REVIEW ARTICLE

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Electrochemical technologies for per- and polyfluoroalkyl substances mitigation in drinking water and water treatment residuals

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Abstract

Water treatment technologies are needed that can convert per- and polyfluoroalkyl substances (PFAS) into inorganic products (e.g., CO_2, F^-) that are less toxic than parent PFAS compounds. Research on electrochemical treatment processes such as electrocoagulation and electrooxidation has demonstrated proof-of-concept PFAS removal and destruction. However, research has primarily been conducted in laboratory matrices that are electrochemically favorable (e.g., high initial PFAS concentration [μg/L–mg/L], high conductivity, and absence of oxidant scavengers). Electrochemical treatment is also a promising technology for treating PFAS in water treatment residuals from nondestructive technologies (e.g., ion exchange, nanofiltration, and reverse osmosis). Future electrochemical PFAS treatment research should focus on environmentally relevant PFAS concentrations (i.e., ng/L), matrix conductivity, natural organic matter impacts, short-chain PFAS removal, transformation products analysis, and systems-level analysis for cost evaluation.

KEYWORDS
electrocoagulation, electrooxidation, perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA)

1 | INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are anthropogenic contaminants of major focus in the water industry. PFAS are broadly defined as organic compounds containing perfluoroalkyl moieties ($C_nF_{2n+1}-$), which are generally linear or branched-chain alkanes with a perfluorinated (CF_2) backbone and a functional group such as carboxylate, sulfonate, phosphonate, or alcohol (Cousins et al., 2020; Kwiatkowski et al., 2020). This broad definition applies to

over 4700 PFAS compounds currently in use (Cousins et al., 2020). Many PFAS, such as perfluoroalkyl acids, are designed to be highly stable, which is the basis of their use in nonstick cookware and aqueous film-forming foam used for firefighting. The stability of the carbon-fluorine bonds and compound hydrophobicity render PFAS highly resistant to environmental degradation, leading to high persistence, bioaccumulation, and occurrence in drinking water sources (Boone et al., 2019; Giesy & Kannan, 2001; Rahman et al., 2014).

A nationwide study measured 17 PFAS from 25 drinking water treatment plants at levels from 1 to 1102 ng/L in all treatment plants studied (Boone et al., 2019). The median PFAS concentration was 19.5 ng/L in the final drinking water (Boone et al., 2019). These values exceed maximum contaminant levels in some state-level regulations, for example, 6–18 ng/L perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) set by Michigan, New Hampshire, and New Jersey (Michigan Code R. 325.1064g, N.J.A.C.7:10, NH HB1264). The two most commonly studied PFAS compounds are PFOA and PFOS, both of which are 8-carbon chain (C8) compounds. Despite being phased out of production in the U.S., these compounds persist in the environment and in drinking water at ng/L to μg/L concentrations, with the higher end of the range representing cases of groundwater contamination (Kwiatkowski et al., 2020; Rahman et al., 2014). An estimated 6 million people are served by drinking water supplies containing PFAS concentrations higher than the current U.S. Environmental Protection Agency (EPA) advisory level of 70 ng/L (sum of PFOA and PFOS concentrations) (Hu et al., 2016). Many more people in the U.S. face sub-EPA advisory PFAS levels, with 10–18 million people served by water supplies containing >10 ng/L PFOA and PFOS, and more than 200 million people receive drinking water containing PFOA and PFOS concentrations higher than 1 ng/L (Andrews & Naidenko, 2020).

The drinking water industry could face a major challenge in widely implementing technology to remove PFAS to ng/L levels if PFAS become more widely regulated. The proposed treatment target (i.e., below 70 ng/L [the current EPA health advisory] or lower maximum contaminant levels depending on the state) is among the lowest contaminant concentrations monitored in treated drinking water (EPA, 2016). When comparing to other regulated organics in drinking water, disinfection byproducts are regulated at 60 and 80 μg/L for haloacetic acids and trihalomethanes, respectively, which are an order of magnitude higher than PFAS advisory levels. In February of 2020, the EPA announced a proposed decision to regulate PFOA and PFOS (https://www.epa.gov/newsreleases/epa-announces-proposed-decision-regulate-pfoa-and-pfos-drinking-water). Accordingly, meeting the

Article Impact Statement
Electrochemical treatment is capable of destroying per- and polyfluoroalkyl substances, but future research should reflect more realistic drinking water sources.

potential ng/L-level regulatory targets will require innovative solutions informed by comprehensive PFAS mitigation research that reflects intended treatment goals.

Conventional drinking water treatment plants are generally ineffective for PFAS mitigation (Boone et al., 2019; Rahman et al., 2014; Takagi et al., 2011). Due to these limitations, alternative treatment technologies such as granular activated carbon, ion exchange, nanofiltration, and reverse osmosis may be needed for PFAS mitigation based on their demonstrated PFAS removal capabilities (Belkouteb et al., 2020; Dixit et al., 2021; Gagliano et al., 2020; Glover et al., 2018; Park et al., 2020; Rahman et al., 2014). PFAS treatment technology can be divided into two categories: nondestructive treatment and destructive treatment. Nondestructive treatment technologies such as granular activated carbon, ion exchange, nanofiltration, and reverse osmosis can remove PFAS. However, nondestructive technology can be limited by the presence of PFAS in concentrated waste streams resulting from treatment (e.g., ion exchange regenerant, membrane concentrate/backwash, and reverse osmosis concentrate), which may require additional treatment before the waste streams are discharged (Radjenovic et al., 2020; Stoiber et al., 2020). For example, Glover et al. (2018) measured 400 ng/L total PFAS in ultrafiltration and nanofiltration membrane backwash water and 600–1800 ng/L in reverse osmosis concentrate. Alternately, destructive technologies utilize redox reactions to transform PFAS into smaller organic and inorganic compounds, ideally with complete defluorination (conversion to fluoride) and mineralization (carbon conversion to CO_2) (Lu et al., 2020). In this review, the term "destructive removal" refers to a series of PFAS redox reactions that result in transformation to inorganic products that are less toxic than the initial PFAS compounds.

Electrochemical drinking water treatment processes such as electrocoagulation and electrooxidation are capable of PFAS mitigation through nondestructive and destructive (or oxidative) pathways, potentially with lower energy inputs compared to other destructive PFAS treatment technologies such as sonolysis, ultraviolet (UV) advanced oxidation, advanced reduction, and photocatalysis (Chaplin, 2019; Cui et al., 2020; Niu et al., 2016). Electrochemical technologies can be advantageous for drinking water treatment because they generate

chemicals on site. Electrochemical treatment may also be applied at various points in the drinking water treatment train, such as after particle separation or for treating the water treatment residuals. Electrocoagulation and electrooxidation have primarily been studied in the context of wastewater, contaminated groundwater, and fundamental electrolyte matrices (i.e., buffered matrices free of scavengers and interfering parameters) While they have recently started to be evaluated in the context of drinking water treatment (Chaplin, 2019; Garcia-Segura, Nienhauser, et al., 2020; McBeath, Mohseni, & Wilkinson, 2020; Radjenovic et al., 2020; Ryan et al., 2021), improved understanding of the performance of electrochemical processes for water treatment is needed to assess their feasibility for use in the water sector.

