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Nano-enhanced treatment of per-fluorinated and poly-fluorinated alkyl substances (PFAS)☆

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Per-fluorinated and poly-fluorinated alkyl substances (PFAS) are environmentally pervasive and persistent. They have been associated with adverse health effects and are a major public health concern. Water contamination is a highly challenging problem due to the large number of PFAS and the limitations of conventional treatments. Nanoscale technologies offer new approaches such as high-capacity, selective sorbents with rapid uptake and regeneration, and integrated methods that capture and destroy PFAS. Nano-enhanced materials can improve the kinetics and selectivity of PFAS uptake (physical removal) and destruction, and the treatment materials can potentially be reused/recycled. Nanoscale technologies also offer opportunities to improve the performance of most conventional treatments. Some recent nano-enhanced approaches for PFAS treatment of aqueous media are discussed in this paper.

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Introduction

Per-fluorinated and poly-fluorinated alkyl substances (PFAS) are a group of synthetic chemicals with useful properties and many industrial and consumer applications [1]. Their numerous applications, widespread use, and high stability due to C–F bonds make PFAS environmentally pervasive and persistent. They have been found in food and drinking water and bioaccumulate [2]. Widespread contamination is a major public health concern as numerous studies associate PFAS exposure with potential health effects [3–5]. Drinking water contamination is an incredibly challenging problem due to the large number of PFAS, lack of consolidated source data, limitations in treatments, and limited studies on some PFAS. Strategies to assess exposure, persistence, and treatability can prioritize health and water treatments studies [6]. Current practices usually target a subset of PFAS for which in-depth studies are available. Approaches such as risk-based geospatial studies and a broader research and management program focused on total PFAS content will expedite mitigating exposure to PFAS for which data are lacking [6]. The US Agency for Toxic Substances and Disease Registry (ATSDR) finalized health risk levels for four PFAS [7], which translate to drinking water levels of 11 parts per trillion (ppt) for perfluorooctanoic acid (PFOA) and 7 ppt for perfluorooctanesulfonic acid (PFOS). The US Environmental Protection Agency's (EPA's) current advisory safe daily dose levels for these compounds is 70 ppt, individually or in combination [7].

Drinking water treatment is usually based on physical removal by granular activated carbon [GAC], ion exchange, and reverse osmosis [RO], and physical and biological processes are used to treat wastewater. These processes have varying efficiencies for PFAS removal and generate PFAS wastes [8,9]. Sludge and biosolids from wastewater treatment plants (WWTPs) can contain high levels of PFAS because PFAS' high stability makes them resistant to conventional degradation treatments [8,9]. Contaminated effluent, biosolids applications, and waste disposal can be important release pathways [10]. Newer technologies for wastewater treatment include membrane separation [11,12] and advanced oxidation/reduction processes (AOPs/ARPs) [13–15]. Nanofiltration (NF) membranes can remove PFAS with molecular weights larger than 300 g mol^{-1} [11]. Reverse osmosis can reduce PFAS concentration to 0.4 ng L^{-1} [12]. Both GAC and AOPs show satisfactory performance for PFOA and PFOS at

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$\mu g\,L^{-1}$ levels [16,17]. However, because ion exchange [18], NF, RO, and GAC are nondestructive processes, treatment of spent media and concentrated PFAS waste is required. Also, GAC is less effective for short-chain compounds. Ultrasonic irradiation can degrade PFAS at a lab-scale [19] but with considerable energy cost. Some thermal and nonthermal methods destroy PFAS but form undesirable byproducts [20,21]. Given the limitations of existing technologies, new treatment technologies are urgently needed (e.g. Refs. [9,17,22]). The central challenge in PFAS destruction is the breakage of their strong C–F bonds (485 kJ/mol) [23]. In this regard, methods based on metal catalysts, sulfate radicals, and rigorous heating have shown some success [24]. Innovative methods based on nanoscale technologies are up-and-coming due to critical properties at the nanoscale. An overview of some recent approaches to PFAS treatment by nano-enhanced processes is given in this paper.

Nano-based systems for PFAS treatment

Advanced materials significantly contribute to developing new technologies for PFAS treatment (e.g. Refs. [9,24–28]). In particular, the high surface area and associated reactivity of nanoscale materials make them especially promising for the treatment of PFAS-contaminated water. Nano-enabled treatment and safer alternatives to PFAS were highlighted at a recent public health symposium [4]. Nanoscale particles/structures can provide high-energy reaction pathways in electrolysis, thermolysis, and photolysis processes [24]. They can improve kinetics and selectivity for target pollutants and potentially be reused/recycled. Nanoscale technologies also offer many possibilities for PFAS removal by sorption. Non-destructive/destructive methods have been reported in recent reviews (e.g. Refs. [9,24,29,30]). Saleh *et al.* [24] reviewed removal from aqueous media by nano-enabled strategies, including high surface area sorbents such as carbon nanomaterials, photocatalysts for hydrodefluorination, and AOPs. Several of these and other nano-enhanced approaches to PFAS removal are highlighted in this section. A schematic overview of nano-enhanced and traditional treatments by nondestructive and destructive processes is presented in Figure 1. In principle, as well as novel approaches, nanoscale technologies offer opportunities to enhance most conventional processes.

