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

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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

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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., In_2O_3), 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 Fe_3O_4@SiO_2@CTAB–SiO_2 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 ^{0}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 H_2O (E^0=2.7V). 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=1.9V), which results in negligible mineralization.[63-68]. Synergistically coupling OH• with other radicals may result in favorable decomposition, (e.g., aqueous electrons (e_{aq}^-), which forms perfluoroalkyl radicals with e_{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 (pK_a = 3.2) and ClO_3^-[72]. On the contrary, PFOS and PFHxS was reported inert under all heat activated persulfate oxidation conditions tested [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[55].

As an alternative to chemical oxidation, thermolysis is known to degrade PFOA and PFOS[67] in controlled conditions. Cleavage of C_7-C_8 bonds in PFOA at temperatures less than 1000 °C is reported[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_2, short-chain fluoroalkanes (e.g., CHF_3, CF_4, C_2F_6), fluorobenzene, and 1,1-difluoroethene, have been observed during lab-scale gasification (4000 °C) and incineration (900 °C)[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[74-77]. *P. chrysosporiuym* was reported to partially degrade polyfluorinated compounds but was not able to convert perfluoroalkyl substances[54]. A few fungal isolates related to *Geomyces* mineralizes some PFAS, possibly via hemicellulose activity[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, achieveing further degradation is being debated.

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

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[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[23, 79, 81]. Particularly, there is a paucity of studies on sorptive removal of perfluorononanoic acid (PFNA) and perfluoroheptanoic acid (PFHpA), despite these being part of EPA's UCMR 3[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[32]. Inorganic oxides (e.g., iron, silicon, titanium, and aluminum oxides)[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[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 m^2/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[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[87], suppress natural organic matter competition, and improve multiple-point attachment onto the ultimate sorption sites[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[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[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-Fe_2O_3)[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[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[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).[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.[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.

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[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[91]. We believe that electron delivery with nano-carbon is a promising but undervalued technology for PFAS remediation.

Utilizing inherent electronic and band properties of nano-photocatalysts: Nano-scale photocatalysts (i.e., TiO_2 nanoparticles, nanostructured In_2O_3) are commonly used for degrading synthetic organic compounds[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[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[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[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_2O_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. β-Ga_2O_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

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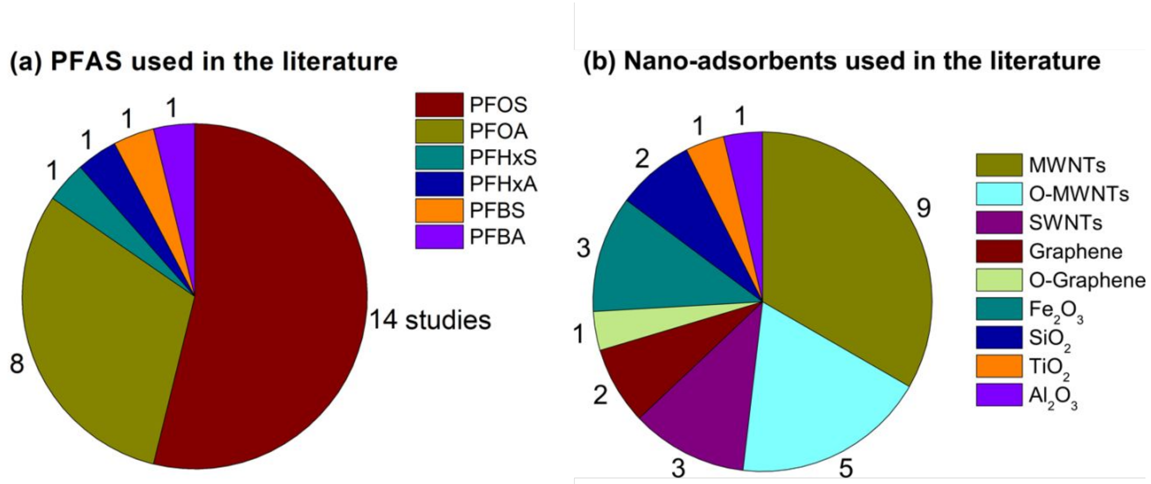


(c) Reported PFOS concentration ranges compiled from nano-adsorbent experiments

(d) Reported PFOA concentration ranges compiled from nano-adsorbent experiments

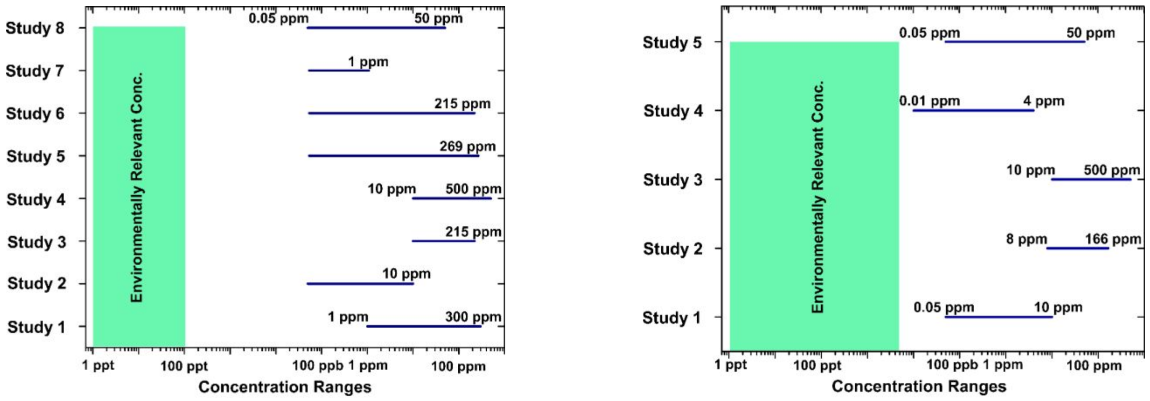


Figure 1. Types of **(a)** PFAS and **(b)** and adsorbents tested in the recent adsorption studies and concentration ranges for adsorption experiments using **(c)** PFOS and **(d)** PFOA by nano-adsorbents reported between 2011 and 2018[81].

