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Electrochemical remediation of perfluoroalkyl substances from water

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ABSTRACT

Organic anthropogenic pollutants such as per- and polyfluorinated alkyl substances (PFAS) present a severe threat to bodies of water and neighboring ecosystems, due to their toxicity and recalcitrance to current treatment methods. PFAS have highly stable carbon-fluorine bonds that contribute to the persistence of these compounds in the environment. Conventional separation methods based on membranes or adsorption materials can often be inefficient at targeting PFAS, or require significant energy or chemical consumption for regeneration. . Electrochemical approaches offer a sustainable and potentially energy-efficient solution to PFAS capture and degradation, with rapid development of new electrode materials and electrochemically-driven processes for the separation and reaction of these compounds. Here, we review electrochemical approaches for PFAS removal and degradation, including electrosorption and electrochemical oxidation/reduction processes. In particular, we discuss investigations using porous carbon electrodes and functional polymers for PFAS electrosorption, as well as electrodes used for PFAS defluorination such as boron-doped diamond. Finally, we present a perspective on emerging topics in electrochemical PFAS remediation, such as the integration of electrochemical reaction and separations, and the urgent need for remediation studies of short-chain PFAS.

1. Introduction

1.1. Background on poly and perfluoroalkyl substances

Recently, bans on the manufacture and use of per- and polyfluoroalkyl substances (PFAS) in consumer products have become increasingly prevalent due to the growing presence of PFAS in water sources worldwide. Referred to as "forever chemicals" due to their persistence in the environment, PFAS are a group of over 4700 synthetic chemicals [1] characterized by a hydrophobic-oleophobic carbon chain, in which the hydrogen atoms can be partially (polyfluoroalkyl) or completely (perfluoroalkyl) substituted by fluorine atoms [2, 3, 4]. According to their end group functionalities, these compounds can be classified as perfluoro carboxylic acids (PFCAs) or perfluoroalkane sulfonic acids (PFSAs). PFAS, due to their unique structures, exhibit properties such as thermal stability, chemical resistance, oil and water repellency, and surfactant properties, making them attractive for applications such as coatings, adhesives, and industrial products [5]. The existence of these chemicals dates back to the 1940s, having been used since then for commercial products, including paints, nonstick cookware, and cosmetics [6–8, 9]. A prevalent application for PFAS is aqueous film-forming foams (AFFFs) for extinguishing fires, which is also amongst the most significant PFAS sources for contamination of drinking water (DW) and groundwater (GW) [10].

The widespread usage of PFAS and recalcitrance to degradation has made them ubiquitous in the environment, wildlife, and even our bodies. Studies have found PFAS present in human blood, plasma, and urine [11,12], with more than 95% of Americans displaying detectable levels of PFAS in their bodies [13]. Epidemiological and toxicity studies have associated perfluorinated compounds with harmful health effects, including liver and testicular cancer, increased cholesterol levels, preeclampsia, and decreased vaccine responses in children [13,14]. These findings have led manufacturers to phase out the production of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in the US in the early 2000s [4]. Since then, regulations for PFOA and PFOS have been issued globally [8].

1.2. PFAS occurrence, transport, and regulations

Emissions of perfluoroalkyl carboxylates have ranged from 3200 to 7300 tons in the United States of America, during a period from 1951 until 2004 [15]. Studies showed that several perfluorinated compounds have been detected in groundwater, surface water, soil, and aquifers in areas neighboring firefighter training, military bases, and wastewater treatment plants (WWTP) [10,16,17]. Therefore, the U.S. Environmental Protection Agency established an advisory level of 70 ng/L for PFOA and PFOS, while the European

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Parliament and Council set a limit of 0.5 μg/L for these same PFAS [18, 19, 20]. However, water sources at different locations around the world have often exceeded these advisory limits [20, 21, 22]. In Veneto, Italy, PFAS concentration levels have ranged from 319 to 1475 ng/L in drinking water [21]. Similarly, in Nevada, USA, surface water contained levels of up to 2234.3 ng/L of PFAS [23]. In groundwater, PFAS have been encountered at concentrations of up to 5200 ng/L in areas of proximity to industrial point sources [24]. To prevent bioaccumulation, new regulations have led to the development of chemical substitutes containing similar properties, but presenting higher volatility and mobility than legacy PFAS [25,26].

The fate and transport of perfluorinated chemicals mainly depend on their amphiphilic properties, given by the length of their fluorinated chain [4]. PFAS are typically classified into *short-chains* if they contain seven or fewer carbon atoms for PFCAs and six or fewer carbon atoms for PFSAs, or *long-chains* for PFCAs with C > 7 or PFSAs with C > 6 [27]. As a result of the new regulations for long-chain PFAS (especially PFOS and PFOA), manufacturers have moved to substitute long-chain PFAS with short-chain PFAS [28,29]. Although their toxicity has not been thoroughly studied, several short-chain PFAS were found to be recalcitrant to biological degradation and just as persistent as long-chain PFAS, thus increasing the concern towards shorter-chain PFAS, which are currently not regulated [29,30].

1.3. Overview of environmental remediation technologies

Due to their environmental persistence, several separations processes for PFAS have been explored. These include membrane processes such as reverse osmosis, nano and ultrafiltration, as well as solvent extraction and adsorption [31–33, 34]. However, many conventional treatment methods (i.e., biodegradation, reverse osmosis, coagulation) can be ineffective when separating perfluorinated substances from water [3,5,31,32,35], and often require high energy input and/or may need the use of organic solvents or regeneration chemicals that generate additional waste [5,36]. Thus, there is a critical need for research and development of sustainable and energy-efficient separation/reaction processes for remediating PFAS-impacted water.

The development of efficient PFAS remediation methods from water is now of more interest than ever, with publications on the topic increasing exponentially over the past few years. There has been extensive work on combining conventional methods, such as integrating activated carbon (AC) adsorbents with nanofiltration [37,38]. Ion exchange resins (IERs) and reverse osmosis (RO) membranes are other techniques that have garnered the attention of many and have been proven to adddress PFAS at low concentrations effectively [39]. However, these methods present various limitations. Membrane fouling can be a potential limitation that increases the cost of RO processes [3,40]. Despite its wide utility in adsorption processes, activated carbon often necessitates long equilibration times, and chemically-intensive treatments to release the contaminants and regenerate the adsorbents [5]. In addition, AC has been shown to capture higher molecular weight compounds with more ease than lower molecular weight compounds. Therefore, when treating mixed PFAS streams, it becomes difficult to completely remove shorter chain PFAS using AC adsorption due to the preferential adsorption of longer-chain PFAS and longer-chain PFAS precursors [38]. For PFAS destruction, advanced oxidation processes (AOPs) have been a promising candidate approach which have been used for a range of emerging organic contaminants. Most AOPs employ catalysts to generate hydroxyl radicals (OH·), which destroy the target contaminants. These processes can often be mediated by ozone (O_3), hydrogen peroxide (H_2O_2), metal oxide catalysts, and even photons [41,42]. Among these, light-induced AOPs have been extensively investigated as an alternative for PFAS degradation because of the high efficiency of photocatalytic materials [43].

Electrochemical separation and electrocatalytic processes have shown to be promising approaches for pollutant removal from water, as they provide a modular approach alternative to conventional methods requiring chemical or thermal input[44]. For example, electrosorption-based separation methods have been shown to efficiently remove different pollutants, including perfluorinated compounds, via electrochemical input [45,46]. Electrochemical advanced oxidation processes (EAOPs), such as electro-Fenton processes and photoelectrocatalysis, provide new degradation pathways that avoid the need for chemical input from conventional AOPs [47,48]. Electrochemically-mediated processes also provide other advantages such as integration with renewable energy sources, which could assist in off-grid deployment, as well as reduced chemical costs due to electrical-field driven regeneration.

With the rapid growth of research on PFAS remediation, several reviews have addressed the PFAS occurrence and environmental impact [25,27,29,49,50], fate and transport [3,7], and different water remediation technologies [2,35,51]. These comprehensive reviews on treatment technologies have discussed adsorption using different materials like activated carbon, ion exchange resins, minerals, biomaterials, polymers, and nanomaterials [4,5,32,52,53]. Despite recent publications on electrochemical water treatment technologies for organic pollutant remediation [45,54–57, 58], only a handful of reviews on PFAS have discussed electrochemical approaches [8,25,35,49,59].

Thus, with the growing interest and applicability of electrochemical approaches for PFAS remediation, we focus this perspective review on the discussion of electrochemically-driven methods for PFAS removal from water. We discuss advances in electrosorption and electrochemical degradation methods including electrocoagulation (EC), Electro-Fenton (EF), and electrochemical oxidation (electrooxidation or EO) for PFAS remediation. We also present electrically-driven methods such as photoelectrochemical and plasma-based methods, and highlight the importance of developing hybrid methods that can synergistically integrate advantages of different approaches, while overcoming limitations. Finally, we discuss current challenges with PFAS removal using electrochemical methods, including energy consumption, monitoring byproduct formation during degradation, and the need for more rigorous comparative studies and technoeconomic analyses.

