composites. SiC/graphene. \(\beta\)-Ga\(_2\)O\(_3\) and zero valent iron have also been used to remove PFOA\[^{103-105}\]; however, the underlying mechanisms of removal are not completely delineated. Photocatalyst design and development should continue its search for unique material properties to achieve higher degradation efficiency of these persistent molecules.

The critical and comparative analyses presented in this perspective are intended to contribute in developing nano-enabled PFAS removal strategies. Removal and degradation of PFAS can be empowered by engaging nano-enabled techniques, where a more holistic removal approach can take advantage of the widening properties at the nano-scale with practical considerations (e.g., operation at near-ambient conditions such as pH, temperature and pressure, inexpensive and accessible nanomaterials with low environmental and public health risks). Though it has been highlighted in many earlier nano-application studies, the aspect of nano-safety needs to be considered in PFAS removal as well. For example, nanosorbents should be immobilized into a matrix to prepare a usable device. Otherwise, the release of the sorbent material into treated water will likely facilitate transport of PFAS. Similarly, catalyst materials should also be bound to surfaces to achieve effective delivery of degradation agents and harnessed energy at the C-F bond. Metal and metal oxide nanocrystals if applied to remediating PFAS, should ensure minimal to no release of toxic metal ions into the treated water. Thus thoughtful device engineering should be integrated with the intelligent material design for any successful and sustainable nano-enabled remediation approach.
Conflicts of Interest

There are no conflicts to declare

Acknowledgements

This work was partially supported by a research grant from the National Science Foundation (CBET 1511826) and by New Faculty Award and faculty start-up grants from Washington State University and start-up grant from University of Massachusetts Lowell. However, the manuscript has not been subjected to the peer and policy review of the agencies and therefore does not necessarily reflect their views.
Figure 1. Types of (a) PFAS and (b) and adsorbents tested in the recent adsorption studies and concentration ranges for adsorption experiments using (c) PFOS and (d) PFOA by nano-adsorbents reported between 2011 and 2018.[81].
Figure 2. Pseudo-equilibrium adsorption capacity comparison of carbon-based nanoparticles at 10 mg/L aqueous concentration for (a) PFOS and (b) PFOA. (c) Sorption capacity (mg/g) and (d) surface normalized sorption capacity (µg/m²) of carbonaceous compared to inorganic-oxide nano-adsorbents for PFOS removal in the literature at Cₑ = 0.5 mg/L.
Table 1. Physicochemical properties of six commonly studied PFAS.

<table>
<thead>
<tr>
<th>PFAS</th>
<th>Abbreviation</th>
<th>Molecular Formula</th>
<th>Molecular Weight (g/mol)</th>
<th>Aqueous Solubility* (g/L)</th>
<th>pK&lt;sub&gt;a&lt;/sub&gt;</th>
<th>log K&lt;sub&gt;ow&lt;/sub&gt;&lt;sup&gt;*a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluorooctanesulfonic acid*</td>
<td>PFOS</td>
<td>CF&lt;sub&gt;3&lt;/sub&gt;(CF&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;7&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;H</td>
<td>500.13</td>
<td>0.57</td>
<td>-3.27</td>
<td>5.26</td>
</tr>
<tr>
<td>Perfluorooctanoic acid*</td>
<td>PFOA</td>
<td>CF&lt;sub&gt;3&lt;/sub&gt;(CF&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;COOH</td>
<td>414.07</td>
<td>3.40</td>
<td>-0.20</td>
<td>4.59</td>
</tr>
<tr>
<td>Perfluorohexanesulfonic acid*</td>
<td>PFHxS</td>
<td>CF&lt;sub&gt;3&lt;/sub&gt;(CF&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;H</td>
<td>400.11</td>
<td>1.40</td>
<td>0.14</td>
<td>4.34</td>
</tr>
<tr>
<td>Perfluorohexanoic acid</td>
<td>PFHxA</td>
<td>CF&lt;sub&gt;3&lt;/sub&gt;(CF&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;COOH</td>
<td>314.05</td>
<td>15.7</td>
<td>-0.16</td>
<td>3.12</td>
</tr>
<tr>
<td>Perfluorobutanesulfonic acid*</td>
<td>PFBS</td>
<td>CF&lt;sub&gt;3&lt;/sub&gt;(CF&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;SO&lt;sub&gt;3&lt;/sub&gt;H</td>
<td>300.10</td>
<td>46.2</td>
<td>0.14</td>
<td>2.73</td>
</tr>
<tr>
<td>Perfluorobutanoic acid</td>
<td>PFBA</td>
<td>CF&lt;sub&gt;3&lt;/sub&gt;(CF&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;COOH</td>
<td>214.04</td>
<td>NA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.40</td>
<td>2.32</td>
</tr>
</tbody>
</table>