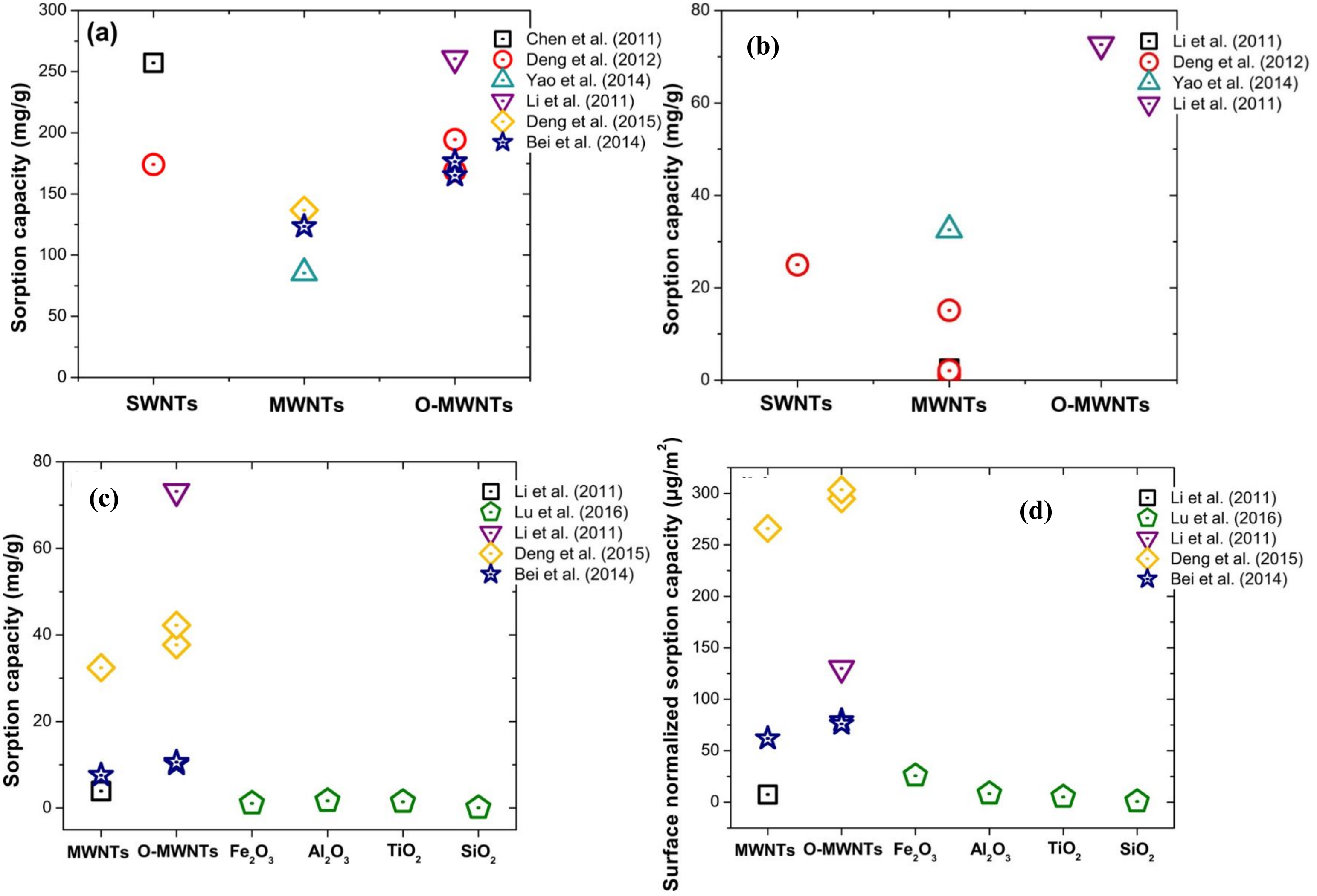


Figure 2. Pseudo-equilibrium adsorption capacity comparison of carbon-based nanoparticles at 10 mg/L aqueous concentration for **(a)** PFOS and **(b)** PFOA. **(c)** Sorption capacity (mg/g) and **(d)** surface normalized sorption capacity (μg/m^2) of carbonaceous compared to inorganic-oxide nano-adsorbents for PFOS removal in the literature at C_e = 0.5 mg/L.

Table 1. Physicochemical properties of six commonly studied PFAS.