2. Electrosorption

Electrochemical adsorption, also referred to as electrosorption, is used to describe a process in which a dissolved species binds onto the surface of a polarized electrode by means of an induced electric field [60]. The potential difference between electrodes allows for ions to be separated from the bulk solution, and adsorb to the charged electrode surface. Next, removing or reversing the potential drives the release of the ions back into solution, thereby regenerating the electrodes without any addition of chemicals or requirement for a physical process (**Fig. 1**). Electrosorption-based separation methods have demonstrated remarkable selectivity towards different pollutants (i.e., heavy metals [61, 62, 63], and organic anions [64]).. However, electrosorption has only recently been studied as a possible remediation method for PFAS. **Table 1** summarizes recent studies on PFAS removal using electrosorption and other electrochemically driven methods. As with the majority of current PFAS remediation studies, most of these investigations have focused on long-chain PFAS, like PFOA and PFOS, because of their historicaly heavy use and recent prohibition from manufacturing. This section reviews studies involving electrosorption of PFAS using different materials, and their advantages and disadvantages compared to other technologies.

Table 1
Summary of electrochemically driven techniques for PFAS remediation in the literature.

Method	Electrode (anode || cathode)	Water Matrix	Target PFAS	Initial Conc. (ng/L)	Performance			Refs.
					RE (%)	DR (%)	Time (hr)	
Electro-sorption	Redox copolymer/ CNT || Pt wire	DI water +20 mM NaCl	PFOA /	4.1×10^7	> 90	q_e >600	> 5	[45]
			PFNA /	4.6×10^7	-	q_e >400	0.5	
			PFSA /	4.9×10^7	-	q_e >350	0.5	
			PFOS	5.0×10^7	-	q_e =500	0.5	
Electro-sorption	Redox copolymer/ CNT || Pt wire	DI water +20 mM NaCl	PFOA	4.1×10^7	> 90	q_e >600	>5	[45]
			PFNA	4.6×10^7	-	q_e >400	0.5	
			PFSA	4.9×10^7	-	q_e >350	0.5	
			PFOS	5.0×10^7	-	q_e =500	0.5	
		Secondary WW	PFOA	1×10^5	> 82.5	--	3	
	Graphene/ CNT || Ti	DI water	PFOA /	4.1×10^7	96.9	q_e =492	4	[66]
			PFOS	5.0×10^7	97.0	q_e =556	2	
		Secondary WW	PFOA	1×10^5	> 82.5	-	3	
	Graphene/ CNT || Ti	DI water	PFOA	4.1×10^7	96.9	q_e =492	4	[66]
			PFOS	5.0×10^7	97.0	q_e =556	2	
	AC felt || Pt plate	DI water +10 mM Na_2SO_4	PFOA	1×10^6	–	q_e ~85	48	[68]
	AC felt || Pt plate	DI water +10 mM Na_2SO_4	PFOA	1×10^6	-	q_e ~85	48	[68]
	MWCNT || MWCNT	DI water +1 mM Na_2SO_4	PFOA	5×10^4	89	-	0.5[a]	[73]
			PFOS		90			
	MWCNT || MWCNT	DI water +1 mM Na_2SO_4	PFOA	5×10^4	89	-	0.5[a]	[73]
			PFOS	5×10^4	90			
EO	PbO_2 || Pt wire	DI water +10 mM Na_2SO_4	PFOA	4×10^6	99	59	4	[91]
EO	PbO_2 || Pt wire	DI water +10 mM Na_2SO_4	PFOA	4×10^6	99	59	4	[91]
	Ce-doped PbO_2 || Pt wire	DI water +100 mM $NaClO_4$	PFBA	1×10^8	31.8	14.9	1.5	[92]
			PFPeA		41.4	27.5		
			PFHxA		78.2	62.5		
			PFHpA		97.9	86.2		
			PFOA		96.7	81.7		
	Ce-doped PbO_2 || Pt wire	DI water +100 mM $NaClO_4$	PFBA	1×10^8	31.8	14.9	1.5	[92]
			PFPeA		41.4	27.5		
			PFHxA		78.2	62.5		
			PFHpA		97.9	86.2		
			PFOA		96.7	81.7		
	Ti/RuO_2 || SS	GW +500 mg/L Na_2SO_4	PFOA /	1.3×10^4	–	58	> 6.7	[93]
			PFOS	1.8×10^4		98		
	Ti/RuO_2 || SS	GW +500 mg/L Na_2SO_4	PFOA	1.3×10^4	-	58	> 6.7	[93]
			PFOS	1.8×10^4		98		
	Ti/SnO_2-Sb-Bi || Pt sheet	DI water +1.4 g/L $NaClO_4$	PFOA	5.0×10^7	99	63.8	3	[94]
	Ti/SnO_2-Sb-Bi || Pt sheet	DI water +1.4 g/L $NaClO_4$	PFOA	5.0×10^7	99	63.8	3	[94]
	Ti/TiO_2-NTs/Ag_2O/ PbO_2 || Ti	DI water +1.4 g/L $NaClO_4$	PFOS	4.6×10^7	74.9	11.5	3	[95]
	Ti/TiO_2-NTs/Ag_2O/ PbO_2 || Ti	DI water +1.4 g/L $NaClO_4$	PFOS	4.6×10^7	74.9	11.5	3	[95]
	BDD || Pt-deposited Ti plate	DI water +10 mM $NaClO_4$	PFOA	3.3×10^9	–	–	10	[96]
	BDD || Pt-deposited Ti plate	DI water +10 mM $NaClO_4$	PFOA	3.3×10^9	-	-	10	[96]
	BDD || BDD	DI water	PFBS /	2.9×10^6	45	66[b]	43	[97]
			PFHxS /	1.1×10^7	91			
			PFOS	1.5×10^7	98			
	BDD || BDD	DI water	PFBS	2.9×10^6	45	66[b]	43	[97]
			PFHxS	1.1×10^7	91			
			PFOS	1.5×10^7	98			

(*continued on next page*)

Table 1 (*continued*)

Method	Electrode (anode || cathode)	Water Matrix	Target PFAS	Initial Conc. (ng/L)	Performance			Refs.
					RE (%)	DR (%)	Time (hr)	
	Si/BDD || Ti sheet	DI water	PFBA /	2.4×10^7	-	~80	2	[98]
			PFBS /	3.4×10^7	-	~50		
			PFHxA /	3.6×10^7	-	~70		
			PFHxS /	4.6×10^7	-	~65		
			PFOA /	5.0×10^7	97.5	~65		
			PFOS /	5.7×10^7	-	~70		
			PFDeA	5.9×10^7	-	~55		
	Si/BDD || Ti sheet	DI water	PFBA	2.4×10^7	-	~80	2	[98]
			PFBS	3.4×10^7	-	~50		
			PFHxA	3.6×10^7	-	~70		
			PFHxS	4.6×10^7	-	~65		
			PFOA	5.0×10^7	97.5	~65		
			PFOS	5.7×10^7	-	~70		
			PFDeA	5.9×10^7	-	~55		
EF	Pt wire || HPC	DI water + 0.3–1.5 mM $FeSO_4$ + 50 mM Na_2SO_4	PFOA	5.0×10^7	90.7	64.8	4	[85]
EF	Pt wire || HPC	DI water + 0.3–1.5 mM $FeSO_4$ + 50 mM Na_2SO_4	PFOA	5.0×10^7	90.7	64.8	4	[85]
EF/ EC	Fe plate || Fe plate	DI water +35 mM NaCl	PFOA	9.9×10^6	100	60	6	[87]
EF/ EC	Fe plate || Fe plate	DI water +35 mM NaCl	PFOA	9.9×10^6	100	60	6	[87]
Solar photo-EF	Pt wire || MOF/CNF composite membrane	DI water +20 mmol H_2O_2	PFOA	2×10^7	99	59	2	[88]
Solar photo-EF	Pt wire || MOF/CNF composite membrane	DI water +20 mmol H_2O_2	PFOA	2×10^7	99	59	2	[88]
EC	Zn || SS rod	DI water +10 mM NaCl	PFOS	10^5–10^8	> 95	q_e =3496	0.2	[107]
			PFOA		96.7	q_e =2286	0.2	
Plasma	HV power supply	Effluent from GWTP	PFOA	~994	> 90	–	0.5	[113]
			PFOS	~250	> 90			
			PFHxS	~400	~60			
	Plasma reactor	GW in fire training area	PFNA	70–1060	100	–	0.2 - 0.3	[115]
			PFOA		95-100			
			PFHpA		90-95			
			PFHxA		55-70			
			PFPeA		45-55			
			PFBA		0			
			PFNS	17-4100	100			
			PFOS		90-95			
			PFHpS		95-100			
			PFHxS		100			
			PFPeS		85-90			
			PFBS		75-85			

RE= removal efficiency.
DF= Defluorination ratio.
EO= electrooxidation.
EF= electro-Fenton.
EC= electrocoagulation.
q_e= uptake capacity (mg/g).
HPC= hierarchically porous carbon electrode.
(a) Hydraulic retention time.
(b) Total defluorination of all species in solution.