The objective of this literature review is to highlight advances and limitations in electrocoagulation and electrooxidation research for PFAS mitigation in drinking water. Fundamental aspects of treatment are discussed, including both destructive and nondestructive removal mechanisms, in addition to providing examples of treatment applications for different process streams relevant to drinking water treatment. Additionally, the limitations of electrochemical treatment processes and research barriers to implementation are identified, leading to a roadmap for future research.
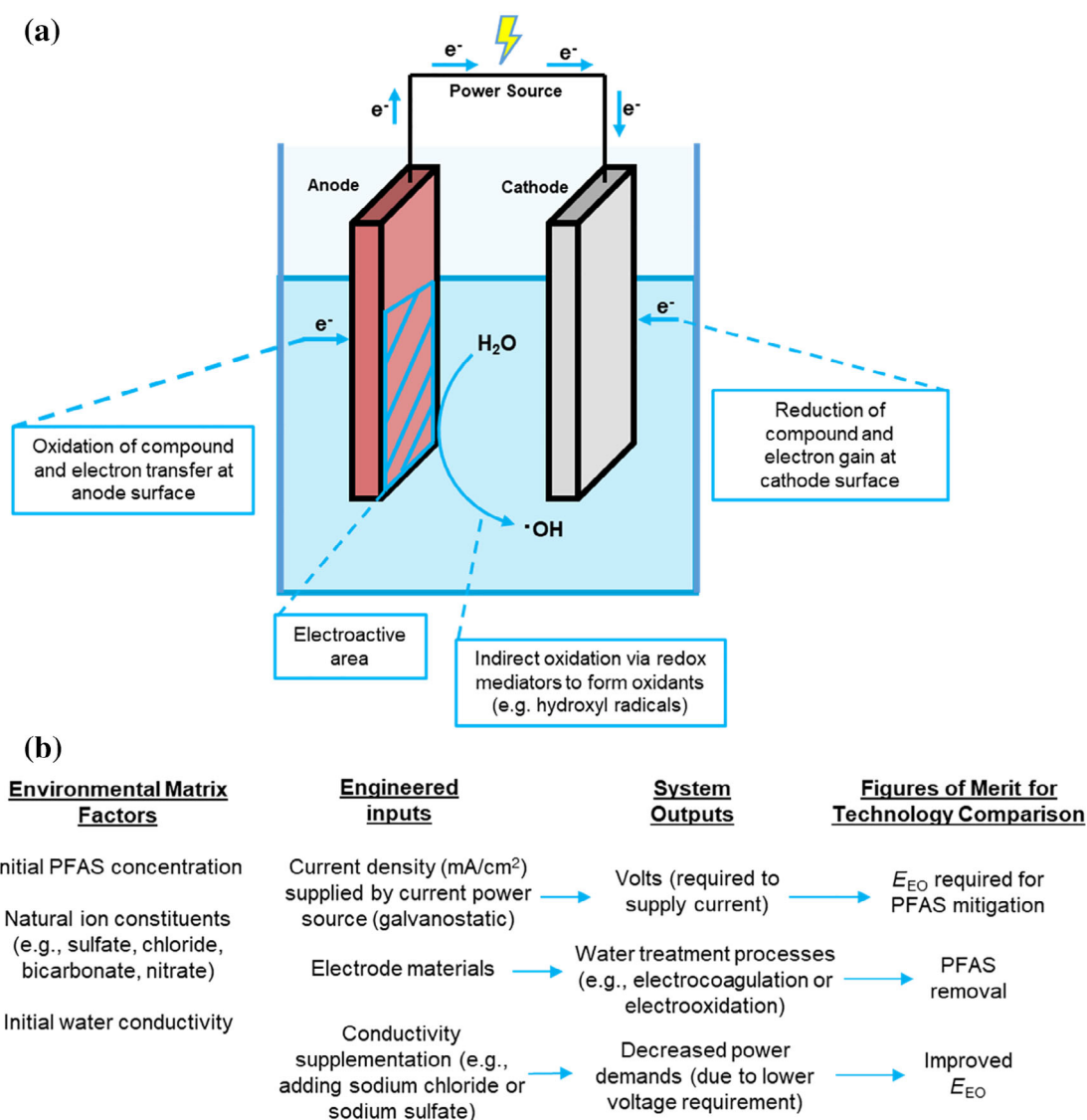
FIGURE 1 (a) Electrolytic cell schematic for electrochemical water treatment reactors. In these cells, oxidation reactions occur at the anode and electrons flow to the cathode, where reduction reactions occur. In these systems, the current density (mA/cm^2) is determined by the amount of current (mA) that passes through the electroactive surface area. (b) Additional information is provided for environmental inputs to the electrolytic cell, in addition to engineered inputs and corresponding system outputs and figures of merit for comparing technology. E_{EO} = electrical energy per order

2 | ELECTROCHEMICAL TREATMENT AS A PFAS MITIGATION TECHNOLOGY

2.1 | Overview of electrochemistry relevant to drinking water treatment

Electrochemical water treatment can offer advantages over conventional water treatment through on-site generation of water treatment chemicals, which negates the costs associated with chemical transportation and storage. These benefits are particularly useful for decentralized operations such as small and rural water treatment facilities (Chaplin, 2019; Ryan et al., 2020). Other advantages of electrochemical reactors include that they are scalable depending on the electrode material and associated costs (e.g., niobium, tantalum, and tungsten for boron-doped diamond production may be too costly to scale), and may be operated as modular processes that can add capacity (Barazesh et al., 2015; Chaplin, 2019). For example, Stirling et al.'s (2020) techno-economic analysis showed that electrooxidation was more economic for point-of-use treatment of atrazine compared to carbon block technology, primarily due to higher performance and the lack of maintenance and replacement fees using electrochemical treatment (Stirling et al., 2020).

Electrochemical treatments utilize electrolytic cells composed of at least one anode, one cathode, and a source of electrons (Figure 1). Oxidation reactions occur on the anode and reduction reactions occur on the cathode, with the type of electrode materials determining the specific reactions occurring. Sufficient thermodynamic energy (e.g., working electrode potential, or standard potential [E^0] reported as Volts [V] vs. standard hydrogen electrode [SHE]) must be available for these reactions to occur.

This review focuses on electrocoagulation and electrooxidation processes, which are the most widely studied electrochemical water treatment processes to date. Although not detailed here, a range of electrochemical alternatives are also being developed and evaluated for PFAS treatment, with most investigations currently at the lab-scale without supporting studies in scaled-up and/or water/wastewater matrices. For example, electroreduction relies on hydrated electrons for reductive defluorination of PFAS using materials such as carbon nanotubes (Su et al., 2019). While efficient defluorination of PFAS proceeds via reductive processes, after complete dehalogenation occurs, it has been observed that oxidation is required for any further degradation of the organic species (Vecitis et al., 2009). Cui et al. (2020) further reviews advanced reductive processes (not electrochemical treatment) for PFAS mitigation.