PFAS	**Abbreviation**	**Molecular Formula**	**Molecular Weight (g/mol)**	**Aqueous Solubility**[a] **(g/L)**	**pK_a**[a]	**log K_{ow}**[a]
Perfluorooctanesulfonic acid*	PFOS	$CF_3(CF_2)_7SO_3H$	500.13	0.57	-3.27	5.26
Perfluorooctanoic acid*	PFOA	$CF_3(CF_2)_6COOH$	414.07	3.40	-0.20	4.59
Perfluorohexanesulfonic acid*	PFHxS	$CF_3(CF_2)_5SO_3H$	400.11	1.40	0.14	4.34
Perfluorohexanoic acid	PFHxA	$CF_3(CF_2)_4COOH$	314.05	15.7	-0.16	3.12
Perfluorobutanesulfonic acid*	PFBS	$CF_3(CF_2)_3SO_3H$	300.10	46.2	0.14	2.73
Perfluorobutanoic acid	PFBA	$CF_3(CF_2)_2COOH$	214.04	NA[b]	0.40	2.32

[a] Source[14]
[b] Not available (miscible)
[*] Listed under EPA UCMR 3[83]

Table 2. Summary of nanomaterials utilized for PFAS destruction

Nanomaterials	Methods	Nano-benefit	PFAS types	Performance	References
Carbon nanotube	Electrochemical oxidation and hydrolysis	PFOA is adsorbed on the CNT, increasing the concentration in anode interface.	PFOA (100µg/L)	3 hours, >90%	[91]
Nanoporous In_2O_3 nanosphere	Photocatalytic decomposition	Better performance due to larger specific surface area and nanoporous structure.	PFOA (30mg/L)	3 hours, 71% at pH 3.9	[99]
Titanate nanotubes	Photocatalytic decomposition	Titanate nanotubes act mainly as adsorbents.	PFOA (50mg/L)	24 hours, Defluorination ratio 85% at pH 4 68% at pH 7 55% at pH 10	[106]
SnO_2-Sb/carbon aerogel	Electrochemical oxidation	Nanomaterials with high surface area, electrical conductivity can enhance decomposition.	PFOA (100mg/L)	5 hours, 91%	[57]
Titanium dioxide with multiple wall carbon nanotubes (TiO_2-MWCNT)	Photocatalytic degradation	The adsorption ability and electron transport capacity of MWCNT enhanced photocatalytic degradation of PFOA.	PFOA (30mg/L)	8 hours, ~100% in acid medium.	[100]
Zr-doped nanocrystalline PbO_2 (Zr-PbO_2)	Electrocatalysis	The lower charge transfer resistance of Zr-PbO_2 improve the oxidation performance.	PFOA (20mg/L)	1.5 hours, 81.8% at pH 4.8	[107]
Graphene quantum dots (GQDs) attached to SiC nanoparticles (SiC/GQDs)	Photocatalytic decomposition	The efficient electron transitions of GQDs and band gap of SiC/GQDs provide strong reductive potential to degrade PFOS.	PFOS (0.019mM)	20 hours, 88.5% at pH 7	[108]
Nano-ZnO	Electrochemical oxidation	Nano-ZnO coated anode showed higher efficiency than Ti-anode.	12 PFCs (0.03ng/L – 6.37ng/L)	40min, 38.95% - 65.84% at pH 7	[109]
Nano-structured In_2O_3	Photocatalytic decomposition	Nano-structured In_2O_3 enhanced the electron transfer between PFOA and catalyst.	PFOA (30mg/L)	40 – 120 min, ~100% at pH 3.9	[101]
Transition-metal modified TiO_2 nanoparticle (Fe-TiO_2 and Cu-TiO_2)	Photocatalytic decomposition	Introducing metals reduced band gap energy of TiO_2 and improved electron trapping.	PFOA (50mg/L)	12 hours, 91% at pH 5	[93]
Nanostructured gallium oxide (Ga_2O_3)	Photocatalytic decomposition	Nanoporous structure of Ga_2O_3 enhanced the decomposition.	PFOA (0.5mg/L)	<1 hour, ~100% at pH 4.7	[103]
In_2O_3-graphene composite	Photocatalytic decomposition	Exposed surface of In_2O_3 and enwrapping of graphene are main factor for decomposition.	PFOA (30mg/L)	3 hours ~90%	[105]
Nanoscale zero-valent iron (nZVI)	Reductive degradation	Nanoparticle with large surface area, and reduction via dehydrohalogenation are main factors.	PFOA, PFOS, PFNA, PFDA (0.2mg/L)	1 hour, 38% - 96% at pH 3	[110]
Noble metallic nanoparticle modified TiO_2 (M-TiO_2, M = Pt, Pd, Ag)	Photocatalytic decomposition	Noble metallic nanoparticles can capture electrons more effectively.	PFOA (60mg/L)	7 hours, 57.7% - 100% pH 3	[92]
BiOCl nanosheets	Photocatalytic defluorination	PFOA was bonded to the BiOCl through carboxyl	PFOA (20µM)	12 hours, ~100% at pH 4.8	[111]

		group. The build-in electric field in BiOCl nanosheets enhance the separation of electron-hole pair.			
Pb-doped $BiFeO_3$ nanoparticles on reduced graphene oxide sheets (Pb-$BFeO_3$/rGO)	Microwave enhanced Fenton process	Production of hydroxyl radicals enhanced by Pb doping and rGO planes.	PFOA (50mg/L)	5 min ~90% at pH 5, 90°C	[112]
Platinum modified indium oxide nanorods (Pt/IONRs)	Photocatalytic degradation	Pt-doping and rod-like structure enhanced the light harvesting.	PFOA (200mg/L)	1 hour, 98% to 5% as pH increased from 1.85 to 9.27	[95]
SiC/graphene	Photocatalytic defluorination	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.	PFOA (0.12mM)	8 hours 40.5% - 58.5% at pH 7	[24]
CeO_2-doped indium oxide (CeO_2/In_2O_3)	Photocatalytic decompostion	The effective inhibition of recombination of photo-generated electron-holes enhance the decomposition.	PFOA (100mg/L)	1 hour, >90% at pH <4.6	[94]
Ce-doped modified porous nanocrystalline PbO_2	Electrochemical mineralization	Porous and nanostructures can improve the decomposition performance.	PFBA, PFPeA, PFHxA, PFHpA, PFOA (100mg/l)	1.5 hour 49% - 95%	[60]