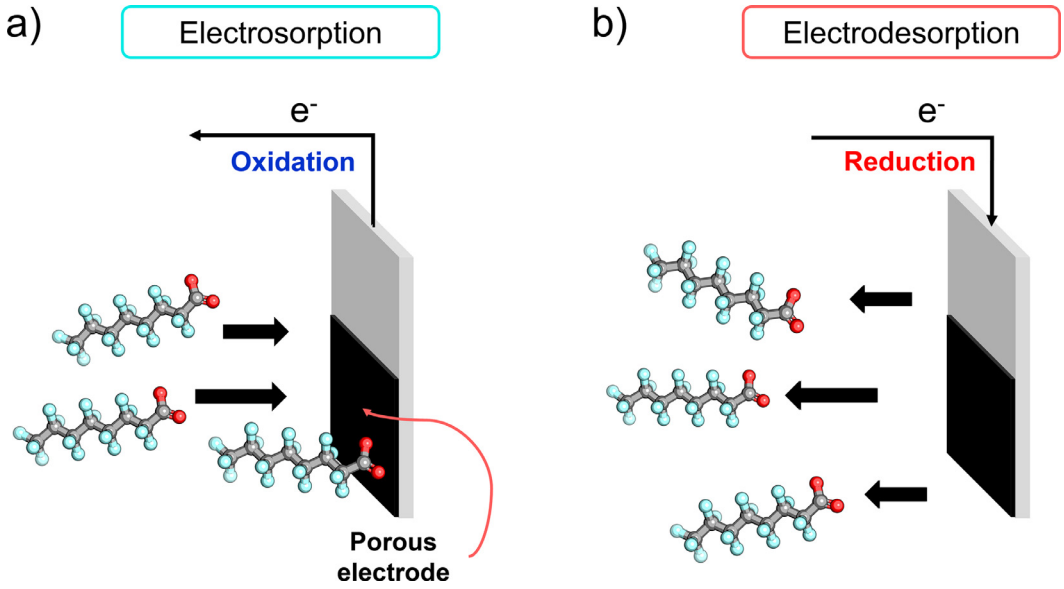

Fig. 1. (a) Electrosorption of PFAS on a positively polarized electrode and (b) electrodesorption of PFAS on a negatively polarized electrode.

2.1. Electrosorption using carbon materials

Most studies on electrochemical adsorption of perfluorinated compounds have focused on carbon materials. Carbon-based electrodes have been extensively used in electrochemical separations, such as capacitive deionization, due to their high surface area, porosity, electrochemical stability, conductivity, and abundance [59]. In general, carbon materials with net positive surface charges exhibit a better PFAS adsorption capacity than those with zero net charge, due to counter-ion attraction with deprotonated PFAS. Also, carbon materials with mesopores have showed better adsorption for hydrophobic PFAS, while microporosity has been observed to be more important for more hydrophilic PFAS [65]. Possible mechanisms proposed for these effects include competitive adsorption between PFAS and dissolved organic matter (DOM), which often results in blocking or narrowing of the micropores and subsequent exclusion of larger PFAS over smaller PFAS. Another possibility is that more hydrophobic PFAS and larger molecules tend to have a lower mobility compared to the more hydrophilic ones and DOM, which leads to faster transport of smaller molecules into the micropores. Typically, mesoporous carbon suffers less from pore blocking, allowing PFAS to access the micropores which are the primary adsorption sites [65]. While most studies have investigated PFAS removal using carbon materials without applied potential, recent research has showed that applying an electrochemical potential can greatly enhance the adsorption of PFAS on materials like activated carbon, carbon nanotubes (CNTs), and graphene oxide [46,52,66].

Activated carbon (AC) has been extensively used in water purification applications because of its low price and high surface area (1000–2000 m^2/g) [67]. Although electrosorption using activated carbon has been studied for other pollutants [54], electrosorption of PFAS using activated carbon has only recently been investigated. Saeidi et al. studied the adsorption of PFOA and perfluorobutanoic acid (PFBA) via electrification of commercial AC felts [68]. In this study, electrosorption at +0.5 V and electrodesorption at −1.0 V of PFOA were performed at concentrations ranging from 1 µg/L to 1 mg/L, which showed maximum uptakes of ~85 mg/g. However, an experiment conducted for 10 cycles applying 0.3 V for adsorption and −0.1 V for desorption showed a significant decrease in electrosorption of PFOA through the course of the ten cycles. This decrease was attributed to the partial attrition of the carbon electrodes due to the direct oxidation and reduction over prolonged times, which decreases the lifetime of the AC in the system. The deterioration of carbon electrodes has been observed in multiple studies with CDI cells [68, 69, 70], and the stability of these electrodes has been shown to increase by using milder positive potentials [69]. The same behavior was observed in the previous study, where a more stable performance over a course of 10 cycles was achieved by adsorbing the PFAS without potential and then desorbing at −0.1 V [68]. Thus, the implementation of AC electrodes for electrosorption of the anionic PFAS is limited by the mostly neutral to negative potentials that can be applied to such electrodes to avoid their deterioration.

The lack of extensive electrosorption studies on PFAS remediation using AC could also be due to the challenges involved in the electrode fabrication. For example, a challenge of using AC is the high manufacturing costs and lower performance of the electrodes since their fabrication usually requires polymeric binders to hold the carbon powders together, which results in a lower electrical conductivity and lower uptake capacities [67]. In addition, the conductivity of activated carbon is relatively low compared to other carbon electrode materials [46,71].

Many PFAS electrosorption studies have used carbon nanotubes (CNTs) due to their unique nanostructures, conductivity, and high surface area [46,52,66,72]. PFOA and PFOS sorption using multi-walled carbon nanotubes (MWCNTs) was studied under both open circuit potential (OCP) and applied potential of +0.6 V [46]. Results showed that the adsorption rates increased by a factor of 60 and 41 for PFOA and PFOS, respectively, compared to the rates at OCP for concentrations ranging from 50 µg/L to 10 mg/L (**Fig. 2**) [46]. Although the study did not investigate PFAS desorption electrochemically, it was found that the electrodes could be regenerated by cleaning in an aqueous solution at 90 ºC. Enhanced adsorption of PFOA and PFOS under applied potential was also observed using MWCNTS in continuous flow and concentrations ranging from 20 to 100 µg/L [73]. A ~5-time increase over open circuit conditions with removal efficiencies of 89% (134 µg adsorbed) and 90% (154 µg adsorbed) for PFOA and PFOS, respectively, were obtained at optimal conditions of +1.0 V and 30-minute hydraulic retention time [73]. Despite the high removal efficiencies, carbon nanotubes can be economically restrictive due to the difficulty in

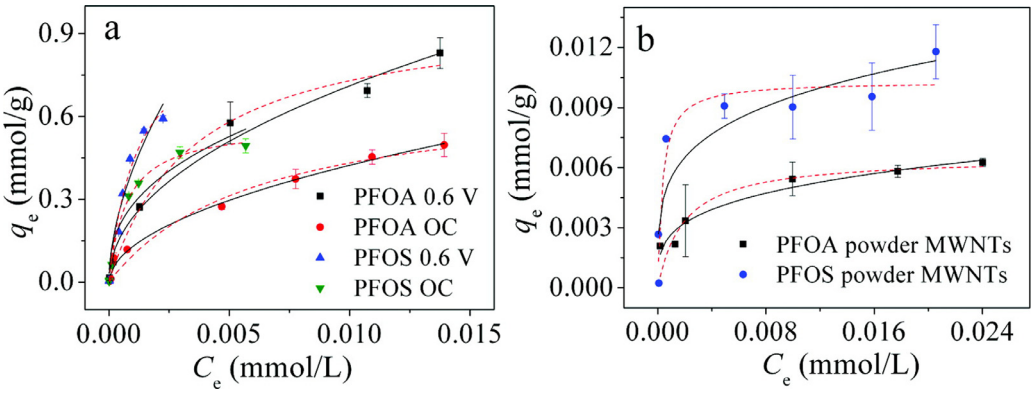

Fig. 2. (a) Electrosorption isotherms of PFOX on MWCNTs electrode at 0.6 V and OCP adsorption. (b) Adsorption isotherms of PFOX on powder MWCNTs. Simulation by Langmuir model (- - -) and Freundlich model (—). Reprinted with permission from X. Li, S. Chen, X. Quan, Y. Zhang, Enhanced Adsorption of PFOA and PFOS on Multiwalled Carbon Nanotubes under Electrochemical Assistance, Environmental Science and Technology, 45 (2011) 8498–8505. Copyright 2011 American Chemical Society.