Physical removal: membranes, sorbents/resins, and surface modification

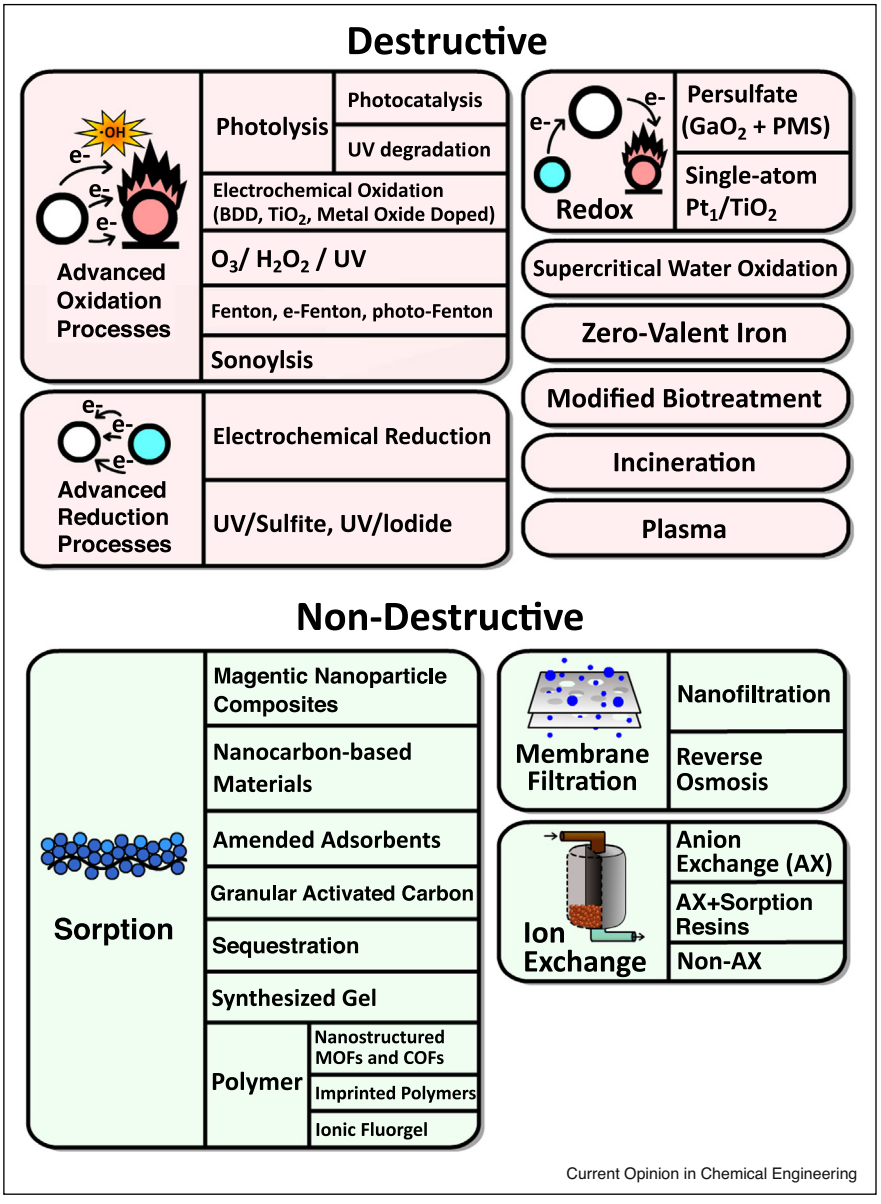
The sorption behavior of PFAS is complex because they have hydrophilic groups and C–F chains with hydrophobic and oleophobic properties and because there are many types. Hydrophobic and hydrophilic properties give them surfactant-like behavior, and sorbent retention depends on a range of factors not usually considered with other pollutants (e.g. Refs. [29,31]). Sorption mechanisms include electrostatic and hydrophobic interactions. Various solution parameters (pH, ionic strength, natural organic matter [NOM]) can affect PFAS sorption, and co-contaminants can induce their release [31].

Though PFAS sorption depends on many factors, it can be a highly effective method for PFAS removal, as has been shown for carbonaceous nanomaterials (CNMs) [32]. In general, nanoscale technologies offer an attractive platform for developing sorbents with high surface area and adjustable chemistries. Unmodified carbon nanotubes exhibited higher PFAS sorption rates and capacities than other sorbents. Sorption on multiwalled carbon nanotubes (MWCNT) increased when surface-borne metal catalysts were present, and MWCNT modified with Mg^{2+} showed significantly enhanced electrosorption relative to the powder form [29]. Several recent studies of PFAS removal from aqueous samples by various nano-enhanced sorbents are listed in Table 1. A sorbent based on a fluorine-doped graphene aerogel with Cu NPs (Cu/F-rGA) was reported [33]. Relative to the unmodified rGA, the adsorption rate for PFOA was enhanced 2.68-fold.

Nanofiltration membrane separation technologies are effective for PFAS that traditional water treatments could not remove. A pilot study at a drinking water plant showed NF to be efficient (>98%) in removing PFAS [41]. The average concentration (total) of seven PFAS found in raw groundwater fed to the NF plant was 160 ± 53 ng/L. However, NF may not ensure the limits for drinking water and the membranes are still prone to fouling. Nanocomposite, mixed-matrix membranes with advanced materials could revolutionize RO/NF processes [42]. For example, adding metal oxide frameworks (MOF) to the polymeric membrane can provide a more selective and efficient capture of PFAS [34,36], and similar approaches can be applied to sorbents. A zirconium-based MOF was found to have characteristics (capacity, kinetics, regeneration) that significantly outperformed current sorbents. For the tested PFAS, rapid sorption and nearly quantitative removal and recovery were obtained [36] (Table 1). Rapid removal and release by this material make it an excellent candidate for developing integrated processes for the collection and destruction of PFAS.