References

1. Concawe, *Environmental fate and effects of poly- and perfluoroalkyl substances (PFAS).* 2016. **8**(16).

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

3. Paul, A.G., K.C. Jones, and A.J. Sweetman, *A First Global Production, Emission, And Environmental Inventory For Perfluorooctane Sulfonate.* Environmental Science & Technology, 2009. **43**(2): p. 386-392.

4. 3M, *The Science of Organic Fluorochemistry.* 1999.

5. Prevedouros, K., et al., *Sources, Fate and Transport of Perfluorocarboxylates.* Environmental Science & Technology, 2006. **40**(1): p. 32-44.

6. Smithwick, M., et al., *Circumpolar Study of Perfluoroalkyl Contaminants in Polar Bears (Ursus maritimus).* Environmental Science & Technology, 2005. **39**(15): p. 5517-5523.

7. Boiteux, V., et al., *Concentrations and patterns of perfluoroalkyl and polyfluoroalkyl substances in a river and three drinking water treatment plants near and far from a major production source.* Science of The Total Environment, 2017. **583**: p. 393-400.

8. Zareitalabad, P., et al., *Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater – A review on concentrations and distribution coefficients.* Chemosphere, 2013. **91**(6): p. 725-732.

9. Post, G.B., et al., *Occurrence of Perfluorinated Compounds in Raw Water from New Jersey Public Drinking Water Systems.* Environmental Science & Technology, 2013. **47**(23): p. 13266-13275.

10. Zhang, X., et al., *Source Attribution of Poly- and Perfluoroalkyl Substances (PFASs) in Surface Waters from Rhode Island and the New York Metropolitan Area.* Environmental Science & Technology Letters, 2016. **3**(9): p. 316-321.

11. Hu, X.C., et al., *Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants.* Environmental Science & Technology Letters, 2016. **3**(10): p. 344-350.

12. Lindim, C., J. van Gils, and I.T. Cousins, *Europe-wide estuarine export and surface water concentrations of PFOS and PFOA.* Water Research, 2016. **103**: p. 124-132.

13. Lam, J.C.W., et al., *Perfluoroalkyl Substances (PFASs) in Marine Mammals from the South China Sea and Their Temporal Changes 2002–2014: Concern for Alternatives of PFOS?* Environmental Science & Technology, 2016. **50**(13): p. 6728-6736.

14. Xiao, F., et al., *Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in soils and groundwater of a U.S. metropolitan area: Migration and implications for human exposure.* Water Research, 2015. **72**: p. 64-74.

15. Yeung, L.W.Y., et al., *Part I. A Temporal Study of PFCAs and Their Precursors in Human Plasma from Two German Cities 1982–2009.* Environmental Science & Technology, 2013. **47**(8): p. 3865-3874.

16. Giesy, J.P. and K. Kannan, *Global Distribution of Perfluorooctane Sulfonate in Wildlife.* Environmental Science & Technology, 2001. **35**(7): p. 1339-1342.

17. Gobelius, L., et al., *Per- and Polyfluoroalkyl Substances in Swedish Groundwater and Surface Water: Implications for Environmental Quality Standards and Drinking Water Guidelines.* Environmental Science & Technology, 2018. **52**(7): p. 4340-4349.

18. Xiao, F., M.F. Simcik, and J.S. Gulliver, *Mechanisms for removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from drinking water by conventional and enhanced coagulation.* Water Research, 2013. **47**(1): p. 49-56.

19. Eschauzier, C., et al., *Impact of Treatment Processes on the Removal of Perfluoroalkyl Acids from the Drinking Water Production Chain.* Environmental Science & Technology, 2012. **46**(3): p. 1708-1715.

20. Nancy, M., et al., *Degradation and Removal Methods for Perfluoroalkyl and Polyfluoroalkyl Substances in Water.* Environmental Engineering Science, 2016. **33**(9): p. 615-649.

21. Choi, J., et al., *Net Oxidative Addition of C(sp<sup>3</sup>)-F Bonds to Iridium via Initial C-H Bond Activation.* Science, 2011. **332**(6037): p. 1545.

22. Sabater, S., J.A. Mata, and E. Peris, *Hydrodefluorination of carbon–fluorine bonds by the synergistic action of a ruthenium–palladium catalyst.* Nature Communications, 2013. **4**: p. 2553.

23. Deng, S., et al., *Sorption mechanisms of perfluorinated compounds on carbon nanotubes.* Environmental Pollution, 2012. **168**: p. 138-144.

24. Huang, D., L. Yin, and J. Niu, *Photoinduced Hydrodefluorination Mechanisms of Perfluorooctanoic Acid by the SiC/Graphene Catalyst.* Environmental Science & Technology, 2016. **50**(11): p. 5857-5863.

25. Gomez-Ruiz, B., et al., *Photocatalytic degradation and mineralization of perfluorooctanoic acid (PFOA) using a composite TiO2 −rGO catalyst.* Journal of Hazardous Materials, 2018. **344**: p. 950-957.