Electrochemical reactions relevant to water treatment include coagulant generation, oxidant generation, reductive defluorination, and direct electron transfer. Coagulants are generated using iron or aluminum electrodes ($Fe^0 \rightleftharpoons Fe^{2+} + 2e^-$, $E^0 = 0.441$ V vs. SHE; $Al^0 \rightleftharpoons Al^{3+} + 3e^-$, $E^0 = 1.67$ V vs. SHE) (Bagotsky, 2005). Oxidants are generated using nonactive electrode materials such as boron-doped diamond or Ti_4O_7 (e.g., $2Cl^- \rightleftharpoons Cl_2 + 2e^-$, $E^0 = 1.35$ V vs. SHE; $H_2O \rightleftharpoons \cdot OH + H^+ + e^-$, $E^0 = 2.73$ V vs. SHE) (Bagotsky, 2005). Additionally, boron-doped diamond and Ti_4O_7 electrodes can oxidize compounds directly on the anode surface via direct electron transfer (Bagotsky, 2005; Chaplin, 2014). Electrolysis of other ions in water, such as sulfate, carbonate, ferrous iron, and manganese, can also generate additional oxidants and radical species (Barazesh et al., 2016; McBeath, Wilkinson, & Graham, 2020b, 2020c; Radjenovic & Petrovic, 2016). Higher levels of ions (e.g., chloride, sulfate, and nitrate) result in higher electrical conductivity that can decrease electrical power demands. For drinking water treatment, low conductivity can be a barrier to implementation due to higher power demands. This issue can be mitigated by supplementing conductivity with salts (e.g., NaCl, Na_2SO_4, etc.) within acceptable ranges of secondary drinking water standards. In summary, the ions in water matrices have a major impact on electrochemistry reaction pathways by affecting which oxidants are generated during treatment and the electrical energy demands attributed to matrix conductivity.

Electrical inputs can be parameterized and compared using the current density (mA/cm^2) applied to the cell and the corresponding voltage. Accordingly, electrochemical treatment is recommended to operate galvanostatically (i.e., constant current) for scaled systems (dos Santos et al., 2014). Current density is the current (mA) applied to the electroactive area of the electrodes in an electrochemical cell (Figure 1). In galvanostatic systems, a given current density yields an analogous potential (V) based on cell resistance, which is primarily influenced by matrix conductivity which corresponds to the system power demands (Power = Potential × Current). The electrical energy demands can be evaluated based on the electrical energy per order of magnitude removal (E_{EO}) (reported as kWh/order—m^3; i.e., kWh hours required to decrease contaminant concentration by 90% per cubic meter of water treated), which provides a means to compare contaminant treatability across technologies (Bolton et al., 2001).

2.2 | Electrocoagulation

Electrocoagulation may offer both nondestructive and destructive PFAS treatment by electrolysis of sacrificial

anode materials such as iron, aluminum, or zinc (Figure 2). Electrocoagulation has classically been studied as a phase separation/nondestructive removal technology although several studies indicated that it may also serve as a destructive/oxidative removal technology for trace organic compounds that are recalcitrant to sorption such as estrogenic compounds, acetaminophen, atenolol, and bronopolol (Bocos et al., 2016; Govindan et al., 2020; Kim et al., 2020; Maher et al., 2019; Qian et al., 2019). Electrocoagulation has previously been applied for drinking water treatment studies focused on heavy metals, estrogens, natural organic matter (NOM), and disinfection byproducts; these studies are beneficial for demonstrating performance based on drinking water metrics (Dubrawski & Mohseni, 2013a; Heffron et al., 2016; Maher et al., 2018; McBeath, Mohseni, & Wilkinson, 2020; Mohora et al., 2012; Ryan et al., 2020; Vik et al., 1984).

2.2.1 | Electrocoagulation as a nondestructive technology

The majority of electrocoagulation studies for PFAS have focused on nondestructive removal mechanisms via sorption to metal hydroxide flocs produced using sacrificial electrodes typically made from iron or aluminum. Additional electrode materials that have been tested in laboratory research include zinc and magnesium (Figure 2) (Lin et al., 2015). A comparison among these electrode materials demonstrated that zinc yielded greater PFOA removal (96.7%) relative to iron (10.6%) and aluminum (11.3%) after 10 min of treatment (Table 1) (Lin et al., 2015). PFAS sorption to hydroxides was primarily attributed to hydrophobic interactions between PFAS species and the metal hydroxide surface rather than other sorption processes such as ligand exchange, van der Waals forces, π-π interactions, or electrostatic interactions
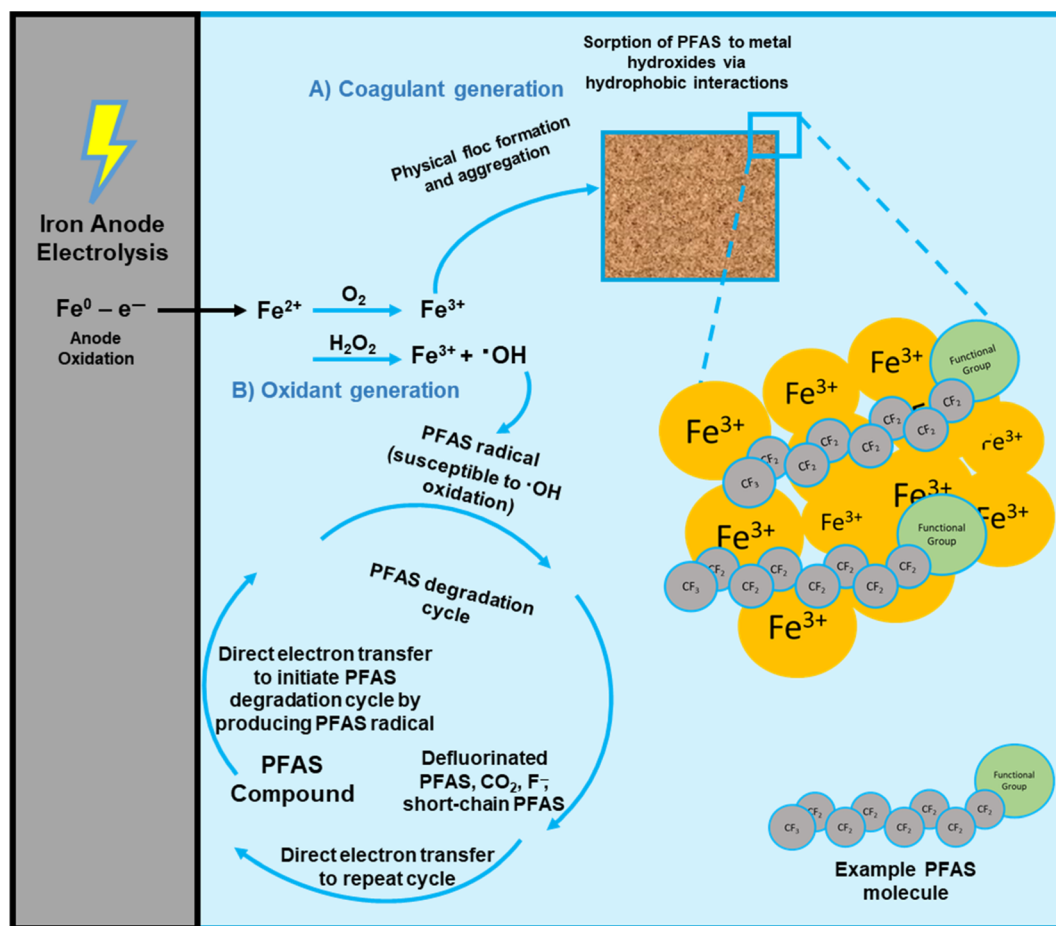
FIGURE 2 Per- and polyfluoroalkyl substances (PFAS) removal mechanisms using electrocoagulation (iron electrodes are shown). The first iron-based reaction occurs due to the dissolution of the anode material to form ferrous iron (Fe^{2+}), which is then oxidized to form ferric iron (Fe^{3+}) and may form hydroxyl radicals (depending on oxidant and pH conditions). (a) Coagulant generation: The ferric iron can aggregate to form flocs capable of sorbing PFAS due to hydrophobic interactions. (b) Oxidant generation: The hydroxyl radicals can participate in the PFAS degradation cycle initiated by a direct electron transfer at the electrode surface. Additional information regarding the PFAS degradation cycle is provided in Figure 3