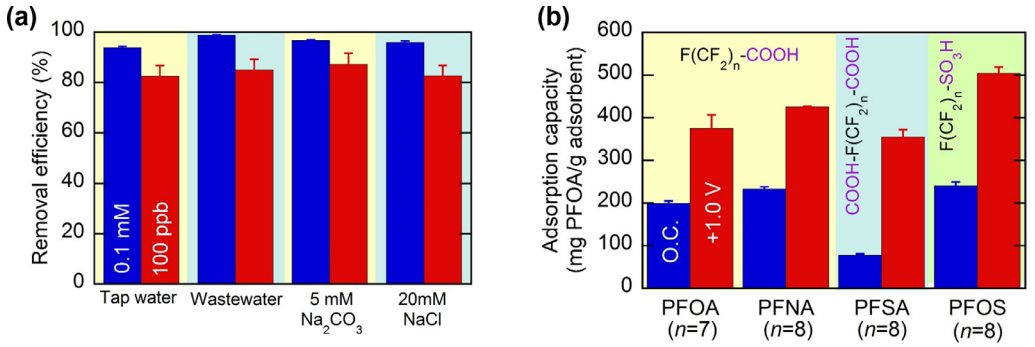

Fig. 3. Uptake capacity of different PFAS with P(TMA51-co-TMPMA49)-CNT electrode at open circuit and +1.0 V (adsorption: 0.1 mM PFAS + 20 mM NaCl for 0.5 h). Reprinted with permission from K. Kim, P. Baldaguez Medina, J. Elbert, E. Kayiwa, R.D. Cusick, Y. Men, X. Su, Molecular Tuning of Redox-Copolymers for Selective Electrochemical Remediation, Advanced Functional Materials, 30 (2020) 1–10. Copyright 2020 John Wiley and Sons.

controlling large-scale synthesis, and associated costs required for bulk production [74]. Furthermore, the performance of these electrodes can depend on the oxygen content in the carbon nanotubes. For example, the adsorption of PFOA, PFOS, perfluorooctanesulfonamide (PFOSA), 2,4-dichlorophenoxyacetic acid (2,4-D), and 4-n-nonylphenol (4-NP) was found to decrease with increasing oxygen content on MWCNTs [75].

2.2. Electrosorption using functionalized carbon materials

Recently, the functionalization of different carbon materials on electrodes has been explored as an alternative method to enhance the selectivity and capture of PFAS from water. Redox-active materials have been leveraged as ion-selective platforms for a number of applications [76, 77, 78], ranging from rare-earth element recovery to contaminant capture and degradation [79–82, 83]. Recently, Kim et al. focused on long-chain PFAS capture using 4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TMA) and 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine (TMPMA) redox copolymer-CNT electrodes [45]. The electrodes showed high PFOA uptake capacities (>600 mg/g) and separation factors (500 vs chloride ions) at +1.0 V potentials and 0.1 mM PFOA + 20 mM NaCl concentrations. More than 80% regeneration of the adsorbent was achieved by applying −1.0 V vs. Ag/AgCl, which allowed the release of the anions by charge repulsion and polarization of the electrode surface [45]. The study also investigated the adsorption of other PFAS, including PFOS, perfluorononanoic acid (PFNA), and perfluorosebacic acid (PFSA) (**Fig. 3**). Results showed overall higher uptake for applied potential conditions (> 300 mg/g), suggesting electrostatic interactions played a key role in the electrosorption mechanism.

Graphene-functionalized CNT electrodes showed that adding 20% graphene into CNTs electrodes improved the electrode capacitive behavior and led to higher adsorption capacities for 0.1 mM PFOA and PFOS (491.9 mg/g and 555.8 mg/g, respectively) [66]. The study also investigated the effects of applied potential (+1.5 V) versus pure adsorption at OCP conditions, and found a higher uptake after electrosorption compared to PFOA and PFOS adsorption experiments with no applied potential. The adsorption mechanism was explained by the enhanced electromigration of PFAS from the bulk of the solution to the electrode surface [66].

Functionalized carbon materials have also been used to explore PFAS adsorption mechanisms, and surface interactions with various chemical groups [71,84]. Although electrostatic and hydrophobic interactions between PFAS and different adsorbents have been extensively studied [4,5,65,85,86], the influence of fluorophilic interactions in PFAS adsorption mechanisms is not fully understood [84]. Interestingly, the role of fluorophilic interactions was studied via electrosorption of PFOA using fluorine-functionalized electrodes [71]. Graphene oxide aerogels doped with copper nanoparticles and fluorine were prepared via a one-step hydrothermal process using HF as the fluorination source. The fluorine was used to leverage fluorophilic interactions between PFOA and the functionalized aerogel electrodes, while copper was added to increase the aerogel conductivity. The electrosorption capacity of modified electrodes was enhanced significantly (**Fig. 4**) due to ligand-exchange reactions and electrostatic interactions between the electrode and PFOA anions [71]. Applying a potential of +0.8 V increased the adsorption of PFOA when compared to the OCP experiments, while

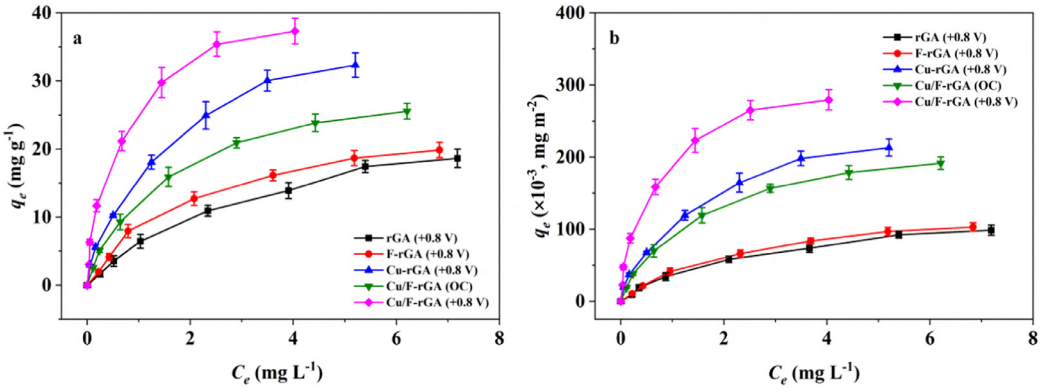

Fig. 4. Electrosorption isotherms of PFOA on reduced graphene oxide aerogel (rGA), F doped rGA (F-rGA), Cu nanoparticle-doped rGA (Cu-rGA) and F and Cu nanoparticle modified rGA (Cu/F-rGA) electrodes. (a) Solid-phase concentrations are expressed by the unit of mg g^{-1}, and (b) solid-phase concentrations are expressed by the unit of mg m^{-2} (normalized by surface area). Reprinted with permission from L. Liu, Y. Liu, N. Che, B. Gao, C. Li, Electrochemical adsorption of perfluorooctanoic acid on a novel reduced graphene oxide aerogel loaded with Cu nanoparticles and fluorine, Journal of Hazardous Materials, 416 (2021) 125,866–125,866. Copyright 2021 Elsevier.

the electrode regeneration was >75% after 10 cycles of electrosorption and electrodesorption experiments. However, the adsorption capacities were relatively low (<50 mg/g) for PFOA concentrations ranging from 0.5 mg/L to 10 mg/L.

3. Electrochemically-mediated degradation techniques

Electrochemically-mediated degradation processes have been widely used for water remediation purposes [87]. For perfluorinated substances, degradation processes have become a leading technique that has garnered much attention in the recent decade (**Table 1**). The most studied electrochemical method for PFAS degradation has been the generation of free radicals that serve as catalytic agents for defluorination. Electrochemical defluorination can be modular, scalable, and greener, often not requiring the addition of external chemicals. In general, electrochemically-mediated degradation methods can be divided into two categories: electrochemical advanced oxidation processes (EAOPs) and advanced reduction processes (ARPs), with the former one being the most widely studied. This section will discuss how EAOPs and ARPs have been implemented to degrade PFAS in different water matrices.