Modified magnetic iron oxide nanoparticles have high sorption capacity and were demonstrated as effective, recyclable sorbents. Magnetic nanoparticles (MNPs) have been extensively studied, and a review of recent work on their synthesis, modification, and environmental applications has been published [43]. Surface modification with specialized coatings could significantly improve the capacity and selectivity of MNPs, their composites, and other nanoscale (and larger) sorbents. For example, an ionic fluorogel rapidly removed 21 PFAS (including short-chain) from wastewater at >95% efficiency, with high affinity and selectivity [44]; amine-based sorbents

Figure 1



Opportunities for nanoscale technologies in nondestructive/destructive treatments of PFAS in aqueous media (non-exhaustive list of common treatment methods illustrated).

have also been applied [45]. Highly specialized chemistries can be designed for MNPs and other NPs, and these materials can serve as a platform for various applications. Ideally, recovery of MNPs from complex matrices is realized by applying a magnetic field [43,46,47].

Nano-based degradation/defluorination: materials and process integration

Nanoscale materials have demonstrated potential for PFAS separations [24], offering superior sorption and selectivity relative to the much larger GAC and ion exchange media. The development of nanoscale technologies for PFAS destruction also is an active research area. Recent studies of destructive and combined (i.e. capture and degrade) methods are presented in Table 2. For example, magnetically retrievable ferrite photocatalysts have been fabricated for wastewater treatment (e.g. Refs. [46,47]). Synthesis of nanocrystalline ferrite catalysts ($Zn_xCu_{1-x}Fe_2O_4$) for photocatalytic degradation of PFOA in water was reported [47]. Degradation in the innovative

Table 1

Recent studies of nano-enhanced water treatments for PFAS: nondestructive methods

Study	Method	Materials	Substance(s) and concentration(s)	Efficiency
Azmi *et al.* [34]	Adsorption on novel metal organic framework (MOF)	Modified Al-based MOF (MIL-96) with hydrolyzed polyacrylamide (to add surface amine groups)	PFOS: 1000 mg/L (20 mg adsorbent with 20 mL solution)	Adsorption capacity: - PFOS: 340 mg/g (72 hour) - PFOS not easily desorbed.
Hassan *et al.* [35]	Adsorption on modified biochar	Red mud sawdust biochar (RMSDN600) with magnetites (Fe_3O_4), ferrihydrites, and desilicated minerals	PFOS (0.5–325 mg/L) 0.57–0.67 g/L sorbent	Adsorption capacity (pH 3.1, 24 hour): RMSDN600:194.6 mg/g SDN600 (unmodified): 178.6 mg/g
Li *et al.* [36]	Adsorption on MOF	Zirconium-based MOF NU-1000 10 mg–50 mL PFAS solution	Aqueous mix at ~0.1 mg/L each: PFSAs (C4, 6, 8); PFCAs (C1, 3, 4, 6, 7, 9)	Adsorption capacities: - PFSAs: 400–620 mg/g, PFCAs: 201–604 mg/g Removal capacities: - Clean water: 90–100% (<1 min typical) - Groundwater: 75–98% (<10 min)
Liu *et al.* [33]	Adsorption on CNM aerogel. Modeling.	F-doped reduced graphene aerogel with Cu NPs (Cu/F-rGA)	PFOA 10 mg/L (6 mg adsorbent), pH 6.07	Adsorption on Cu/F-rGA was enhanced 2.68-fold relative to rGA
Omo-Okoro *et al.* [37]	Adsorption on activated media	Physically and chemically activated maize tassel silver (PAMTAg and CAMTAg)	PFAS-simulated water PFHxS, PFOS, PFBA, PFDA, PFHpA, PFHxA. PFNA, PFOA, PFPeA, PFBS	Adsorption capacities: - PFOS: 454.1 mg/g; PFOA: 321.2 mg/g Removal: PAMTAg: 79.2–81%; CAMTAg: 81.2–83%
Wang *et al.* [38]	Adsorption on modified clay	Edible, nutrient-amended montmorillonite clays	5 μg/L individual PFAS, PFOA (protonated or not [nH]), PFOS, GenX, PFBS	Binding estimates for modified (and parent) clay (GenX and PFBS were lower): - PFOA-H 54% (28%), PFOA-nH 34% (20%) - PFOS: 28% (18%)
Xing *et al.* [39]	Adsorption on magnetic nanocomposite	Hydrolytically stable magnetic core-shell aminosilane nanocomposite for PFOS and PFOA	PFOS or PFOA solution (100 mL, 1–15 mg/L) with 0.02 g composite	Rapid removal: PFOS 78%, PFOA 65% - Regenerated and used 15 cycles (>70%) - Optimal removal: pH ≤ 5 - Easy magnetic separation from water
Xu *et al*. [40]	Adsorption on carbon-supported Fe_3O_4 NPs	GAC-magnetite NP composite (Fe_3O_4@GAC) prepared by hydrothermal method	Sorption tests: 0.241 mmol/L PFOA (with different molar ratios of Fe^{2+} and Fe^{3+}).	2:1 Fe^{2+}/Fe^{3+} had best removal (79%) of the tested composites [GAC: 59%, Fe_3O_4: 10%). - 4 times faster and 28.8% greater capacity than GAC at pH 4. - Ca^{2+} increased uptake (>2x, pH ≥ 5) - 91% recovery from material and reusable