TABLE 1 Electrocoagulation treatment performance for per- and polyfluoroalkyl substances (PFAS) mitigation

PFAS compound	Electrode material	Initial PFAS conc, mg/L	Water matrix	Current density, mA/cm²	Electrolysis time, min	% Removal	Comments	References
Perfluorooctane sulfonic acid (PFOS)	Iron	125	2 g/L NaCl, pH = 5.2	25	50	99.6		Yang et al. (2016)
Perfluorooctanoic acid (PFOA)	Iron	103	2 g/L NaCl, pH = 3.8	25		78.3		Lin et al. (2015)
PFOA	Zinc	207	10 mM NaCl, pH = 5	100 mA (electroactive area not provided)	10	96.7	PFAS removal rate was higher for 1.5 mM than 0.5 mM, indicating high concentration leads to higher kinetics	Lin et al. (2015)
	Iron					10.6		
	Aluminum					11.3		
PFOA	Iron	10	35 mM NaCl, pH = 3	40	360	>99	Redox focus, 60% total organic carbon (TOC) removal	Kim et al. (2020)

Note: All studies conducted electrocoagulation in parallel plate batch reactors or jar tests.

(Lin et al., 2015). The hydrophobic interactions resulted from PFAS' hydrophobic tail sorbing onto the flocs via multilayer sorption (Lin et al., 2015). Electrocoagulation of waters using iron and aluminum with high PFAS concentrations can yield high removal efficacy (e.g., 90%), as shown in Table 1. Of note, the applied iron and aluminum doses in Yang et al. (2016) and Kim et al. (2020) are much higher than Lin et al. (2015) which may contribute to the higher PFAS removal via iron and aluminum. Other factors which may account for the differences in PFAS removal during iron and aluminum electrocoagulation summarized in Table 1 include the speciation of Fe/Al oxide and hydroxide formation, which have varying affinities to function as coagulant chemicals. Iron and aluminum speciation can be affected by a number of variables including, but not limited to, anode potential, pH, temperature, DO, [Fe(II)]:[Fe(III)], and co-occurring solute concentration and ratios (Dubrawski & Mohseni, 2013b).

2.2.2 | Iron-electrocoagulation as a destructive technology

In addition to nondestructive PFAS removal, electrocoagulation could potentially be used for destructive PFAS removal. Electrocoagulation may produce oxidation reactions via anode surface oxidation, reactive iron intermediates, or hydroxyl radicals produced by Fenton processes at low pH (presuming there is H_2O_2 in the matrix) (Bocos et al., 2016; Heffron et al., 2019; Kim et al., 2020; Maher et al., 2019). Oxidation mechanisms for electrocoagulation treatment of trace organic compounds were suspected to include anode oxidation, reactive oxygen species, and ferryl iron (Maher et al., 2019). To validate these findings, additional electrochemical mechanism experiments are needed to measure the working electrode potentials in electrocoagulation reactors to substantiate if direct electron transfer reactions of trace organic compounds occur. For example, the direct oxidation of organic pollutants at the anode surface has been observed previously, indicated by an irreversible oxidation peak below the oxygen evolution potential during cyclic voltammetry (Linares-Hernández et al., 2009).

Qian et al. (2019) investigated the oxidizing capacity of iron-electrocoagulation using a combination of kinetic modeling and quantifying the conversion of benzoate to *p*-hydroxybenzoic acid (an oxidation byproduct for mechanism analysis). The authors concluded that electrocoagulation may yield reactive oxidants (such as hydroxyl radicals) via Fenton-like mechanisms (Qian et al., 2019). A combination of electrochemical experiments to verify working electrode potentials and oxidation byproducts

parameterization is needed to substantiate the production of oxidants during iron-electrocoagulation. The redox removal mechanisms in electrocoagulation may be similar to the electrooxidation PFAS removal mechanisms, as discussed in Section 2.2.1 (Kim et al., 2020).

Kim et al. (2020) investigated the oxidative ability of iron-electrocoagulation for PFOA mitigation, and reported removal via direct electron transfer and oxidant generation using high current loading and long electrolysis times. Oxidation mechanisms were verified by measuring final transformation products including formate (a byproduct of organic oxidation), fluoride (a byproduct of PFAS defluorination), and short-chain PFAS (indicative of long-chain PFAS degradation into shorter chain compounds) (Kim et al., 2020). The transformation product analyses indicated that shorter chain PFAS (perfluoropentanoic acid [PFPeA, C5], perfluorohexanoic acid [PFHxA, C6], and perfluoroheptanoic acid [PFHpA, C7]) were produced via the oxidation of PFOA (Kim et al., 2020). Only 20% defluorination was achieved after 6 h of electrolysis at a high current density of 40 mA/cm^2 (Kim et al., 2020). The PFOA removal rate was independent of solution pH, which may open up opportunities for electrocoagulation as an oxidative process during drinking water treatment at neutral conditions (rather than acidic Fenton oxidation conditions of pH 3–4). Additional research efforts to improve the yield of reactive oxygen species (i.e., hydroxyl radicals, hydrogen peroxide, etc.) in electrocoagulation would benefit destructive PFAS treatment (Garcia-Segura et al., 2017).

2.3 | Electrooxidation

Electrooxidation is an advanced oxidation process that proceeds via the electrolysis of nonactive or active anode electrode materials. Nonactive electrodes are electrocatalytic materials in which the oxidation state of the electrode substrate does not change over the course of electrolysis. Nonactive electrodes are capable of mineralization (Chaplin, 2014; Comninellis, 1994; Garcia-Segura et al., 2018). For active electrodes, the oxidation state of the substrate metals shift oxidation states during electrooxidation and higher oxide metals participate in the reaction; however, active electrodes are less likely to achieve mineralization of organics (Chaplin, 2014; Garcia-Segura et al., 2018). This review focuses on nonactive electrode materials, specifically boron-doped diamond and Ti$_4$O$_7$.