3.1. Electrochemical advanced oxidation processes (EAOPs)

3.1.1. Electro-fenton reactions

Fenton reactions were studied for the first time in 1894 by Henry Fenton (hence the name) [88]. Still, it was not until 1931 that the hydroxyl radical mechanism that explains the AOP process was elucidated [89]. The mechanism consists of the oxidation of Fe^{2+}into Fe^{3+} after reacting with H_2O_2 (Eq. (1)). This reaction then produces OH· that react with the targeted species (**Fig. 5a)**). A slower reaction (Eq. (2)) is also generated and produces HO_2· radicals that can also react with the targeted species.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + H^+ \quad (2)$$

Fenton processes have been used for AOPs since the 60 s [90]. Since it has been extensively studied for several decades, most of the significant drawbacks of this process have been overcome (i.e., generation of iron sludge from the slower reaction and low mineralization caused by intermediates species). The electro-Fenton (EF) process was developed in the early 2000s and has helped prevent most of the byproducts within iron sludge that decrease the reaction's efficiency [91]. In an EF process, the method is enhanced by the in-situ electro-generation of H_2O_2 (produced by reducing O_2), thus eliminating the need of H_2O_2 additives throughout the reaction. During the reduction reaction, O_2 combines with $H+$ and solvated electrons to generate the H_2O_2 (Eq. (3)). This process can also be classified as an electrocoagulation process since it combines Fenton reactions with sludge generation [92].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (3)$$

The EF process was implemented for degrading PFOA by Liu et al. in 2015 [93]. The study used hierarchically porous carbon to promote O_2 reduction, a material which provided a high surface area to carry out the electrocatalytic process. The process was able to mineralize PFOA up to 90.7% after four hours of operation. Wang et al. more recently established a tandem process, in which a Fe/Mn cathode was used to generate H_2O_2 while BDD was used in the anode to accelerate OH· generation [94]. The tandem system resulted in a mineralization of 93% within four hours. Similarly, a study by Kim et al. 2020 showed the application of iron-based electrodes to enhance the electrocatalytic process [95]. Both cathode and anode were composed of iron plates, with the side reactions proposed are depicted in **Fig. 6**. The system was shown to degrade 60% of the PFOA.

The efficiency of the EF process, and OH· generation, can be strongly influenced by the choice of the cathode material. Recent advances have combined porous electrodes with metal-organic frameworks (MOF) to enhance the degradation factor of the EF process [96]. Wang et al. first established a solar-electro-Fenton process for PFAS degradation [96]. The study showed 91% of the PFOA was mineralized in only two hours. Photo-Fenton processes have been used previously for water treatment, showing high efficiencies for total organic compound removal [97]. Although this technique seems very promising, only a handful of studies have been carried out so far for PFAS. In the future, more extensive studies could expand the applicability of these processes towards shorter chain PFAS.

3.1.2. Electrochemical oxidation

Electrochemical oxidation (electrooxidation, EO) is a process that involves the production of hydroxyl radicals by means of water splitting, without the need of applying any chemical additives [98]. During the process, OH radicals are produced on a material that causes an overpotential high enough for the oxygen evolution reaction to occur when applying lower potentials. Such materials often include boron-doped diamonds (BDD) and metal oxides materials such as titanium oxides (TiO_2), lead oxide (PbO_2), ruthenium oxide (RuO_2), and tin oxide (SnO_2). Metal oxide materials have become more popular because they are much cheaper

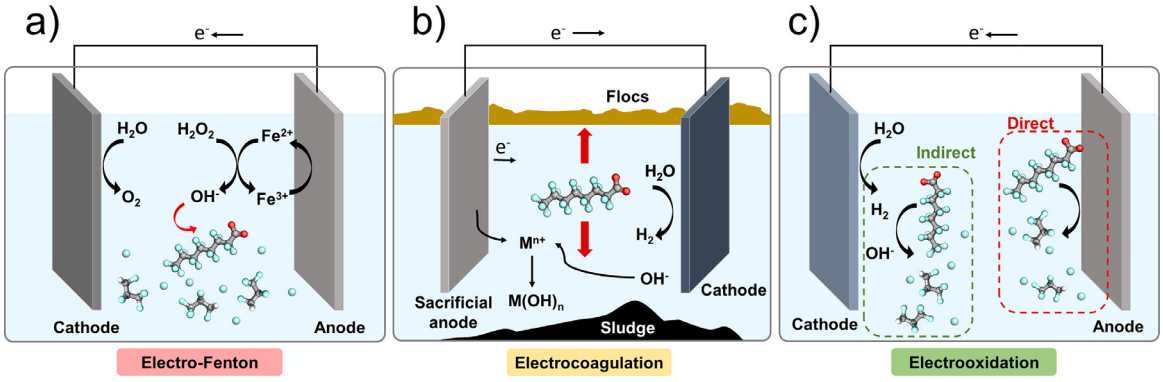

Fig. 5. Electrochemical advanced oxidation processes used for PFAS degradation (a) Electro-Fenton mechanism, (b) electrocoagulation methods and (c) indirect and direct electrooxidation.

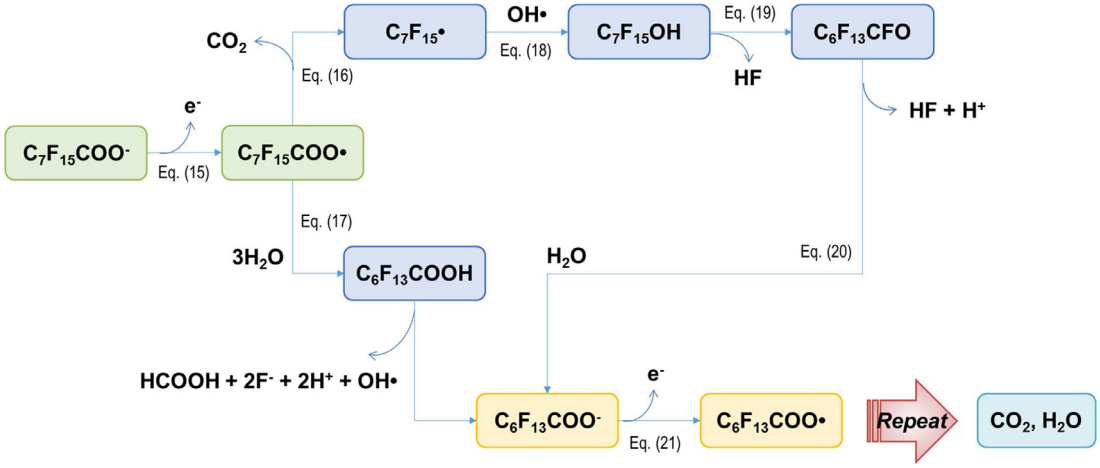

Fig. 6. Proposed mechanism of PFOA degradation in a electrocoagulation process using iron electrodes. Reprinted with permission from M.-K. Kim, T. Kim, T.-K. Kim, S.-W. Joo, K.-D. Zoh, Degradation mechanism of perfluorooctanoic acid (PFOA) during electrocoagulation using Fe electrode, Separation and Purification Technology, 247 (2020) 116,911. Copyright 2019 American Chemical Society.

and durable than BDD [99–102, 103]. Despite this, the impressive ability of BDD to defluorinate PFAS has led to its ongoing studies [104, 105, 106].

The degradation kinetics of BDD electrodes have been extensively studied under different conditions. Evaluation on current densities indicated that degradation rates are increased when larger current densities are applied [107,108], yet this effect is not observed in phosphate buffer solutions, possibly because phosphate is a less reactive ion than chlorine which is usually present in the oxidative process [107]. Uwayezu et al. explored the degradation of BDD in wastewater and found that sulfonic acids can be more readily degraded than carboxylic acids [108]. Although this behavior differed from previously reported data [105,107,109], the higher degradation for sulfonic acids over carboxylic ones was attributed to the presence of PFCAs precursors in real water matrixes,which can increase the concentration of PFCAs upon reaction [107,109]. Material properties such as BDD particle size has also shown to influence PFAS degradation. For example, a higher degradation was observed when conducting experiments with micronanocrystals versus ultrananocrystals [109], yet the degradation efficiency was not affected by the amount of boron doping in BDD electrodes with varying quantities of boron [107].

Metal oxides such as TiO_2, and PbO_2, have been evaluated as electrocatalytic electrode materials for PFAS degradation. For example, PbO_2 can be obtained from lead-acid batteries and is also a commercially available product since large quantities have been produced to generate the batteries [110]. An electrode created using PbO_2 extracted from a lead-acid battery led to a PFOA degradation of 99% with a defluorination of ~59% [99]. Other interesting materials are Magnéli phase titanium suboxide (TSO) anodes due to their low commercial cost and high conductivity. TSO consists of a titanium oxide structure with the formula Ti_nO_{2n-1}, with Ti_4O_7 being the most common structure [111]. Wang et al. developed a method to utilize TSO electrodes to analyze the degradation pathway of different PFAS [112]. The study reported a faster and complete degradation in experiments that contained longer chain PFAS, and showed that PFAS degradation can be achieved while using cheaper alternatives to BDD electrodes.