UV–vis/$Zn_xCu_{1-x}Fe_2O_4$/oxalic acid system was attributed to oxidative dissociation and defluorination through UV light-mediated generation of hydroxyl radicals in a heterogeneous photo-Fenton-like process, without added H_2O_2. Photocatalytic processes are generally less practical for treating trace PFAS in a large volume of water, and conventional photocatalysts (e.g. TiO_2) have limitations (e.g. Ref. [48]). As an alternative, wastewater treatment by ozonation of PFAS adsorbed onto ferric NPs formed *in-situ* was investigated [49]. For testing, firefighting foam concentrate was used to prepare synthetic contaminated water samples over a PFAS concentration range from 8.33 to 133 μg/L. The maximum PFAS loading (80%) was higher than that for conventional sorbents, but the maximum removal was 44%. Titanate nanotubes also have attracted interest as adsorbents/photocatalysts due to their photoelectron response. Li *et al.* [48] tested an iron-modified composite of activated carbon and titanate nanotubes (Fe/TNTs@AC) to concentrate and destroy PFOA. The material degraded >90% of surface-concentrated PFOA in 4 hours under UV irradiation, of which 62% was mineralized to F^-. Photodegradation regenerated the material without added chemicals, and no significant decrease in performance was found after six cycles. Composites of magnetite and ferrites offer high surface area, durability, and improved electron transfer. Advances in heterogeneous Fenton catalysis are discussed in a recent review [50]. Zhu *et al.* [51] reported

Table 2

Recent studies of nano-enhanced water treatments for PFAS: destructive methods

Study	Method	Materials	Substance(s) and concentration(s)	Efficiency
Barisci and Suri [60]	Electrooxidation	Si/BDD electrode	- PFCAs: Short (C3–C6) and Long (C7–C18) chains. - PFOA: 10 mg/L, 200 μg/L - DI water, river water, WWTP effluent	PFOA (10 mg/L, 1 hour. pH 5, optimum conditions): - 80% removal (90% at 200 μg/L), 74% TOC removal - 37% defluorination PFCA: Long-chain: >95% removal (C7 = 85%). Short: C3: 39%, C4: 41%, C5: 66%, C6: 70%
Barisci and Suri [61]	Electrooxidation	Ti/RuO_2 electrode	PFCAs/PFSAs (100 μg/L) PFCAs: C3–C7, PFOA (C8), C9–C14, C16, C18 PFSAs: C4, C6, PFOS (C8)	Degradation Ranges: - Short-chain: 16%–67% - Long-chain: 64%–91%
Deng *et al.* [62]	Mechanochemical degradation	Co-milling reagents: ZVI Ferrate (VI)	0.1 g of PFHxS and 1.4 g of reagents	100% degradation, 95% defluorination after 4 hour milling at the optimum ratio
Duan *et al.* [25]	Photocatalytic degradation	Boron Nitride (BN)	PFOA: 5 ppm	16% of shorter-chain PFAS byproducts remained
Eke *et al.* [63]	Membrane filtration UV Irradiation, oxygenation (liquid aerobic oxidation)	SPEEK and phosphorene nanocomposite membranes	PFOA: 100 mg/L solution	99% membrane rejection, 84% recovery of adsorbed PFOA (by reverse flow), and 99% recovery of adsorbed residual by UV photolysis and oxidation
Hou *et al.* [59]	- Membrane composite - Solar light irradiation	Lignin/polyvinyl alcohol MOFs membrane (PVA/Co/Fe)	PFOA: 20 mg/L solution	89.6% degradation within 3 hour
Huang *et al.* [26]	Electrocatalytic oxidation (electron transfer without radical involvement)	Ti_4O_7 anode with fluorinated surface and amorphous Pd clusters of single Pd atoms	PFOA: 0.12 mM solution	86.7 ± 6.3% degradation after 1 hour (81.3 ± 6.5% of C to CO_2). - 77.9 ± 3.2% of fluorine released as F^- - C3–C6 PFCA products negligible. Slightly lower F than C mass balance suggests volatile loss
Li *et al.* [48]	'Concentrate and destroy' - Adsorption - Photocatalysis	Adsorptive photocatalyst Fe/TNTs@AC (based on activated carbon and TiO_2)	PFOA: 100 μg/L solution (pH 7)	>90% degradation in 4 hour under UV - 62% mineralized to F^-
Liu *et al.* [64]	Mechanochemical stirring - adsorption - Reduction	Bimetallic catalyst on carbon (AlC). Also tested AlC_{Ni} with PMS @ 60 °C (oxidant) and UV/sulfite (reductant).	1 mg/L PFOA.as test for wastewater treatment	Best with no additives and pH around 4: - 98% removal after 3 hour - 70.43% release of Fl^- $AlC_{Ni} > AlC_{Ni}/SO_3^{2-} \rightarrow AlC_{Ni}$/PMS
Liu *et al.* [65]	ZVI + biochar	ZVI with biochar (BC) under environmental conditions.	PFOA and PFOS: 18.6 mg/L	Removal: 17–94% PFOA: 20–60% PFOS: 90–94% (by ZVI or ZVI + BC).
	- Sorption (H bonding)		3 PFCAs: PFHxA, PFHpA, PFOA	Short-chain: - PFCAs (C6, C7): 0–17%; PFSAs (C4–C7): 20–70%
	- Reductive DF by ZVI		4 PFSAs: PFBS, PFHxS, PFHpS, PFOS	PFSAs (up to 94%) better removed than PFCAs (60%) - 5–10% DF by ZVI alone.
Masud *et al.* [66]	Redox on nanohybrid (NH) material: adsorption, reduction. AOP (with H_2O_2)	ZVI NPs on 2D rGO nanosheets (rGO-nZVI NH) with and without H_2O_2	200 μg/L of individual PFAS (PFOS, PFOA, PFPeS, and PFPeA) in DI water	Removals (10 min, room temperature): - Long-chain: 85% for PFOS, 39% for PFOA - Short-chain: 19% for PFPeS, 18% for PFPeA H_2O_2 improved removal 10–18% (NH-generated ROS)
Parenky *et al.* [67]	Redox	ZVI NPs (strong reductant) + common oxidants: PS, PMS, HP	10 mg/L PFOS solution	PS: 7% @20°C, 31% @ 40°C, 54% @60°C PMS: 8% @20°C, 22% @ 40°C, 53% @60°C HP: 12% @ 20°C, 59% @ 40°C, 74% @ 60°C