26. Urtiaga, A., et al., *Kinetics of the electrochemical mineralization of perfluorooctanoic acid on ultrananocrystalline boron doped conductive diamond electrodes.* Chemosphere, 2015. **129**: p. 20-26.

27. Soriano, Á., D. Gorri, and A. Urtiaga, *Efficient treatment of perfluorohexanoic acid by nanofiltration followed by electrochemical degradation of the NF concentrate.* Water Research, 2017. **112**: p. 147-156.

28. Tang, C.Y., et al., *Use of Reverse Osmosis Membranes to Remove Perfluorooctane Sulfonate (PFOS) from Semiconductor Wastewater.* Environmental Science & Technology, 2006. **40**(23): p. 7343-7349.

29. Tang, C.Y., et al., *Effect of Flux (Transmembrane Pressure) and Membrane Properties on Fouling and Rejection of Reverse Osmosis and Nanofiltration Membranes Treating Perfluorooctane Sulfonate Containing Wastewater.* Environmental Science & Technology, 2007. **41**(6): p. 2008-2014.

30. Zhao, C., et al., *Perfluorooctane sulfonate removal by nanofiltration membrane—the effect and interaction of magnesium ion / humic acid.* Journal of Membrane Science, 2016. **503**: p. 31-41.

31. Yu, J., et al., *Removal of perfluorinated compounds by membrane bioreactor with powdered activated carbon (PAC): Adsorption onto sludge and PAC.* Desalination, 2014. **334**(1): p. 23-28.

32. Meng, P., et al., *Role of Air Bubbles Overlooked in the Adsorption of Perfluorooctanesulfonate on Hydrophobic Carbonaceous Adsorbents.* Environmental Science & Technology, 2014. **48**(23): p. 13785-13792.

33. Yu, Q., et al., *Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: Kinetic and isotherm study.* Water Research, 2009. **43**(4): p. 1150-1158.

34. Chularueangaksorn, P., et al., *Adsorption of perfluorooctanoic acid (PFOA) onto anion exchange resin, non-ion exchange resin, and granular-activated carbon by batch and column.* Desalination and Water Treatment, 2014. **52**(34-36): p. 6542-6548.

35. Rattanaoudom, R., C. Visvanathan, and S.K. Boontanon, *Removal of concentrated PFOS and PFOA in synthetic industrial wastewater by powder activated carbon and hydrotalcite*. Vol. 2. 2012. 245-258.

36. Ochoa-Herrera, V. and R. Sierra-Alvarez, *Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge.* Chemosphere, 2008. **72**(10): p. 1588-1593.

37. Senevirathna, S.T.M.L.D., et al., *Adsorption of perfluorooctane sulfonate (n-PFOS) onto non ion-exchange polymers and granular activated carbon: Batch and column test.* Desalination, 2010. **260**(1): p. 29-33.

38. Senevirathna, S.T.M.L.D., et al., *A comparative study of adsorption of perfluorooctane sulfonate (PFOS) onto granular activated carbon, ion-exchange polymers and non-ion-exchange polymers.* Chemosphere, 2010. **80**(6): p. 647-651.

39. Gao, X. and J. Chorover, *Adsorption of perfluorooctanoic acid and perfluorooctanesulfonic acid to iron oxide surfaces as studied by flow-through ATR-FTIR spectroscopy.* Environmental Chemistry, 2012. **9**(2): p. 148-157.

40. Tang, C.Y., et al., *Effect of solution chemistry on the adsorption of perfluorooctane sulfonate onto mineral surfaces.* Water Research, 2010. **44**(8): p. 2654-2662.

41. Yao, Y., Volchek, K., Brown, C.E., Robinson, A., Obal, T., *Comparative study on adsorption of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) by different adsorbents in water.* Water Science and Technology, 2014. **70**(12): p. 1983-1991.

42. Gong, Y., et al., *Removal of aqueous perfluorooctanoic acid (PFOA) using starch-stabilized magnetite nanoparticles.* Science of The Total Environment, 2016. **562**: p. 191-200.

43. Johnson, R.L., et al., *The Adsorption of Perfluorooctane Sulfonate onto Sand, Clay, and Iron Oxide Surfaces.* Journal of Chemical & Engineering Data, 2007. **52**(4): p. 1165-1170.

44. Zhang, X., et al., *Chitosan-Coated Octadecyl-Functionalized Magnetite Nanoparticles: Preparation and Application in Extraction of Trace Pollutants from Environmental Water Samples.* Analytical Chemistry, 2010. **82**(6): p. 2363-2371.

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.

46. Deng, S., et al., *Removal of perfluorooctane sulfonate from wastewater by anion exchange resins: Effects of resin properties and solution chemistry.* Water Research, 2010. **44**(18): p. 5188-5195.

47. Chen, H., et al., *Sorption of perfluorooctane sulfonate (PFOS) on marine sediments.* Marine Pollution Bulletin, 2012. **64**(5): p. 902-906.

48. Jia, C., C. You, and G. Pan, *Effect of temperature on the sorption and desorption of perfluorooctane sulfonate on humic acid.* Journal of Environmental Sciences, 2010. **22**(3): p. 355-361.

49. Arias Espana, V.A., M. Mallavarapu, and R. Naidu, *Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA): A critical review with an emphasis on field testing.* Environmental Technology & Innovation, 2015. **4**: p. 168-181.