3.1.3. Electrocoagulation

Electrocoagulation (EC) is a process that relies on the dissolution of cations (e.g., Zn^{2+}, Al^{3+}, Fe^{3+}), which are formed in the anode, often called the sacrificial electrode (**Fig. 5b**). The methodology of the EC process consists of three main steps: (1) the sacrificial electrode oxidizes to form the coagulants that will then (2) destabilize the contaminants or targeted species and produce an aggregation and suspension of the targeted compounds to subsequently (3) form the flocs that will be eliminated from the solution via sedimentation and filtration [113].

The formation of these complexes allows for the adsorption of a target molecule for successful water remediation. For PFAS degradation, EC methods have been studied in tandem with AOPs. For example, a study by Shi et al. generated PFAS-containing flocs by using a sacrificial anode of zinc and applying a direct current method [114]. Zinc was selected as the sacrificial anode according to a previous study that compared the behavior of different sac-

rificial anode materials including zinc, iron, magnesium, and aluminum, which found that PFAS were aggregated into the zinc hydroxide flocs faster than with the aforementioned anode materials [115]. Then, to fully mineralize the PFAS, EC was followed by electrooxidation using a Ti_4O_7 electrode, which showed over 90% degradation of the longer chain PFAS in only 60 min [114]. Yang et al. developed a tandem EC system by adding metal cation Fe in the form of $FeCl_3{\cdot}6H_2O$ to promote a neutralization effect. This effect facilitates the aggregation step by eliminating the electrostatic ingress towards the adsorbates. The system could remove 99% of PFOA using a Fe anode and through intermittent addition of H_2O_2 [116]. This type of treatment could also be classified as an electro-Fenton process since the removal is enhanced by using an oxide material which favors OH· production.

3.2. Advanced reduction processes (ARPs)

Advanced reduction processes (ARPs) have advanced the field as emerging techniques capable of destroying PFAS in a rapid fashion. The process is done by producing highly reactive species, similar to AOPs, but ARPs require reducing hydrated electrons [117,118]. In addition to the hydrated electrons, other reductive catalysts involved in the reduction process include H· and sulfite radicals.

In the specific case of PFAS, ARPs mainly use hydrated electrons to destroy the compounds [119]. Photodegradation is one of the most studied ARPs for PFAS destruction due to its capability of using simple solar energy, thus increasing the energy efficiency of the process. A study by Lyu et al. suggested that photochemical degradation of PFSAs using the reductive process is highly affected by the pH of the solution, and that degradation would be more favorable in alkaline solutions and anoxic conditions [120]. Since most of these processes occur in neutral to mildly acidic environments, new strategies should be focused on developing ARPs in real-water matrixes.

Plasma-based degradation processes are ARPs that have also shown excellent degradation performance towards PFAS. The Thagard group has carried out several studies on plasma degradation of PFAS, ranging from lab scale to pilot plant scale applications [121, 122, 123]. These studies have shown the high degradation efficiency and fast kinetics of plasma processes for PFAS degradation. For example, Stratton et al. showed that 90% of PFOA was degraded in just 30 min by using electrical discharge plasma [121]. Therefore, to understand the degradation pathways, a mechanistic study explored the main components affecting the mineralization of the C–C and C-F bonds' wrecking [122]. It showed that hydrated electrons break down the PFAS into shorter chain PFAS to fully degrade the system (**Fig. 7**) [122]. Separately, an industrial scaleup study used plasma treatment for long-chain, short-chain, and PFAS precursor removal. More than 90% of long-chain perfluoroalkyl acids and PFAS precursors were removed while short-chain perfluoroalkyl acid concentrations were reduced by 88% [123]. Therefore, plasma-based treatment can be an impactful, emerging electrically-driven approach for large-scale PFAS remediation.

4. Hybrid Methods for PFAS remediation

While electrochemical separation and oxidation processes present advantages over conventional water treatment methods (i.e., reversible sorption, improved selectivity, modularity, and scalability) [44], these techniques do not offer a holistic solution on their own. For example, although some EAOPs have shown superior performance for the degradation of perfluorinated substances [8,59,124], the large operation costs due to high energy consumption and restricted mass transfer limitations prevent their implementation for large scale applications [8]. Another drawback of using EAOPs is the potential formation of toxic organo-chlorinated byproducts and short-chain PFAS, due to incomplete mineralization and possibly other reactive ions in the water matrix [8,49,124, 125, 126].

On the other hand, electrosorption techniques require further treatment of the waste stream to fully defluorinate or mineralize. As such, any single method can often be insufficient to address the complexity of the reaction/separation problem. Recent advances have focused on coupling electrochemical processes with different water remediation techniques by exploiting the advantage of individual approaches. For instance, recent studies have shown that integration of EAOPs with membrane separation enhances the overall removal efficiency and mitigates membrane fouling [127,128]. As a result, significant research on the development of combined electrochemical technologies for the removal of PFAS has become an area of growing interest. This section reviews integrated approaches using electrochemical methods and discusses the advantages of coupling distinct systems for synergistic performance. **Table 2** presents a summary of studies on PFAS removal using integrated electrochemical methods.

4.1. Membrane pre-concentration followed by electrochemical degradation

Due to the very low concentrations of PFAS in different water matrices [3,17], most water treatment methods are unable to efficiently remediate streams at naturally occurring concentrations [35]. A possible solution is to implement a pre-concentration step, to facilitate removal at low concentration streams, and thus reduce energy consumption. These approaches have been used for addressing the treatment of PFAS contaminated water. For example, the integration of membrane separation with BDD electrooxidation for perfluorohexanoic acid (PFHxA) removal showed that pre-concentration before the electrooxidation stage significantly reduced the energy consumption (15.2 kWh/m^3) while obtaining a 90% removal ratio [129]. A similar case study for PFHxA remediation showed that pre-concentration using a nanofiltration (NF) membrane followed by BDD electrochemical oxidation of the concentrate saved 77% and 59% of the energy compared to direct BDD oxidation for removal ratios of 90% and 99%, respectively [130]. The study combined simulation techniques with laboratory data to study the mass transfer and electrolysis kinetics. However, a 99% removal efficiency was only achieved using a selective NF90 membrane. Interestingly, no improvement was noted when a less selective NF membrane was used, showing the importance of materials selection during integration (**Fig. 8**). These studies were performed using simulated industrial process water with relatively high PFAS concentrations (60–204 mg/L), so further research may be needed to evaluate these integrated approaches for other environmental contexts (e.g. PFAS occurrence in the µg/L-ng/L range).

Similarly, removal of hexafluoropropylene oxide dimer acid (HFPO-DA, also known as GenX) was achieved using an NF90 membrane and subsequent treatment of the retentate via electrooxidation [131]. A 99.5% removal of 1 mg/L HFPO-DA was observed when using a combined treatment, and the energy consumption was lowered by more than an order of magnitude when compared with an electrochemical oxidation step by itself. The treatment of a mixture of six PFAS in groundwater (initial concentrations of 10 µg/L each) was also carried out using membrane pre-concentration and BDD electrooxidation [132]. The integrated approach used a cascade of four reverse osmosis (RO) membranes stages followed by electrooxidation of the concentrate, and yielding a total PFOA and PFOS concentration lower than 70 ng/L while obtaining a lower energy consumption than using solely an electrochemical treatment.

Table 2
Summary of coupled electrochemical methods for PFAS removal in the literature.

Method	Electrode (anode || cathode)	Water Matrix	Target PFAS	Initial Conc. (ng/L)	Performance			Refs.
					RE (%)	DR (%)	Time (hr)	
Electro-sorption/ EO	BDD || redox copolymer /CNT	DI water + 20 mM NaCl	PFOA	4.1×10^7	> 90	80	5	[45]
EF/ EO	BDD || Fe/Mn	DI water +50 mM Na_2SO_4	PFOA	5.0×10^7	97	93	4.5	[94]
		Wastewater from DWTP	PFOA	61.6	96	91	4	
RO/ EO	BDD || BDD	RO retentate of GW	PFBS	1.6×10^4	83	42[a]	18	[105]
			PFHxS	1.2×10^5	92			
			PFOS	7.0×10^4	96			
EC/ EO	EC: Zn || SSEO: Ti_4O_7 || SS	DI water +20 mM Na_2SO_4	PFOA	10^4–10^5	> 95	-	1	[114]
			PFOS		> 95			
			PFNA		> 95			
			PFHpA		> 95			
			PFHxA		> 95			
			PFHxS		> 95			
			PFBS		73.4			
NF/ EO	p-Si/BDD || p-Si/BDD	Industrial Process water	PFHxA	10^7–10^8	98	–	1.5	[129]
	BDD || SS	NF retentate	GenX	1×10^6	99.5	–	4	[131]
REM	Ti_4O_7 REM || SS	DI water, 100 mM K_2HPO_4	PFOA	4.14×10^6	> 99	75.3	11.3 s [b]	[58]
			PFOS	5×10^6	> 99	68.9		
HTEO	BDD || Pt wire	DI water +50 mM Na_2SO_4	PFOA	2×10^8	93.6	90	6	[136]
Electro-sorption/ EO	BDD || redox copolymer /CNT	DI water + 20 mM NaCl	GenX	3.3×10^7	> 95	100	24	[139]

RE= removal efficiency.
DF= Defluorination ratio.
EO= electrooxidation.
EF= electro-Fenton.
RO= reverse osmosis filtration.
EC= electrocoagulation.
NF=nanofiltration.
REM= reactive electrochemical membrane.
HTEO= hydrothermally enhanced electrooxidation.
(a) Total defluorination of all species in solution.
(b) Residence time (s).