Boron-doped diamond and Ti$_4$O$_7$ are preceded by other electrode materials for PFAS electrooxidation, including tin oxide (SnO$_2$) electrodes, lead oxide (PbO$_2$) electrodes, and dimensionally stable anodes (DSA) (e.g., RuO$_2$,IrO$_2$,IrO-RuO$_2$) (Barisci & Suri, 2021; Lin et al., 2012; Lin et al., 2013). Performance of these electrode materials for PFAS mitigation was reviewed by Niu et al. (2016), whereas this review specifically focuses on boron-doped diamond and Ti$_4$O$_7$ electrodes in the context of the drinking water treatment sector. Of note, prior electrode materials such as SnO$_2$ and PbO$_2$ may not have feasible application for drinking water treatment due to the potential risk of secondary metal contamination (such as lead) which is recommended to be excluded from water infrastructure. DSA electrodes (also described as mixed metal oxide in the literature) are generally not feasible for PFAS electrooxidation compared to boron-doped diamond due to poor anode stability when operating at high current densities / potentials required for PFAS mitigation (Radjenovic et al., 2020).

During electrooxidation, oxidation can occur by two different pathways: (1) Direct oxidation on the electrode surface, and (2) indirect oxidation by hydroxyl radicals or other oxidants generated in situ (e.g., free chlorine, chlorine radicals, sulfate radicals, etc.) (Chaplin, 2014). Electrooxidation can be advantageous for oxidant generation because it is capable of supplying oxidants based on ions present in solution without the addition of auxiliary chemicals (such as hydrogen peroxide or chlorine), which can mitigate costs and hazards associated with chemical handling and storage.

2.3.1 | Fundamentals of electrooxidation for PFAS mitigation

Elucidating the mechanisms of PFAS mitigation using electrooxidation is an active field of research, with different pathways under discussion. One line of thinking is that PFAS mitigation occurs due to a combination of direct electron transfer reactions at the electrode surface followed by oxidation by homogenous electrogenerated oxidants (Niu et al., 2016; Radjenovic et al., 2020). In the initiation step, PFAS mitigation may occur by an initial direct electron transfer with the electrode surface, which forms a perfluorinated radical then undergoes decarboxylation and desulfonation reactions to remove the carboxylic acid and sulfonate groups (Figure 3) (Niu et al., 2016). After the head group is removed, hydroxyl radicals near the electrode's diffusion layer break down the CF$_2$ backbone into shorter chain PFAS compounds until defluorination is achieved via a series of hydrolysis reactions and hydroxyl radical oxidations (Niu et al., 2016). Thus, both direct electron transfer and hydroxyl radicals may be needed for PFAS transformation, and reactors should be designed to maximize contact with the electrode surface, thereby enhancing direct electron transfer to initiate PFAS degradation.
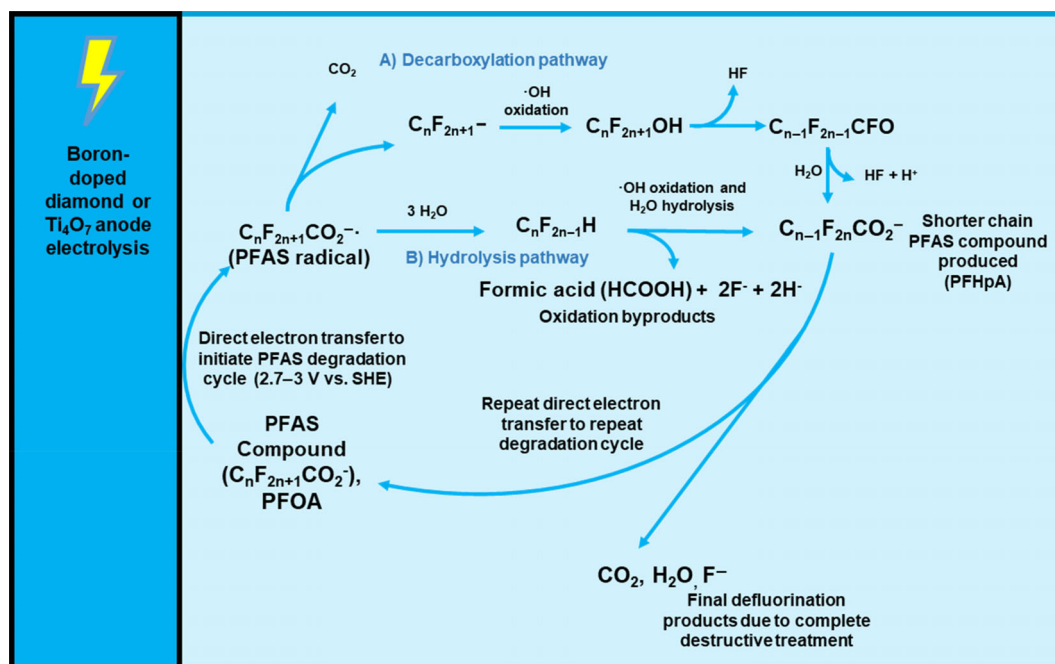
FIGURE 3 Proposed per- and polyfluoroalkyl substances (PFAS) destruction mechanisms for perfluorooctanoic acid in electrooxidation adapted from Kim et al. (2020), Niu et al. (2016), and Radjenovic et al. (2020). In the initial reaction, parent PFAS compounds undergo direct electron transfer reactions at the electrode surface to yield an unstable PFAS radical ($C_nF_{2n+1}O_2\cdot$). The radical then reacts via pathways (a) and (b). (a) Decarboxylation pathway: The PFAS radical undergoes Kolbe decarboxylation to remove the carboxylic head group compound. The decarboxylated compound is oxidized by hydroxyl radicals or undergoes hydrolysis to yield formic acid (HCOOH) and fluoride via chain shortening reactions. (b) Hydrolysis pathway: The PFAS radical is oxidized by hydroxyl radicals or undergoes hydrolysis to yield formic acid (HCOOH) and fluoride via chain shortening reactions. Following these reactions, the short-chain compound can undergo direct electron transfer reactions to repeat the chain shortening process

2.3.2 | Electrooxidation as a destructive technology for PFAS in laboratory matrices and groundwater

Electrooxidation, most commonly using boron-doped diamond electrodes, can treat PFAS in environmental source waters such as groundwater at initial concentrations ranging from 10 μg/L to higher levels of 15 mg/L (Table 2). The majority of existing studies focused on PFOA and PFOS removal with fewer studies addressing short-chain PFAS and other PFAS compounds (Barisci & Suri, 2020; Schaefer et al., 2017; Trautmann et al., 2015). Trautmann et al. (2015) found that short-chain PFAS (perfluorohexanesulphonic acid [PFHxS] and perfluorobutanesulfonic acid [PFBS]) were more resistant to electrooxidation compared to PFOS in both laboratory and field samples from groundwaters contaminated with aqueous film-forming foam. For example, 44% removal of PFBS (C4) was achieved following 120 h of electrooxidation compared to 99% PFOS removal. Although approximately 99% PFOS was removed, the resulting defluorination was only 66%, indicating that PFOS was converted into shorter chain PFAS (Trautmann et al., 2015). Schaefer et al. (2017)

analyzed electrooxidation treatment of environmental groundwaters initially containing 300–600 μg/L, representative of concentrations in aqueous film-forming foam-contaminated waters and found roughly 80% PFOA and 50% PFOS removal following 8 h of electrolysis.