50. Chaplin, B.P., *Critical review of electrochemical advanced oxidation processes for water treatment applications.* Environmental Science: Processes & Impacts, 2014. **16**(6): p. 1182-1203.

51. Fernandez, N.A., et al., *Effect of chemical structure on the sonochemical degradation of perfluoroalkyl and polyfluoroalkyl substances (PFASs).* Environmental Science: Water Research & Technology, 2016. **2**(6): p. 975-983.

52. Gole, V.L., et al., *Treatment of perfluorooctane sulfonic acid (PFOS) using a large-scale sonochemical reactor.* Separation and Purification Technology, 2018. **194**: p. 104-110.

53. Liu, J., et al., *Thermal- and photo-induced degradation of perfluorinated carboxylic acids: Kinetics and mechanism.* Water Research, 2017. **126**: p. 12-18.

54. Tseng, N.S., *Feasibility of Biodegradation of Polyfluoroalkyl and Perfluoroalkyl Substances.* 2012.

55. Hori, H., et al., *Efficient Decomposition of Environmentally Persistent Perfluorooctanesulfonate and Related Fluorochemicals Using Zerovalent Iron in Subcritical Water.* Environmental Science & Technology, 2006. **40**(3): p. 1049-1054.

56. Sahu, S.P., et al., *Rapid Degradation and Mineralization of Perfluorooctanoic Acid by a New Petitjeanite Bi3O(OH)(PO4)2 Microparticle Ultraviolet Photocatalyst.* Environmental Science & Technology Letters, 2018. **5**(8): p. 533-538.

57. Zhao, H., et al., *Fabrication of novel SnO2-Sb/carbon aerogel electrode for ultrasonic electrochemical oxidation of perfluorooctanoate with high catalytic efficiency.* Applied Catalysis B: Environmental, 2013. **136-137**: p. 278-286.

58. Carter, K.E. and J. Farrell, *Oxidative Destruction of Perfluorooctane Sulfonate Using Boron-Doped Diamond Film Electrodes.* Environmental Science & Technology, 2008. **42**(16): p. 6111-6115.

59. Trautmann, A., Schell, H., Schmidt, R., Mangold, K. Tiehm, A., *Electrochemical degradation of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in groundwater.* Water Science and Technology, 2015. **71**(10): p. 1569-1575.

60. Niu, J., et al., *Electrochemical Mineralization of Perfluorocarboxylic Acids (PFCAs) by Ce-Doped Modified Porous Nanocrystalline PbO2 Film Electrode.* Environmental Science & Technology, 2012. **46**(18): p. 10191-10198.

61. Cheng, J.-h., et al., *Photochemical defluorination of aqueous perfluorooctanoic acid (PFOA) by VUV/Fe3+ system.* Chemical Engineering Journal, 2014. **239**: p. 242-249.

62. Schaefer, C.E., et al., *Electrochemical treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in groundwater impacted by aqueous film forming foams (AFFFs).* Journal of Hazardous Materials, 2015. **295**: p. 170-175.

63. Mitchell, S.M., et al., *Degradation of Perfluorooctanoic Acid by Reactive Species Generated through Catalyzed H2O2 Propagation Reactions.* Environmental Science & Technology Letters, 2014. **1**(1): p. 117-121.

64. Wardman , P., *Reduction Potentials of One ‐ Electron Couples Involving Free Radicals in Aqueous Solution.* Journal of Physical and Chemical Reference Data, 1989. **18**(4): p. 1637-1755.

65. Ribeiro, A.R., et al., *An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU.* Environment International, 2015. **75**: p. 33-51.

66. Schröder, H.F. and R.J.W. Meesters, *Stability of fluorinated surfactants in advanced oxidation processes—A follow up of degradation products using flow injection–mass spectrometry, liquid chromatography–mass spectrometry and liquid chromatography–multiple stage mass spectrometry.* Journal of Chromatography A, 2005. **1082**(1): p. 110-119.

67. Vecitis, C.D., et al., *Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA).* Frontiers of Environmental Science & Engineering in China, 2009. **3**(2): p. 129-151.

68. Dorfman, L.M. and G.E. Adams, *Reactivity of the hydroxyl radical in aqueous solutions*. 1973, National Standard Reference Data System.

69. Zhang, Z., et al., *Complete mineralization of perfluorooctanoic acid (PFOA) by γ-irradiation in aqueous solution.* Scientific Reports, 2014. **4**: p. 7418.

70. Bruton, T.A. and D.L. Sedlak, *Treatment of Aqueous Film-Forming Foam by Heat-Activated Persulfate Under Conditions Representative of In Situ Chemical Oxidation.* Environmental Science & Technology, 2017. **51**(23): p. 13878-13885.

71. Lutze, H.V., et al., *Degradation of perfluorinated compounds by sulfate radicals – New mechanistic aspects and economical considerations.* Water Research, 2018. **129**: p. 509-519.

72. Bruton, T.A. and D.L. Sedlak, *Treatment of perfluoroalkyl acids by heat-activated persulfate under conditions representative of in situ chemical oxidation.* Chemosphere, 2018. **206**: p. 457-464.

73. UDRI, *Laboratory scale thermal degradation of perfluoro-octanyl sulfonate and related precursors.* 2003.

74. Butt, C.M., D.C.G. Muir, and S.A. Mabury, *Biotransformation pathways of fluorotelomer-based polyfluoroalkyl substances: A review.* Environmental Toxicology and Chemistry, 2014. **33**(2): p. 243-267.