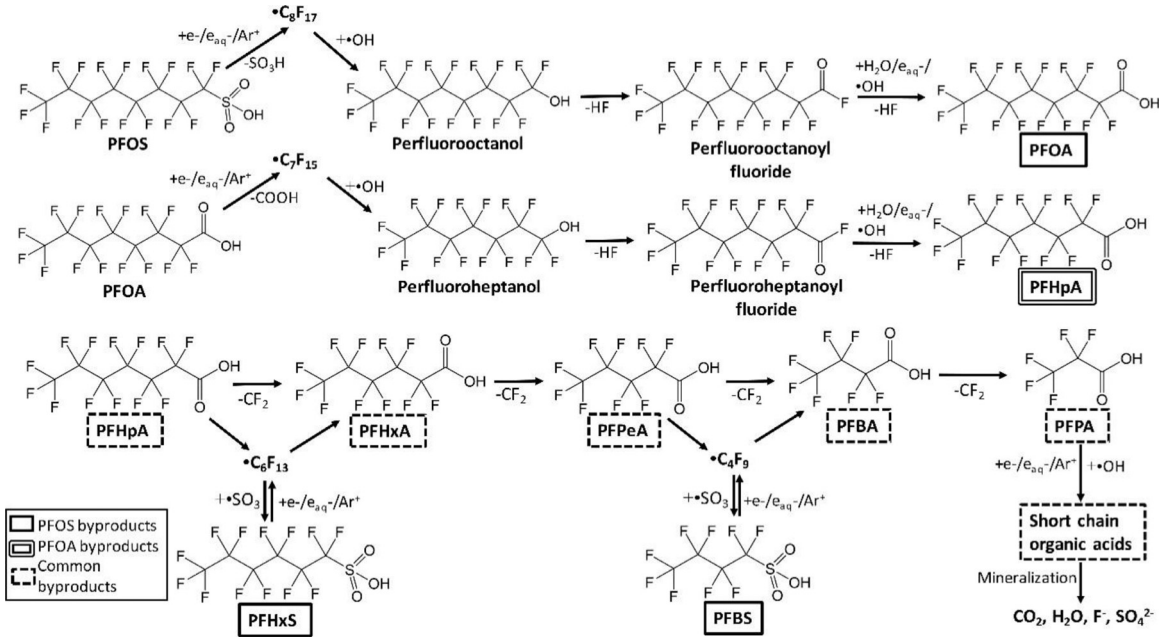

Fig. 7. Proposed mechanism for reductive degradation of PFOA and PFOS in plasma treatment. Reprinted with permission from R.K. Singh et al., Breakdown Products from Perfluorinated Alkyl Substances (PFAS) Degradation in a Plasma-Based Water Treatment Process, Environmental Science & Technology, 53 (2019) 2731–2738. Copyright 2019 American Chemical Society.

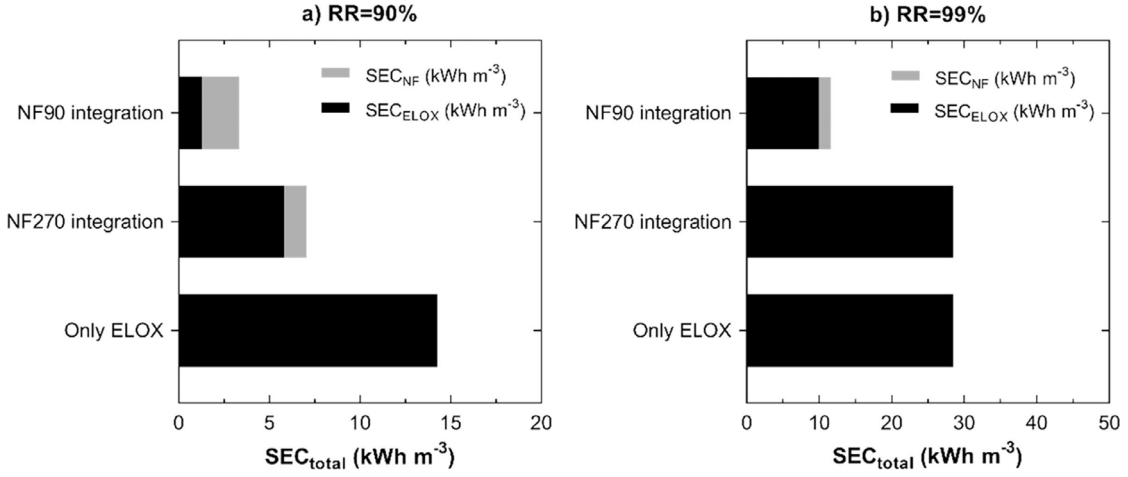

Fig. 8. Comparison of specific energy consumption (SEC) with coupled NF/electrooxidation, and electrooxidation without NF pre-concentration, for the different PFHxA removal efficiencies (referred to as RRs in figure). (a) RR=90%; (b) RR=99%. Reprinted with permission from Á. Soriano, D. Gorri, A. Urtiaga, Membrane pre-concentration as an efficient tool to reduce the energy consumption of perfluorohexanoic acid electrochemical treatment, Separation and Purification Technology, 208 (2019) 160–168. Copyright 2019 Elsevier.

4.2. Alternative electrically-driven methods

4.2.1. Reactive electrochemical membranes

Reactive electrochemical membranes (REMs) have been another prime example of electrochemically-based process intensification for PFAS remediation. REM systems use the membrane as both an electrode and a filter, facilitating the mass transfer to the electrode surface and improving oxidation efficiency within a single step [128,133]. This dual benefit was observed for a Ti_4O_7 REM, which was operated in a single-pass flow-through operation mode for the electrochemical oxidation of PFOA and PFOS [58]. The system achieved a 5-log removal (99.999%) at 3.3 V vs. standard hydrogen electrode (SHE) and 3.6 V vs. SHE, for initial concentrations of 4 and 5 mg/L for PFOA and PFOS, respectively. The dual function of the membrane as a separator and the anode in the system helps lower the energy consumption by an order of magnitude when compared to other advanced oxidation technologies like sonolysis [58,134]. A similar study investigated the degradation of PFOS using an Ebonex REM and a batch operation setup [135]. Results showed a larger removal of PFOS (98%) using a cross-flow REM configuration compared to the batch operation mode under the same potential of 3.15 V vs. SHE.

4.2.2. Coupled electrooxidation techniques

Beyond membranes, other techniques have also been combined with electrochemical oxidation to improve the current efficiency and performance of the PFAS removal process. For example, combining hydrothermal oxidation with electrochemical oxidation enhanced the degradation efficiency for PFOA by improving the rate of ionic migration and conductivity of the solution [136]. The combined hydrothermal-electrochemical oxidation process showed 90% defluorination after 6 h of operation, whereas the defluorination

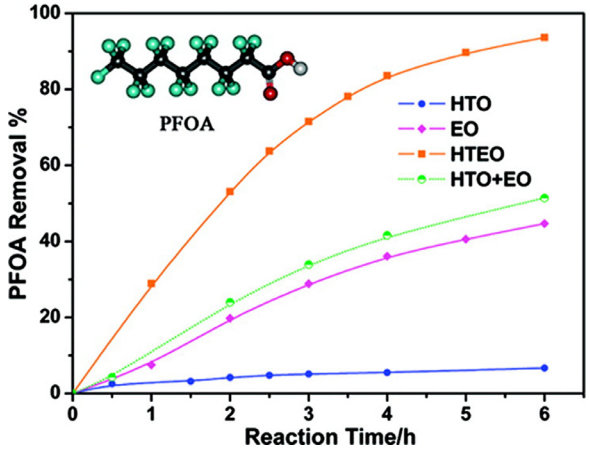

Fig. 9. Removal of PFOA for 400 mL solution of 200 mg/L PFOA using the following methods: hydrothermally-enhanced electrochemical oxidation (HTEO), hydrothermal oxidation (HTO), and electrochemical oxidation (EO). Reprinted with permission from H. Xiao, B. Lv, G. Zhao, Y. Wang, M. Li, D. Li, Hydrothermally Enhanced Electrochemical Oxidation of High Concentration Refractory Perfluorooctanoic Acid, The Journal of Physical Chemistry A, 115 (2011) 13,836–13,841. Copyright 2011 American Chemical Society.

from the electrooxidation process itself was only 48% after 6 h (**Fig. 9**). However, the defluorination of both processes was incomplete, which suggests the formation of other fluorinated intermediates [136]. Ultrasonic irradiation coupled with electrooxidation was also used to degrade PFOA, using SnO2-Sb carbon aerogel electrodes for the electrooxidation [137]. Results showed a 94% increase in PFOA degradation using the combined ultrasonic-electrooxidation method versus the traditional electrooxidation process, after 5 h of electrolysis.