One limitation of these groundwater studies was that they employed relatively high PFAS concentrations compared to most drinking water sources and may not reflect the range of common PFAS contamination levels (e.g., <500 ng/L according to Glassmeyer et al. (2017)). Yang et al. (2019) used initial PFOA/PFOS concentrations of 10 μg/L (an order of magnitude lower than conditions tested in Schaefer et al. (2017)) and found 90% PFOA and PFOS removal after 0.5 h of electrooxidation, which was far less treatment time than Trautman et al.'s (2015) 8 h of electrolysis for 50%–80% removal. Accordingly, more research is needed to determine PFAS treatability under low initial PFAS conditions (i.e., <500 ng/L) to determine the treatment inputs needed to meet potential PFAS regulations of <70 ng/L.

Few studies have focused on the removal and defluorination of shorter chain PFAS during electrooxidation. The inclusion of short-chain PFAS in analyses is important

TABLE 2 Electrooxidation treatment performance table

Compound	Electrode	C_i PFAS, μg/L	Water matrix	Current density, mA/cm²	Electrolysis time, h	Rate constant, 1/min	% Removal	Defluorination ratio, %	E_{EO} kWh/m³	Comments	References
PFOS	BDD	15,000	Synthetic solution: pH = 5.9, conductivity = 1600 μS/cm, DOC = 4.6 mg/L	2.3	48	-	98	66% for mixture	-	78% DOC mineralization; rate constants increased with carbon chain length	Trautmann et al. (2015)
PFHxS		11,000					91				
PFBS		2900					45				
PFOS		70	Contaminated groundwater: pH 6.1, conductivity = 48 μS/cm, DOC = 13 mg/L		120		Below LOQ (99% for both)	-	-	96% DOC mineralization	
PFHxS		120									
PFBS		16					44				
PFOA	BDD	300	Groundwater: pH = 6.7, TOC = 11 mg-C/L, 769 μmhos/cm, electrolyte source either 1500 mg/L Na₂SO₄, or 1500 mg/L Na₂SO₄+ NaCl	15	8	9.16×10^{-5}	80[a]	-	-		Schaefer et al. (2017)
PFOS		600				1.13×10^{-5}	50[a]				
PFOA	BDD	10	Environmental groundwater; TOC = 0.59, pH = 8.1, conductivity = 0.4 mS/cm	10	0.5	-	90 (reported as 1 log reduction) for both	-	E_{EO} ranged from 5.1 to 12.7 kWh/m³	Low EEO for groundwater with 15 mM Na₂SO₄ addition, and higher E_{EO} for raw groundwater	Yang et al. (2019)
PFOS											
PFOA	BDD	207,000	20 mM NaClO₄	5	3	2.7×10^{-2}	98.8	-	-	-	Lin et al. (2018)
PFOA	Ti₄O₇	207,000				3.4×10^{-2}	>99.9	95.0		90.4% of TOC mineralized for Ti₄O₇	
PFOS		50,000				1.3×10^{-4}	93.1	80.9			
L-PFOS, B-PFOS	Ti₄O₇	1000 μg/L (reported as 2 μM)	100 mM Na₂SO₄	10	0.33	$1.43–1.53 \times 10^{-4}$	98.5–98.6	95% after 8 h for 20 μM concentration	E_{EO} = 3.6 kWh/m³	Complete PFOS removal at 4 h, but complete defluorination of PFOS products at 8 h (for 2 μM conc)	Wang et al. (2020)
	BDD					$4.19–4.79 \times 10^{-5}$	84.6–85.7		19.9 kWh/m³. Chloride inhibited Ti₄O₇ removal rate, but increased BDD removal rate		

TABLE 2 (Continued)

Compound	Electrode	C_i PFAS, µg/L	Water matrix	Current density, mA/cm²	Electrolysis time, h	Rate constant, 1/min	% Removal	Defluorination ratio, %	E_{EO} kWh/m³	Comments	References
PFOA	BDD	200	Na$_2$SO$_4$ = 400 mg/L, pH 7	2.5–25	1	-	45 to >90**	Not measured, below fluoride detection limit		Short-chain PFAS were more recalcitrant than long chain in all matrices	Barisci and Suri (2020)
Mixture of C7–C18 PFCAs		10,000 each	Wastewater treatment plant effluent, TOC = 35.96 ± 1.79 mg-C/L, pH = 7, chloride = 177.39 ± 1.04 mg/L	25		-	(Mixture, not reported)	74			
Mixture of C3–C6 PFCAs			Wastewater treatment plant effluent			-	(Mixture, not reported)	35			
Mixture of C7–C18 PFCAs			River water +200 mg/L Na$_2$SO$_4$, TOC = 18.95 ± 4.50 mg-C/L, pH = 7.31, chloride not detected.			-	(Mixture, not reported)	38			
Mixture of C3–C6 PFCAs						-	(Mixture, not reported)	35			
Mixture of C7–C18 PFCAs			Deionized water containing 400 mg/L Na$_2$SO$_4$, pH = 5			-	>80% for all C7–C18 PFCAs[a]	95			
Mixture of C3–C6 PFCAs						-	40% (for C3) to 60% (for C6)[a]	35			

Note: "-" indicates parameter not reported in study.

Abbreviations: BDD, boron-doped diamond; B-PFOS, branched PFOS; DOC, dissolved organic carbon; LOQ, limit of quantification; L-PFOS, linear PFOS; PFAS, per- and polyfluoroalkyl substances; PFBS, perfluorobutanoic sulfonic acid; PFCA, perfluorinated carboxylic acid; PFHxS, perfluorohexanoic sulfonic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulfonic acid.

[a]Value was estimated from a figure in published study.

because long-chain PFAS (C7–C18) are degraded into shorter chains (C3–C6) during incomplete destructive treatment, (Kwiatkowski et al., 2020). The low molecular weight and high water solubility of short-chain PFAS can impede diffusion and mass transfer to the electrode surface and decrease removal via electrooxidation (Barisci & Suri, 2020). Barisci & Suri (2020) studied the removal and defluorination of short- and long-chain PFAS in a range of water matrices including deionized water (as a control), river water, and treated wastewater effluent. In all cases, short-chain PFAS were the most resistant to defluorination (∼35% for all matrices), suggesting that short-chain PFAS may require extensive treatment conditions (such as high-energy inputs and long electrolysis times) for full defluorination (Barisci & Suri, 2020).

Studies comparing across these matrices also help to account for the impact of ions (e.g., chloride and sulfate) and natural/dissolved organic matter, which is ubiquitous in source waters and can impact electrooxidation performance. Barisci & Suri (2020) showed that long-chain PFAS were more readily defluorinated in wastewater effluent (74%) than river water (35%), likely due to the role of additional ions in wastewater that may have increased oxidant generation. Interestingly, the wastewater matrix contained more than double the total organic carbon (36 vs. 19 mg-C/L) of the river water matrix yet had greater PFAS mitigation. In comparison to wastewater and river water, the deionized water yielded the highest defluorination (95%) of long-chain PFAS, indicating that other ions and organics may have inhibited defluorination in wastewater and river water matrices. Accordingly, more research is needed to delineate the impact of each matrix parameters (ion sources, pH, and NOM characteristics) to better understand process performance. Future studies should also consider short-chain PFAS mitigation as short-chain substitutes are being used in product manufacturing, and may introduce additional water treatment challenges. Additional research is also needed to understand the chronic toxicity associated with short-chain PFAS and PFAS transformation products following treatment to substantiate the extent of PFAS treatment required to mitigate adverse impacts due to PFAS (Ateia et al., 2019).