Table 2 (*Continued*)

Study	Method	Materials	Substance(s) and concentration(s)	Efficiency
Tian *et al.* [68]	- Adsorption on photocatalyst - UV degradation (enhanced by 0.5 M H_2O_2)	Adsorption on Fe-doped, activated carbon-supported titanate nanotubes (Fe/TNTs@AC). UV (254 nm) destruction	- Model leachate with PFAS contaminants (18 detected) - Spiked with 100 μg/L PFOA for screening tests.	- Adsorption: >95% of 13 PFAS (74% with 3 uses); >92% of 18 PFAS in 8 hour for field (pilot) test - Degradation: 84% of 16 PFAS in solid phase - Degradation regenerated the material
Verma *et al.* [47]	Heterogeneous photo-Fenton like system (no added H_2O_2) - Photooxidative degradation, photo-defluorination	Nanocrystalline ferrite catalyst in UV-vis, oxalic acid system: UV-vis/ $Zn_xCu_{1-x}Fe_2O_4$ NPs/OA (254 nm)	PFOA (100 ppb, 100 ppm) Used 6 mL + I mL 0.1 M OA (as reductant additive)	- Degradation (UV light, 2 hour, pH 1.7) 100 ppm (high concentration): 32%; 100 ppb: 63% Optimal: 0.1 M OA, pH 1.73, 8.3 mg/mL NPs
Wang *et al.* [69]	Electrochemical oxidation: synergic cathodic e-Fenton and anodic	EC cell with Fe(II)/Mn(II)-doped carbon (Fe/Mn-C) cathode and BDD anode	PFOS: 120 μM (100 mL)	Degradation: 97% over a few hours (pH 3) - 93% loss of TOC indicated mineralization. - Dual Fenton catalysts enhanced oxygen reduction and selectivity of e-Fenton reaction
Wang *et al.* [70]	Electrochemical oxidation	Magnéli phase titanium suboxide (Ti_4O_7) and BDD anodes (tested effects of Cl^-)	Linear and branched PFOS 20 μM	- Nearly complete removal by Ti_4O_7 anode in 4 hour - >95.14% fluorine release in 8 hour - Reported Ti_4O_7 superior to BDD in presence of Cl^- due to slow rates of ClO_3^- and ClO_4^- formation on Ti_4O_7
Wang *et al.* [71]	Electrochemical oxidation	Magnéli phase titanium suboxide (Ti_4O_7) anode (2 SS plates as cathode).	8 linear (L) and branched PFAS at 2.0 μM each PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFHxS, PFOS	- PFOA, PFOS: >90% removed in 30 min (5 mA cm^{-2}) and 10 min (15 mA cm^{-2}). - Defluorination >90% above 10 mA cm^{-2}. PFAAs >90% degraded (15 mA cm^{-2}) except PFBA (50%) after 8 hour - Degradation rates general order: L-PFOS > PFOA > L-PFHxS > PFHpA > PFHxA > L-PFBS > PFPeA > PFBA
Weon *et al.* [54]	Photocatalytic oxidation, reductive hydrodefluorination	Single-atom Pt on TiO_2 having oxidative and reductive facets	PFOA: 100 μM	58% of F from degradation was surface bound (Ti–F bonds). No F^- in solution (i.e. no HF formed)
Wu *et al.* [72]	Photocatalysis	BiOCl nanosheets	PFOA: 50 mL of 0.12 mM	PFOA: 77.3% photodegradation efficiency
Xu *et al.* [57]	Visible and UV Photocatalysis Reported $SO_4^{\bullet-}$ and photoinduced holes as main active species	TiO_2 + PMS ($S_2O_8^{2-}$)	PFOA in water and wastewater 50 mg/L, pH 3	- Water: 100% degraded, 8 hour (400–770 nm); 1.5 hour (254, 185 nm) - Wastewater: 100% under UV (<2 hour); 65–82% degraded, 8 hour vis light, TOC removal 26–44%. TOC removals of 65–69% at 254 nm and 34%–44% at 185 nm
Xu *et al.* [73]	- Adsorption - Photocatalytic degradation	Iron (hydr)oxides carbon sphere (FeO/CS) composite photocatalyst	PFOA: 200 μg/L; pH 7 (160 mL, 1.0 g/L catalyst)	PFOA: >99% adsorbed within 1 hour - 95.2% degraded; 57.2% defluorinated in 4 hour. - Degradation regenerated the material
Xu *et al.* [58]	UV Photocatalysis (redox species: $SO_4^{\bullet-}$, $O_2^{\bullet-}$ and photogenerated e^-)	Gallium Oxide (Ga_2O_3) powder + PMS (reported as better than T_iO_2; environmentally friendly)	PFOA in water and wastewater 50 ng/L to 50 mg/L	PFOA: 100% degraded (pH 3 improved degradation) - 90 min under 254 nm; 60 min under 185 nm - 75–85% TOC removal under 254 nm
Xu *et al.* [74]	- Adsorption - Photocatalytic degradation	Carbon sphere modified bismuth phosphate composite photocatalyst (BiOHP/CS)	PFOA: 200 μg/L; pH 7 (40 mL, 1.0 g/L catalyst)	PFOA: >99% adsorbed within 2 hour (254 nm) - 9% BiOHP/CS had highest degradation: 90% in 1 hour - 32.5% defluorination in 4 hour
Zenobio *et al.* [75]	Reductive defluorination and desulfonation with catalyst	Bimetallic catalyst: ZV nickel and iron NPs on AC (n$NiFe^0$-AC)	PFOS (short-chain and long-chain): 10 mL, 6 μM solution +0.2 g n$NiFe^0$-AC	94 ± 4.1% degradation (50°C); ≥97 of transformed PFOS accounted for by F^- (products gone after 24 hour)