75. Parsons, J.R., et al., *Biodegradation of Perfluorinated Compounds*, in *Reviews of Environmental Contamination and Toxicology Vol 196*, D.M. Whitacre, Editor. 2008, Springer US: New York, NY. p. 53-71.

76. Liou, J.S.C., et al., *Investigating the biodegradability of perfluorooctanoic acid.* Chemosphere, 2010. **80**(2): p. 176-183.

77. Dimitrov, S., et al., *Predicting the biodegradation products of perfluorinated chemicals using CATABOL.* SAR and QSAR in Environmental Research, 2004. **15**(1): p. 69-82.

78. Li, X., et al., *Enhanced Adsorption of PFOA and PFOS on Multiwalled Carbon Nanotubes under Electrochemical Assistance.* Environmental Science & Technology, 2011. **45**(19): p. 8498-8505.

79. Lu, X., et al., *Adsorption behavior and mechanism of perfluorooctane sulfonate on nanosized inorganic oxides.* Journal of Colloid and Interface Science, 2016. **474**: p. 199-205.

80. Bei, Y., Deng, S., Du, B., Wang, B., Huang, J., Yu, G., *Adsorption of perfluorooctane sulfonate on carbon nanotubes: influence of pH and competitive ions.* Water Science and Technology, 2014. **69**(7): p. 1489-1495.

81. Deng, S., et al., *Effect of co-existing organic compounds on adsorption of perfluorinated compounds onto carbon nanotubes.* Frontiers of Environmental Science & Engineering, 2015. **9**(5): p. 784-792.

82. Dai, Y., et al., *Enhanced sorption of perfluorooctane sulfonate (PFOS) on carbon nanotube-filled electrospun nanofibrous membranes.* Chemosphere, 2013. **93**(8): p. 1593-1599.

83. USEPA, *Third unregulated contaminant monitorng rule: Fact sheet for assessment monitoring of List 1 contaminants.* 2012.

84. Li, X., et al., *Adsorption of ionizable organic contaminants on multi-walled carbon nanotubes with different oxygen contents.* Journal of Hazardous Materials, 2011. **186**(1): p. 407-415.

85. Chen, X., et al., *A comparative study on sorption of perfluorooctane sulfonate (PFOS) by chars, ash and carbon nanotubes.* Chemosphere, 2011. **83**(10): p. 1313-1319.

86. Tessmer, C.H., R.D. Vidic, and L.J. Uranowski, *Impact of Oxygen-Containing Surface Functional Groups on Activated Carbon Adsorption of Phenols.* Environmental Science & Technology, 1997. **31**(7): p. 1872-1878.

87. Cao, F., et al., *Synthesis and application of a highly selective molecularly imprinted adsorbent based on multi-walled carbon nanotubes for selective removal of perfluorooctanoic acid.* Environmental Science: Water Research & Technology, 2018. **4**(5): p. 689-700.

88. Liu, L., et al., *Improved sorption of perfluorooctanoic acid on carbon nanotubes hybridized by metal oxide nanoparticles.* Environmental Science and Pollution Research, 2018. **25**(16): p. 15507-15517.

89. Niu, Z., et al., *Electrochemically enhanced removal of perfluorinated compounds (PFCs) from aqueous solution by CNTs-graphene composite electrode.* Chemical Engineering Journal, 2017. **328**: p. 228-235.

90. Oren, Y., H. Tobias, and A. Soffer, *Removal of bacteria from water by electroadsorption on porous carbon electrodes.* Bioelectrochemistry and Bioenergetics, 1983. **11**(4): p. 347-351.

91. Xue, A., et al., *Electro-oxidation of perfluorooctanoic acid by carbon nanotube sponge anode and the mechanism.* Chemosphere, 2015. **141**: p. 120-126.

92. Li, M., et al., *Photocatalytic decomposition of perfluorooctanoic acid by noble metallic nanoparticles modified TiO2.* Chemical Engineering Journal, 2016. **286**: p. 232-238.

93. Chen, M.-J., et al., *Photocatalytic decomposition of perfluorooctanoic acid by transition-metal modified titanium dioxide.* Journal of Hazardous Materials, 2015. **288**: p. 168-175.

94. Jiang, F., et al., *Enhancement of photocatalytic decomposition of perfluorooctanoic acid on CeO2/In2O3.* RSC Advances, 2016. **6**(76): p. 72015-72021.

95. Xu, C., et al., *Platinum modified indium oxide nanorods with enhanced photocatalytic activity on degradation of perfluorooctanoic acid (PFOA).* Journal of the Taiwan Institute of Chemical Engineers, 2017. **80**: p. 761-768.

96. Brown, P.R., et al., *Energy Level Modification in Lead Sulfide Quantum Dot Thin Films through Ligand Exchange.* ACS Nano, 2014. **8**(6): p. 5863-5872.

97. Segets, D., et al., *Determination of the Quantum Dot Band Gap Dependence on Particle Size from Optical Absorbance and Transmission Electron Microscopy Measurements.* ACS Nano, 2012. **6**(10): p. 9021-9032.

98. Tian, A., Y. Wu, and K. Mao, *Enhanced performance of surface modified TiO2 nanotubes for the decomposition of perfluorooctanoic acid*. 2017. 020029.

99. Li, Z., et al., *Different nanostructured In2O3 for photocatalytic decomposition of perfluorooctanoic acid (PFOA).* Journal of Hazardous Materials, 2013. **260**: p. 40-46.