2.3.3 | The impact of electrooxidation electrode materials

The initial cost associated with boron-doped diamond electrode production is a limitation to implementing electrooxidation for PFAS treatment. The Ti_4O_7 electrode can potentially be a cheaper alternative to boron-doped diamond for PFAS mineralization and defluorination (Le et al., 2019; Lin et al., 2018). These Ti_4O_7 electrodes have similar electrochemical properties to boron-doped diamond,

except that they are composed of a porous ceramic material rather than a coated metal (e.g., tantalum, tungsten, or niobium) as used for boron-doped diamond (Lin et al., 2018; Radjenovic et al., 2020). A cost analysis demonstrated that Ti_4O_7 electrodes were cheaper to synthesize relative to boron-doped diamond, at ∼$0.36 per m^2 versus ∼$7125 per m^2 (Chaplin, 2019). Although Ti_4O_7 are cheaper to produce than boron-doped diamond, they are not without limitation; for example, Ti_4O_7 electrodes are a nascent technology with shorter electrode lifespans than boron-doped diamond (Huang et al., 2020; Lin et al., 2021; Stirling et al., 2020). Thus, more research on extending electrode lifespan and stability relative to boron-doped diamond electrodes is essential to facilitate implementation in water treatment applications. In terms of treatment, Ti_4O_7-electrooxidation and boron-doped diamond-electrooxidation perform similarly for PFAS mitigation with respect to removal and defluorination, making Ti_4O_7 electrodes a potentially cheaper alternative for PFAS treatment processes (Lin et al., 2018; Wang et al., 2020). In terms of energy, the E_{EO} for PFOS removal using Ti_4O_7-electrooxidation was 3.6 kWh/m^3 compared to 19.9 kWh/m^3 for boron-doped diamond, demonstrating that PFAS removal using Ti_4O_7-electrooxidation was approximately 80% less energy intensive (Wang et al., 2020).

Additionally, Ti_4O_7 electrodes can also be utilized for emerging treatment technologies such as reactive electrochemical membranes, which integrate the high surface area of membrane filters due to the porous Ti_4O_7 electrode structure with the advanced oxidative pathways of electrooxidation (Trellu et al., 2018). Alternately, boron-doped diamond electrodes are not amenable to reactive electrochemical membrane configuration due to the high costs for production (Misal et al., 2020; Trellu et al., 2018). These novel reactors may be effective for electrochemical treatment by allowing flow-through operation that can treat higher volumes of water faster than batch treatment conditions while also maximizing electrode surface contact. For example, Le et al. (2019) reported ∼5-log removal of PFOS and PFOA after approximately 11 s of treatment using Ti_4O_7 reactive electrochemical membranes. This electrochemical membrane approach had E_{EO} values of 5.1 and 6.7 kWh/m^3 for PFOA and PFOS, respectively (Le et al., 2019), which are in the low-range of E_{EO} values reported in Tables 2 and 3, and are closer to E_{EO} values for other advanced oxidation treatment processes in water treatment (Miklos et al., 2018). However, Le et al. (2019) used high concentrations of PFOA (4.14 mg/L) and PFOS (5 mg/L), which may have enhanced removal. Accordingly, more research is needed using lower PFAS concentrations to substantiate the use of reactive electrochemical membranes for PFAS mitigation, in addition to assessing the performance of Ti_4O_7 in environmentally relevant matrices (Le et al., 2019).

TABLE 3 Electrooxidation of per- and polyfluoroalkyl substances (PFAS) in water treatment residuals

Compound	Electrode material	C_i PFAS, µg/L	Water matrix	Current density, mA/cm² or h	Electrolysis time, min or h	Rate constant, 1/min or m/s[b]	% Removal	Defluorination ratio	E_{EO} kWh/m³	Additional comments	References
PFBA	Ti₄O₇	1660	Spent ion exchange brine: 80% by volume methanol/10% saltStill bottom 1: methanol and NaCl. TOC = 13,280 mg-C/L, pH = 9.57 ± 0.3, chloride = 62,716 mg/L	10	50–200 h	-	−49.6[c]	5.1% after 4 h	-	Total PFAS removal of 61.1% after 40 h. Negative removals due to short chain production	Wang et al. (2021)
PFBS		1450					−6.8[c]				
PFPeA		10,100					−10.2[c]				
PFPeS		2640					10.8				
PFHxA		13,160					−6.9[c]				
PFHxS		40,940				1.26 × 10⁻⁷[b]	95				
PFHpA		3690				3.38 × 10⁻⁷[b]	56.6				
PFHpS		2548				1.30 × 10⁻⁷[b]	96.8				
PFOA		7560				1.71 × 10⁻⁷[b]	94.8				
PFOS		8080				1.71 × 10⁻⁷[b]	98.9				
PFBA		2320	Spent ion exchange brine: 80% by volume methanol/10% salt. Still bottom 2 = methanol/ NaITOC = 201,529 mg-C/L, pH = 9.64 ± 0.5, 3579 mg/L NaCl			2.60 × 10⁻⁸[b]	86.8	16% after 50 h	-	98.1% removal of all PFAS after 200 h of treatment	Wang et al. (2021)
PFBS		2290				5.38 × 10⁻⁸[b]	99.7				
PFPeA		6950				2.74 × 10⁻⁸[b]	100				
PFPeS		1460				1.21 × 10⁻⁸[b]	100				
PFHxA		7170				2.74 × 10⁻⁸[b]	100				
PFHxS		18,710				5.06 × 10⁻⁸[b]	100				
PFHpA		2420				1.21 × 10⁻⁸[b]	100				
PFHpS		1570				3.67 × 10⁻⁸[b]	100				
PFOA		11,920				8.19 × 10⁻⁸[b]	98.7				
PFOS		12,020				1.66 × 10⁻⁷[b]	96.5				
6:2 FTS		9640				1.44 × 10⁻⁷[b]	96.1				
Mixture of PFAS in AFFF substance solution containing: PFOA, PFOS, PFHpSPFHxA, PFPeS, and precursors	BDD	PFOA = 290 µg/L, PFOS = 15,200 µg/L. Overall PFAS of 64 µg/L–15,200 (combination of 11 detected PFAS	1:500 diluted AFFF solution. Ion exchange brines using sodium salts (NaCl, Na₂SO₄, NaHCO₃, at 0.2%,1%, and 5%	40	2.5–8 h	-	(Measured via defluorination)	80%–90% for PFOS, PFOA and PFHpS after 2 h	-	280 kWh/m³ for defluorination in 5% sulfate brine ~0.3 kWh/m³ for total water (i.e., volume treated by ion exchange, and regenerant)	Schaefer et al. (2020)
HFPO-DA (GenX)	BDD	1000	Synthetic source water: 500 mg/L Na₂SO₄ and 100 mg/L NaCl	50	240 min	0.0021	30[a]		1470 kWh/m³		Pica et al. (2019)
		4980	Nanofiltration concentrate: 2475 mg/L Na₂SO₄, 495 mg/L NaCl			0.0041	60[a]	-	237 kWh/m³ for nanofiltration concentrate. 47.5 kWh/m³ for combined nanofiltration and electrooxidation		