Table 2 (*Continued*)

Study	Method	Materials	Substance(s) and concentration(s)	Efficiency
Zhang *et al.* [27]	Photocatalysis	In_2O_3 NPs. Modeled impact of environmental factors and verified results.	PFOA: 20.88 ± 1.43 mg/L Treated under different conditions (e.g. pH, sulfate, Cl^-, H_2O_2)	Model predictive under specified conditions. Experimental results (optimal conditions) were: - Decomposition: pH 4.2: 53.50%, pH 2: 92.20% - Defluorination: pH 4.2: 21.33%, pH 2: 95.99%
Zhang *et al.* [49]	Adsorption Ozonation	*In-situ* formed ferric NP adsorbent, O_3 bubbling 15–45 s	28 PFAS (8.33–133 μg/L total). Solutions prepared with AFFF concentrates	Removal: 44% at 8.33 μg/L (pH 6). Maximum solid-phase loading of 80% at pH 3.
Zhu *et al.* [51]	Adsorption Photocatalytic degradation	Ga-doped C modified titanate nanotubes (Ga/TNTs@AC)	PFOS: 100 μg/L	PFOS: 75% degradation and 66.2% mineralization after 4 hour UV irradiation

a similar approach based on a non-ferrite photocatalyst, gallium-doped carbon-modified titanate nanotubes (Ga/TNTs@AC), for solid-phase photocatalytic degradation of PFOS in water. Duan *et al.* [25] reported photocatalytic degradation of PFOA using boron nitride (BN) and proposed a hole-initiated reaction involving reactive oxygen species (ROS). The BN material was four times more active than TiO_2 and remained effective in degrading GenX and other PFAS over three cycles. Other nano-enabled applications also are relevant to water quality. A sensor-based on covalent organic frameworks (COFs) attached to lanthanide-doped nanocrystals selectively detected PFOS in tap water at a detection limit of 0.15 picomolar [52]. These studies further illustrate the broad applications of nanoscale technologies for sensing, capturing, and destroying PFAS in aqueous systems.

Destruction of PFAS using single-atom catalyst (SAC) materials has also been reported. Single Pt atoms on a silicon carbide substrate (Pt_1/SiC) allowed efficient C–F bond activation for PFAS destruction [53]. The high activity of Pt_1/SiC for hydrodefluorination of PFOA was attributed to effective hydrogen 'spillover' from isolated Pt atoms, where the formed Si–H bond further 'redistributes' with the C–F bond, resulting in photocatalytic hydrodefluorination and covalent attachment of F to the substrate. Photocatalysis with Pt_1/SiC was reported as the most energy-efficient technology to date for PFOA. Other SAC materials include one prepared by site-selective loading of Pt co-catalyst atoms onto facet-engineered TiO_2 for photocatalytic oxidation and reductive hydrodefluorination of PFOA [54]. The degradation rate for Pt_1/facet-engineered TiO_2 was 15 times that for its NP equivalent, and both were superior to facet-engineered TiO_2. A surface-fluorinated titanium oxide (Ti_4O_7) electrode with amorphous palladium clusters of single atoms (Pd) was also tested for electrocatalytic oxidation of PFOA [26]. The electrode outperformed a Ti_4O_7 electrode with crystalline Pd particles due to enhanced electron transfer and binding of PFOA and its degradation intermediates to the fluorinated surface, allowing efficient mineralization. The reaction proceeded without ROS and was therefore not quenched by common anions (e.g. Cl^-) in natural waters. Although SAC technology has potential for concentrated waste treatment, these materials are still in the early development stage [55]. Other investigators reported effective decomposition of PFOA by nano-based photocatalysts such as TiO_2, Ga_2O_3, and In_2O_3 under UV irradiation. Nano In_2O_3 showed the most promise, related to the high surface area of the In_2O_3 nanostructures and the number of photogenerated holes at the surface [56], but environmental factors can affect degradation [27]. Xu *et al.* [57] reported visible and UV photocatalysis of aqueous PFOA by TiO_2 and peroxymonosulfate (PMS). Improved photocatalysis of PFOA in water and wastewater in a Ga_2O_3/UV system assisted by PMS also was described [58]. Hou *et al.* [59] reported catalytic degradation of PFOA using lignin-based, polyvinyl alcohol, bimetallic MOF (lignin/PVA/bi-MOF) nanofiber composite membrane. Sulfate and hydroxyl radicals were generated by activating PMS with transition metals and solar light. The membranes were 89% effective within 3 hours and could be reused after rinsing.