100. Song, C., et al., *Photodegradation of perfluorooctanoic acid by synthesized TiO2–MWCNT composites under 365nm UV irradiation.* Chemosphere, 2012. **86**(8): p. 853-859.

101. Li, Z., et al., *In2O3 nanoporous nanosphere: A highly efficient photocatalyst for decomposition of perfluorooctanoic acid.* Applied Catalysis B: Environmental, 2012. **125**: p. 350-357.

102. Ong, C.B., et al., *Solar photocatalytic and surface enhancement of ZnO/rGO nanocomposite: Degradation of perfluorooctanoic acid and dye.* Process Safety and Environmental Protection, 2017. **112**: p. 298-307.

103. Shao, T., et al., *Photocatalytic decomposition of perfluorooctanoic acid in pure water and wastewater by needle-like nanostructured gallium oxide.* Chinese Journal of Catalysis, 2013. **34**(8): p. 1551-1559.

104. Liu, J., et al., *Removal of PFOA in groundwater by Fe0 and MnO2 nanoparticles under visible light.* Journal of Environmental Science and Health, Part A, 2017. **52**(11): p. 1048-1054.

105. Li, Z., et al., *Synthesis of In2O3-graphene composites and their photocatalytic performance towards perfluorooctanoic acid decomposition.* Journal of Photochemistry and Photobiology A: Chemistry, 2013. **271**: p. 111-116.

106. Chen, Y.-C., S.-L. Lo, and J. Kuo, *Effects of titanate nanotubes synthesized by a microwave hydrothermal method on photocatalytic decomposition of perfluorooctanoic acid.* Water Research, 2011. **45**(14): p. 4131-4140.

107. Xu, Z., et al., *Highly efficient and stable Zr-doped nanocrystalline PbO2 electrode for mineralization of perfluorooctanoic acid in a sequential treatment system.* Science of The Total Environment, 2017. **579**: p. 1600-1607.

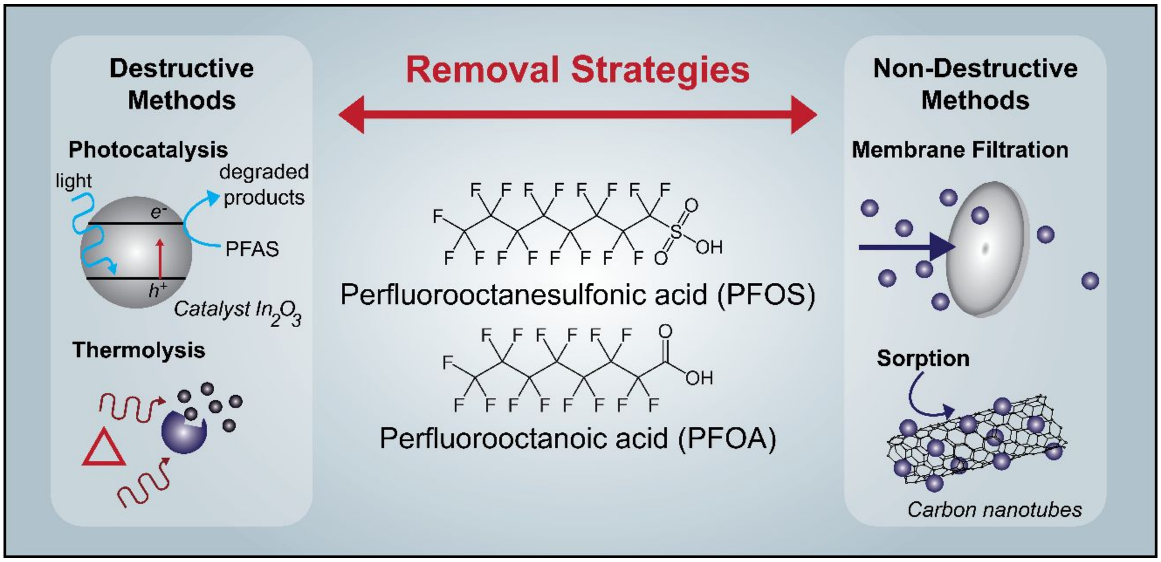
108. Huang, D., et al., *Directional electron transfer mechanisms with graphene quantum dots as the electron donor for photodecomposition of perfluorooctane sulfonate.* Chemical Engineering Journal, 2017. **323**: p. 406-414.

109. Zhang, C., et al., *Degradation of perfluorinated compounds in wastewater treatment plant effluents by electrochemical oxidation with Nano-ZnO coated electrodes.* Journal of Molecular Liquids, 2016. **221**: p. 1145-1150.

110. Arvaniti, O., et al., *Reductive Degradation of Perfluorinated Compounds in Water using Mg-aminoclay coated Nanoscale Zero Valent Iron*. Vol. 262. 2015. 133-139.

111. Song, Z., et al., *Efficient photocatalytic defluorination of perfluorooctanoic acid over BiOCl nanosheets via a hole direct oxidation mechanism.* Chemical Engineering Journal, 2017. **317**: p. 925-934.

112. Li, S., et al., *Microwave enhanced Fenton-like process for degradation of perfluorooctanoic acid (PFOA) using Pb-BiFeO3/rGO as heterogeneous catalyst.* Chemical Engineering Journal, 2017. **326**: p. 756-764.


Destructive Methods
Removal Strategies
Non-Destructive Methods
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Catalyst In2O3
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