<sup>a</sup> Source<sup>[14]</sup>  
<sup>b</sup> Not available (miscible)  
* Listed under EPA UCMR 3<sup>[83]</sup>
### Table 2. Summary of nanomaterials utilized for PFAS destruction

<table>
<thead>
<tr>
<th>Nanomaterials</th>
<th>Methods</th>
<th>Nano-benefit</th>
<th>PFAS types</th>
<th>Performance</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon nanotube</td>
<td>Electrochemical oxidation and hydrolysis</td>
<td>PFOA is adsorbed on the CNT, increasing the concentration in anode interface.</td>
<td>PFOA</td>
<td>3 hours, &gt;90%</td>
<td>[91]</td>
</tr>
<tr>
<td>Nanoporous In$_2$O$_3$ nanosphere</td>
<td>Photocatalytic decomposition</td>
<td>Better performance due to larger specific surface area and nanoporous structure.</td>
<td>PFOA</td>
<td>3 hours, 71% at pH 3.9</td>
<td>[99]</td>
</tr>
<tr>
<td>Titanate nanotubes</td>
<td>Photocatalytic decomposition</td>
<td>Titanate nanotubes act mainly as adsorbents.</td>
<td>PFOA</td>
<td>24 hours, Defluorination ratio 85% at pH 4 68% at pH 7 55% at pH 10</td>
<td>[106]</td>
</tr>
<tr>
<td>SnO$_2$-Sb/carbon aerogel</td>
<td>Electrochemical oxidation</td>
<td>Nanomaterials with high surface area, electrical conductivity can enhance decomposition.</td>
<td>PFOA</td>
<td>5 hours, 91%</td>
<td>[57]</td>
</tr>
<tr>
<td>Titanium dioxide with multiple wall carbon nanotubes (TiO$_2$-MWCNT)</td>
<td>Photocatalytic degradation</td>
<td>The adsorption ability and electron transport capacity of MWCNT enhanced photocatalytic degradation of PFOA.</td>
<td>PFOA</td>
<td>8 hours, ~100% in acid medium.</td>
<td>[100]</td>
</tr>
<tr>
<td>Zr-doped nanocrystalline PbO$_2$ (Zr-PbO$_2$)</td>
<td>Electrocatalysis</td>
<td>The lower charge transfer resistance of Zr-PbO$_2$ improve the oxidation performance.</td>
<td>PFOA</td>
<td>1.5 hours, 81.8% at pH 4.8</td>
<td>[107]</td>
</tr>
<tr>
<td>Graphene quantum dots (GQDs) attached to SiC nanoparticles (SiC/GQDs)</td>
<td>Photocatalytic decomposition</td>
<td>The efficient electron transitions of GQDs and band gap of SiC/GQDs provide strong reductive potential to degrade PFOS.</td>
<td>PFOS</td>
<td>20 hours, 88.5% at pH 7</td>
<td>[108]</td>
</tr>
<tr>
<td>Nano-ZnO</td>
<td>Electrochemical oxidation</td>
<td>Nano-ZnO coated anode showed higher efficiency than Ti-anode. Nano-structured In$_2$O$_3$ enhanced the electron transfer between PFOA and catalyst.</td>
<td>PFOA</td>
<td>12 hours, 91% at pH 5</td>
<td>[109]</td>
</tr>
<tr>
<td>Nano-structured In$_2$O$_3$</td>
<td>Photocatalytic decomposition</td>
<td>Introducing metals reduced band gap energy of TiO$_2$ and improved electron trapping.</td>
<td>PFOA</td>
<td>12 hours, 91% at pH 5</td>
<td>[101]</td>
</tr>
<tr>
<td>Transition-metal modified TiO$_2$ nanoparticle (Fe-TiO$_2$ and Cu-TiO$_2$)</td>
<td>Photocatalytic decomposition</td>
<td>Nanoporous structure of Ga$_2$O$_3$ enhanced the decomposition.</td>
<td>PFOA</td>
<td>&lt;1 hour, ~100% at pH 4.7</td>
<td>[103]</td>
</tr>
<tr>
<td>Nanostructured gallium oxide (Ga$_2$O$_3$)</td>
<td>Photocatalytic decomposition</td>
<td>Exposed surface of In$_2$O$_3$ and enwrapping of graphene are main factor for decomposition.</td>
<td>PFOA</td>
<td>3 hours, ~90%</td>
<td>[105]</td>
</tr>
<tr>
<td>In$_2$O$_3$-graphene composite</td>
<td>Photocatalytic decomposition</td>