Destruction of PFAS by AOPs/ARPs has been intensively studied at the bench scale [13,14]. Their efficacy is strongly dependent on the compound and conditions [76]. Photochemical and photocatalytic degradation is typically slow and energy-intensive, and the pathways are uncertain. Reductive destruction by radiolytically generated aqueous electrons was identified as one of the most promising methods, but it is also energy-intensive, and the mechanisms are uncertain [13]. A recent paper [77] reported electron beam irradiation as a promising technique for destruction of shorter-chain PFAS due to its cost-effective ability to generate high amounts of

reducing and oxidizing species. Samples of perfluoroheptanoic acid (PFHpA) in water (100 μg/L) were exposed to irradiation doses of 0–75 kGy. Nitrate, fulvic acid, and alkalinity did not inhibit the degradation. Highly alkaline conditions favored removal, with complete degradation at 50 (and 75) kGy. Defluorination and decarboxylation were proposed as the main degradation routes. Chemical reduction by zero-valent iron (ZVI) showed potential but had limited applications due to the highly acidic conditions required and short lifetime of iron powder (alone) in aqueous media [78]. Advanced oxidation processes generate powerful ROS, notably hydroxyl radical ($^{\bullet}$OH), that degrades organic pollutants and typically require added chemicals. Photocatalytic AOPs generate ROS by irradiating surfaces with UV/visible light, but limitations in reactor design remain.

Electrochemical oxidation (ECO) processes are widely used AOPs and have been applied to PFAS in water [60,61,69,79–87]. Many applications have involved a boron-doped diamond (BDD) anode. Gomez-Ruiz *et al.* [84] reported 99.7% removal of eight PFAS from WWTP effluent using a BDD anode. Barisci and Suri [60] applied BDD to degrade short-chain (C3–C6) and long-chain (C7–C18) PFCAs (Table 2). Removal was >95% for long-chain compounds, with 37% defluorination, and lower for short-chain (39%–70%). Soriano *et al.* [85] designed an integrated, laboratory-scale system with NF separation followed by ECO in a cell equipped with a BDD anode and two parallel flow compartments. The system was designed to remove perfluorohexanoic acid (PFHxA) (60–200 mg L^{-1}) from industrial process waters. The membrane provided PFHxA rejection without fouling, and the ECO of PFHxA in the concentrate (870 mg/L) reached 98%. The optimized process reduced energy input, possibly allowing operation by solar power [9]. Wang *et al.* [69] reported PFOA degradation by a combined electro-Fenton and EC anodic oxidation process, using a cell with an iron/manganese-doped carbon (Fe/Mn-C) cathode and a BDD anode (Table 2). The dual catalysts enhanced oxygen reduction and selectivity of the electro-Fenton reaction, with a degradation efficiency of 97% over a few hours.

A major challenge in water treatment by oxidative/reductive processes, including faradaic electrocatalytic treatments, is controlling the reaction pathway [55]. The reaction rate depends on complex water chemistry and other parameters (e.g. electrode type, surface area, and voltage; initial concentrations; extent of treatment; co-contaminants), and different pathways and intermediates can occur with the same compound [55]. In addition, many competing constituents in wastewater and environmental waters can decrease the degradation efficiency for target pollutants. For EC applications, BDD electrodes have been considered a gold standard [55]. However, they are expensive, difficult to produce, fouling prone, and give incomplete PFAS destruction [15,28,88]. Studies of PFAS indicate that EC transformations can occur by compound-dependent mechanisms. Degradation at a BDD anode is attributed to oxidation by ($^{\bullet}$OH) from the EC splitting of water. Although $^{\bullet}$OH is a strong oxidant, it was not sufficient for the oxidation of short-chain PFAS [86]. In general, oxidation treatments are slow and inefficient due to the incredible stability of C–F bonds to oxidation. In the case of ECO, poor electron transfer efficiency can limit oxidation. However, if an initiating step can be accelerated, oxidation by $^{\bullet}$OH can be significantly expedited. Nanostructured (and subnano) materials offer opportunities for significant advances in the energy efficiency and selectivity of electrocatalytic degradation of persistent water pollutants. Material science has focused on bandgap engineering to control the activity of semiconductor electrocatalysts, but control of surface nanostructure represents the 'frontier'of nano-engineering [55]. This field has the potential to develop highly specialized electrodes and materials that can selectively remove target pollutants and generate reactive radical species [55]. Recent advances are expected to reduce treatment times significantly. A reactive EC membrane could reduce the process to seconds [88].