4.2.3. Electrosorption with electrochemical degradation

Integration of more than one electrochemical technique has also been employed to obtain more efficient PFAS removal processes. Coupling electrosorption with subsequent electrochemical degradation has shown to be an efficient way to reduce the energy consumption and obtain higher removal rates for PFOA [45,138]. For example, combination of electrosorption using 4-methacryloyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TMA) and 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine (TMPMA) redox copolymer-CNT electrodes coupled with BDD electrooxidation provided a lower energy consumption (62.3 kWh/mol F^- for a 5-hour operation) than other methods like ultrasonic, microwave and UV, while obtaining a high defluorination efficiency (80%) [45]. Electrosorption and defluorination of the short-chain GenX was also studied using the same redox-copolymer-BDD system, achieving 100% defluorination after 24 h of electrooxidation at 10 mA/cm^2 [139]. Another study investigated the combined effect of electrosorption and subsequent electrooxidation using a CNT sponge anode to remove PFOA at 100 µg/L concentrations [138]. The increased concentration on the electrode surface due to PFOA sorption onto the CNT sponge facilitated itsdegradation upon applying a potential of 3.5 V. Despite obtaining a relatively high removal efficiency of 90%, subsequent short-chain perfluorocarboxylic acids were detected in the product water, suggesting incomplete mineralization of PFOA.

5. Conclusions and perspectives

Electrochemical technologies have shown to be promising for PFAS remediation, displaying enhanced removal rates, capability for full mineralization, and reversible regeneration of adsorbents based on electrochemical control. Among electrosorption methods, functionalized carbon materials have shown superior selectivity and energy efficiency to capture PFAS molecules over non-functionalized carbon. Nevertheless, only a handful of electrosorption studies for PFAS have been conducted, and most of these have focused solely on long-chain molecules such as PFOA and PFOS.

Within the class of electrically-driven degradation methods, plasma-based ARPs, and oxidation via BDD and EF processes are the most predominant methods in the literature to treat PFAS-contaminated streams. Despite the recent advances in the field and the advantages electrochemical remediation technologies , research is still needed to address several opportunities and challenges: (i) there is a significant potential for process intensification in PFAS remediation, such as coupling reaction and separation to increase overall removal efficiency, (ii) the evaluation of electrochemical approaches for a range of environmentally relevant concentrations and water matrices, (iii) expanding the studies to short-chain PFAS and other precursors, and finally, (iv) addressing scaleup and the comparative costs between various technologies through rigorous techno-economic modeling.

Development of hybrid electrochemical approaches and integration of reaction with separation. While each PFAS remediation technique can have distinct advantages under constrained conditions, recent studies have shown that a single method may not provide a universal solution to the complex PFAS problem. For instance, while electrosorption provides an effective platform to selectively capture and release PFAS reversibly for concentrating these contaminants, it does not address the subsequent degradation or mineralization challenge. In contrast, while electrochemical degradation methods can mineralize the compounds directly, these approaches often encounter serious mass transfer limitations when treating ultra-dilute PFAS concentrations. They can also produce harmful byproducts due to either incomplete mineralization (leading to the formation of shorter-chain PFAS) or harmful reactions with other existing ions and contaminants in solution like disinfection byproducts. Going forward, we envision an opportunity to move beyond a “one problem, one solution” mindset, in order to properly address the highly-complex challenges of water remediation, especially the opportunity to integrate distinct separation and reaction steps.

Combining multiple steps within a treatment train has shown to be effective for providing clean water by exploiting the individual advantages of each method, with PFAS being a prime emerging opportunity for developing synergistic, multi-thronged approaches for water remediation. Integration of reaction and separations, through a fully electrified platform, can be a promising direction to reduce energy consumption and improve the overall removal efficiency of the process. In particular, using electrosorption as a pre-concentration step combined with subsequent electrooxidation has shown potential for promoting higher PFAS defluorination and reducing overall energy consumption. From a separations perspective, creating materials with even higher selectivity may be needed to concentrate ultra-dilute PFAS at environmentally relevant concentrations, to be subsequently (or simultaneously) treated by electrocatalytic methods.

Evaluating electrochemical methods at environmentally relevant PFAS concentrations. The concentrations of PFAS in water heavily depend on the geographical location and the source of PFAS. Generally, concentrations in natural waters, such as groundwater and surface water, are in the ng/L scale [20–22, 23], yet higher concentrations (µg/L) can be found if the location is close to industrial point sources [24]. Nevertheless, these concentrations are considerably lower (by at least 3 orders of magnitude) than those being used in many studies in the literature. Hence, when developing electrochemically-based PFAS treatment methods for point-of-use application, it is important to evaluate environmentally relevant contaminant concentrations, even if higher concentrations can be used in model studies beforehand. Hence, there may be a growing

need for consensus on performance metrics and materials benchmarks, based on different environmental contexts.

Extending electrochemical approaches to short-chain PFAS. So far, most studies have focused primarily on the transport and removal of the long-chain compounds such as PFOA and PFOS. However, due to rising regulations and concern, there has been a trend among manufacturers to replace long-chain PFAS with short-chain PFAS [28,29]. Short-chain PFAS may pose an even greater challenge when compared to their long-chain analogs, due to their increased mobility, hydrophilicity, and higher intraparticle diffusion rates [4]. The replacement of long-chain PFAS with short-chain homologs, along with the unintended byproducts formed during manufacturing and disposal processes, is expected to increase the occurrence of short-chain PFAS in various water streams [140]. However, there is limited information regarding the mechanisms that drive short-chain PFAS capture, other than the observed lower adsorption efficiencies compared with longer-chained homologs due to hydrophobicity effects [4,5]. Hence, future studies involving PFAS molecules besides PFOA and PFOS are necessary to address the ever-growing classes of these compounds, especially short-chain PFAS, which are of growing usage across the world [4]. Furthermore, methods that do not fully defluorinate long-chain PFAS also contribute to the growing presence of these substances in the environment by generating persistent side-products. Thus, careful analytics and mechanistic studies regarding the final products from electrochemical degradation constituents, and full mass balances, are necessary to ensure environmental feasibility and success of new approaches.

Technoeconomic analyses of PFAS electrochemical remediation approaches and electrode stability. Despite the recent scientific advances, the techneonomic feasibility of many electrochemical remediation methods for large-scale water treatment plants remains unknown [8]. It has been shown that electrooxidation processes can be potentially more energy-efficient than sonolysis, ultrasonication, and microwave treatment methods [58]. Recent technoeconomic assessments and comparative analysis have assisted in evaluating the feasibility and constraints of electrochemical processes for different environmental contexts, including selective removal of contaminants and point-of-source treatment [58,141,142]. However, careful studies which consider practical implementation of electrochemical approaches for PFAS remediation are still limited, and the wide ranges in contaminant concentration and differing energy consumption reports complicates a systematic analysis. In addition, the longevity of many of these electrodes for PFAS remediation is relatively unexplored, including the stability of functionalized carbon, redox-polymers, or even advanced oxidation electrodes such as titanium or boron-doped diamond (BDD).

Designing materials that can be utilized in wide pH ranges, various ionic strengths, and are stable to various corrosive species under electrochemical conditions is key ffor the translation of many of these PFAS remediation approaches to both groundwater and surface water contexts. On the long term, fundamental materials design should be coupled with rigorous techno-economic analysis and process modeling for finding feasible solutions. These challenges will hopefully bring in interdisciplinary collaborations between resarchers working on electrochemistry, environmental engineering, and materials science to solve the complex problems involving PFAS remediation.

Declaration of Competing Interest

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

Credit authorship contribution statement

Anaira Román Santiago: Conceptualization, Writing – original draft, Writing – review & editing. **Paola Baldaguez Medina:** Writing – original draft, Writing – review & editing. **Xiao Su:** Writing – review & editing, Supervision.

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