<td>Nanoparticle with large surface area, and reduction via dehydrohalogenation are main factors.</td>
<td>PFOA, PFOS, PFNA, PFDA</td>
<td>1 hour, 38% - 96% at pH 3</td>
<td>[110]</td>
</tr>
<tr>
<td>Nanoscale zero-valent iron (nZVI)</td>
<td>Reductive degradation</td>
<td>Noble metallic nanoparticles can capture electrons more effectively.</td>
<td>PFOA</td>
<td>7 hours, 57.7% - 100% pH 3</td>
<td>[92]</td>
</tr>
<tr>
<td>Noble metallic nanoparticle modified TiO$_2$ (M-TiO$_2$, M = Pt, Pd, Ag)</td>
<td>Photocatalytic decomposition</td>
<td>PFOA was bonded to the BiOCl through carboxyl</td>
<td>PFOA</td>
<td>12 hours, ~100% at pH 4.8</td>
<td>[111]</td>
</tr>
<tr>
<td>BiOCl nanosheets</td>
<td>Photocatalytic defluorination</td>
<td></td>
<td>PFOA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>Method</td>
<td>Reaction</td>
<td>Product</td>
<td>Conditions</td>
<td>References</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-------------------------</td>
<td>----------------------------------------------------</td>
<td>--------------------------------</td>
<td>-----------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>Pb-doped BiFeO$_3$ nanoparticles on reduced graphene oxide sheets (Pb-BFeO$_3$/rGO)</td>
<td>Microwave enhanced Fenton process</td>
<td>Production of hydroxyl radicals enhanced by Pb doping and rGO planes.</td>
<td>PFOA (50mg/L)</td>
<td>5 min ~90% at pH 5, 90°C</td>
<td>[112]</td>
</tr>
<tr>
<td>Platinum modified indium oxide nanorods (Pt/IONRs)</td>
<td>Photocatalytic degradation</td>
<td>Pt-doping and rod-like structure enhanced the light harvesting.</td>
<td>PFOA (200mg/L)</td>
<td>1 hour, 98% to 5% as pH increased from 1.85 to 9.27</td>
<td>[95]</td>
</tr>
<tr>
<td>SiC/graphene</td>
<td>Photocatalytic defluorination</td>
<td>Surface fluorination through converting Si-H bonds to Si-F bonds. Graphene can reduce the electron cloud density of C-F bonds to accelerate the defluorination.</td>
<td>PFOA (0.12mM)</td>
<td>8 hours 40.5% - 58.5% at pH 7</td>
<td>[24]</td>
</tr>
<tr>
<td>CeO$_2$-doped indium oxide (CeO$_2$/In$_2$O$_3$)</td>
<td>Photocatalytic decomposition</td>
<td>The effective inhibition of recombination of photo-generated electron-holes enhance the decomposition.</td>
<td>PFOA (100mg/L)</td>
<td>1 hour, &gt;90% at pH &lt;4.6</td>
<td>[94]</td>
</tr>
<tr>
<td>Ce-doped modified porous nanocrystalline PbO$_2$</td>
<td>Electrochemical mineralization</td>
<td>Porous and nanostructures can improve the decomposition performance.</td>
<td>PFBA, PFPeA, PFHxA, PFHpA, PFOA (100mg/l)</td>
<td>1.5 hour 49% - 95%</td>
<td>[60]</td>
</tr>
</tbody>
</table>
References


2. KEMI, Occurrence and use of highly fluorinated substances and alternatives. 2015. 7(15).


45. Li, K., et al., *Fabrication of mesoporous Fe3O4@SiO2@CTAB–SiO2 magnetic microspheres with a core/shell structure and their efficient adsorption performance for the removal of trace PFOS from water*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2015. **465**: p. 113-123.


Destructive Methods
- Photocatalysis
  - light
  - PFAS
  - Catalyst In$_2$O$_3$
- Thermolysis

Non-Destructive Methods
- Membrane Filtration
- Sorption
  - Carbon nanotubes

Removal Strategies
Perfluorooctanesulfonic acid (PFOS)
Perfluorooctanoic acid (PFOA)