Studies of two-dimensional SAC (subnano) materials demonstrated their high reactivity and the potential of three-dimensional (3D) nanostructures. A nano-porous 3D Ti_4O_7 electrode gave extremely fast reaction rates for PFAS, assisted by high surface area and efficient mass transport in micro-flow channels. Intra-electrode diffusivity was a rate-limiting step, but careful control of pore structure can improve transport [55]. Many 3D electrodes are engineered to form micro- to macro-size pores for attachment of NP catalysts. Bimetallic NP catalysts have been grown on 3D microporous graphite fiber cloth electrodes, wherein the cloth minimizes intraparticle diffusion and provides a high surface area and NP loading [55]. Importantly, nano-enhanced electrodes that can operate in complex water matrices without fouling or interferences are critical to adopting these technologies. Ideally, surface nanostructures could allow selective preconcentration of target pollutants, followed by localized ROS production for their destruction. In practice, though highly reactive, nanostructured electrodes also may be prone to aging and fouling. Most nano-enhanced EC treatment technologies are largely conceptual and have been tested only at the laboratory scale [24,55]. Potential opportunities and barriers for nanotechnology to enhance EC treatment of PFAS-contaminated water are presented in a recent review [55].

Though usually more favorable than oxidation, slow kinetics and water constituents inhibit the reduction with conventional reducing agents (e.g. ZVI). As an alternative or in a combined (with AO) process, PFAS can be effectively degraded by strong reducing radicals such as

hydrated electrons (e^-_{aq}) [14,89], but their generation has required special equipment [90] and alkaline and anaerobic conditions due to competing reactions. High photon flux UV/sulfite or other photosensitizers, including indole acetic acid in a micelle composite containing PFAS [23], have been used to increase the e^-_{aq} yield. Processes for the reductive destruction of PFAS by e^-_{aq} are summarized in a recent review [14]. A new reductive process for short-chain and long-chain PFOS was recently reported, based on ZV nickel and iron NPs supported on AC (nNiFe^0-AC) [75]. Nickel was selected over Pd due to its low cost, potential to be more reactive, and enhanced stability of Fe^0 NPs relative to Pd particles [75]. Results (Table 2) were found to be promising: $94 \pm 4.1\%$ of PFOS was transformed (50 °C), with $\geq$97% mineralization of the transformed PFOS. Based on the products identified, the reaction proceeds by defluorination and desulfonation pathways. The authors suggested the potential use of the nNiFe^0-AC technology in permeable reactive barriers. Liu *et al.* [64] also reported a bimetallic catalyst on carbon (CNi-Al_2O_3, or AlC_{Ni}), which served as a nanoporous sorbent and catalyst. After 3 hours, 98% of PFOA was removed from wastewater by mechanochemical stirring. The main degradation steps involved adsorption, defluorination-hydroxylation, and decarboxylation, without added chemicals or special activation requirements.

Conclusion

The development of cost-effective, efficient technologies for the treatment of PFAS-contaminated water is a priority research need. Nano-enhanced technologies offer many opportunities for physical/destructive water treatments. Nanoscale materials have much higher sorption capacity and reactivity relative to the macroscale and can be modified to enhance selectivity and efficiency. Novel materials for the physical removal of PFAS are useful but generate contaminated media/waste. Integrated strategies that capture and destroy PFAS are needed. Examples include sorption on high-surface-area nanostructures for rapid, targeted destruction at/near the surface or collection and release for downstream destruction. Mixed-metal photocatalytic systems with iron have the promise to destroy PFAS in photo-Fenton-like reactions, but low pH and high energy are often required. Surface modification of the catalyst and immobilization may enhance PFAS sorption and degradation and allow operation at more neutral conditions.

Unlike many AOPs/ARPs, EC processes are essentially chemical-free and offer cost-effective, sustainable operation, and the equipment can be adapted, and field deployed [55]. Commercially available BDD anodes have been most widely used but they give incomplete PFAS destruction, are expensive, and have other limitations. Porous electrodes based on mixed metal oxides such as Ti_4O_7 are much less expensive and can provide speedy reactions, but they are not widely available [88] and mass transport in their nanostructure can be rate limiting [55]. More open structures and nanocatalyst-modified surfaces could significantly improve performance. Process scalability and cost assessments are critical to practical application of EC technologies and need further consideration. Other needs include low-cost, robust electrodes; improved reactor designs; and integrated byproduct treatment [55]. Improvements in system regeneration and sorbate selectivity are also needed [24].

Although some studies showed high removals with different electrodes/materials, the process times were highly variable, and removal was based on the initial concentration. Confirming mineralization is an essential step in evaluating any treatment process. Byproduct analysis also is critical because it is necessary to understand degradation pathways and problems. Moreover, many studies tested clean water spiked with PFAS. Field samples may require more prolonged treatment, with reduced performance and electrode life. Ultimately, any nano-enhanced technology must provide effective treatment solutions that are safe and energy-efficient.

Conflict of interest statement

Nothing declared.

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