TABLE 3 (Continued)

Compound	Electrode material	C_i, PFAS, µg/L	Water matrix	Current density, mA/cm²	Electrolysis time, min or h	Rate constant, 1/min or m/s[b]	% Removal	Defluorination ratio	E_{EO} kWh/m³	Additional comments	References
PFOA	BDD	8.5 ± 1.3	Model groundwater with no preconcentration; Na₂SO₄ = 0.21 g/L	35	40 min	2.83 × 10⁻⁴[b]	>99[a]	-	23.2 kWh/m³ (to reach 70 ng/L) (includes 4 stage RO)	PFBA increased by 40% before being degraded due to short chain production. Electrical energy costs were 4.3%–7.6% of total costs. PFBA increased by 20% before degradation	Soriano et al. (2020)
PFOS		6.2 ± 0.1			60 min	1.63 × 10⁻⁴[b]	>90[a]				
PFBA		9.3 ± 1.3			120 min		>80[a]				
PFPeA		8.5 ± 1.3			60 min		>80[a]				
PFHxA		9.4 ± 0.9			60 min		>80[a]				
PFHpA		8.0 ± 1.1			60 min		>90[a]				
6:2 FTSA		9.1 ± 2.2			60 min	2.0 × 10⁻⁴[b]	>99[a]				
PFOA	BDD	111.3 ± 8.3	Model groundwater concentrated by 10 times using reverse osmosis, Na₂SO₄ g/L	35	30 min	1.18 × 10⁻⁴[b]	>99%[a]	-	26 kWh/m³ (to reach 70 ng/L treatment target) (value includes 4 stage RO operation) -		
PFOS		31.5 ± 9.7			30 min	5.16 × 10⁻⁵[b]	>90%[a]				
PFBA		147.7 ± 1.2			80 min		>99[a]				
PFPeA		135.7 ± 1.7			60 min		>99[a]				
PFHxA		217.2 ± 4.5			30 min		>90[a]				
PFHpA		87.8 ± 3.2			30 min		>90[a]				
6:2 FTSA		111.2 ± 12.5			30 min	9.66 × 10⁻⁵[b]	>90[a]				
PFOS	BDD	19,000	Reverse osmosis concentrates from groundwater. DOC = 38 mg-C/L, conductivity = 780 µS/cm, pH = 8.4	2.3	18 h	-	96	42	-	DOC mineralization of 47%. After electrolysis the short chain PFAS: PFBA, PFPeA, PFHxA, and PFHpA increased by a factor of 21,6.7, 2.1, and 4.8 due to incomplete defluorination and short chain production	Trautmann et al. (2015)
PFHxS		10,000					92				
PFBS		4000					83				

Note: "-," "indicates parameter not reported in study.

Abbreviations: AFFF, aqueous film forming-foam; 6:2 FTSA, fluorotelomer sulfonic acid; HFPO-DA, hexafluoropropylene oxide dimer; PFBA, perfluorobutanoic acid; PFBS, perfluorobutanoic sulfonic acid; PFHpA, perfluoroheptanoic acid; PFHxA, perfluorohexanoic acid; PFHxS, perfluorohexanesulphonic acid; PFOA, perfluorooctanoic acid; PFOS, perfluorooctane sulfonic acid; PFPeA, perfluoropentanoic acid.

[a]Value was estimated from a figure in published study.

[b]Reported as surface area pseudo first order (m/s).

[c]Negative removal attributed to short-chain PFAS formation.

3 | ELECTROCOAGULATION AND ELECTROOXIDATION FOR TREATING PFAS IN WATER TREATMENT RESIDUALS

Electrochemical treatment may also be feasible for treating PFAS in the water treatment residuals from non-destructive PFAS treatment (e.g., ion exchange regenerant and membrane and reverse osmosis concentrate) as a side-stream treatment process before discharging the residuals. Using this approach, nondestructive technologies sequester PFAS from the drinking water stream and concentrate them into smaller volumes of wastewater that can be treated electrochemically using lower power demands due to higher conductivity, smaller reactors, and improved mass transfer and improved kinetics of degradation due to higher PFAS concentrations (Urtiaga, 2021).

3.1 | Electrocoagulation treatment of water treatment residuals

Electrocoagulation has not been studied for PFAS mitigation in water treatment residuals. However, prior research has shown that electrocoagulation can remove other contaminants in membrane concentrates (Soomro et al., 2020; Subramani & Jacangelo, 2014; Top et al., 2011). Using this approach, electrocoagulation can remove oxidant scavengers in the form of concentrated NOM in water treatment residuals via coagulation and flocculation, while electrocoagulation-generated oxidants may lead to PFAS destruction. Accordingly, more research is needed to evaluate the efficacy of electrocoagulation for treatment of water treatment residuals.

3.2 | Electrooxidation of water treatment residuals

3.2.1 | Electrooxidation for ion exchange regenerants

Electrooxidation has been used to treat PFAS in ion exchange regenerant and still bottom brines (Schaefer et al., 2020; Wang et al., 2021). Regenerants from ion exchange resins for PFAS treatment typically contain a mixture of organic solvents (such as methanol) for desorbing PFAS from the resin and ionic constituents (e.g., chloride, sulfate, etc.) needed to regenerate the resin's active sites (Dixit et al., 2021; Gagliano et al., 2020). Methanol has previously been reported as the most effective regenerant for removing PFAS from anion exchange membranes (Gagliano et al., 2020). "Still

bottom" refers to the liquid remaining after the ion exchange regenerant is distilled to remove methanol (Wang et al., 2021). Following distillation, the concentrated PFAS require secondary treatment to mitigate PFAS contamination. In prior studies, electrooxidation of still bottom wastes resulted in 61% removal of total PFAS after 40 h of electrolysis using Ti_4O_7 electrodes to treat mixtures of PFAS in pilot-scale ion exchange regenerants (Wang et al., 2021). For ion exchange regenerant applications, longer electrolysis times are likely needed due to the inevitably high concentrations of PFAS in regenerant waste streams as well as background regenerants such as methanol, which can lead to oxidant scavenging and background regenerants (such as methanol leading to oxidant scavenging) in regenerant waste streams.

The ion exchange regenerant matrix can also contain concentrated ions and solvents that will impact treatment. For example, background alcohols interfered with PFAS oxidation via indirect oxidants such as hydroxyl radicals and sulfate radicals, which decreased PFAS defluorination in ion exchange regenerant (Schaefer et al., 2020). Chloride in the regenerant (>0.2%) likely interfered with direct electron transfer reactions and inhibited PFAS mitigation (Schaefer et al., 2020). In contrast, bicarbonate and sulfate-rich regenerants were more effectively defluorinated via electrolysis, for both 1% and 5% (based on salt) comparison tests (Schaefer et al., 2020). For electrolysis of 5% sulfate regenerant, the E_{EO} for defluorination was 280 kWh/m^3. However, when these values were normalized to the total volume of water treated by ion exchange (i.e., the volume of drinking water containing PFAS that passes through ion exchange rather than the volume of the regenerant), the E_{EO} for defluorination was roughly 0.3 kWh/m^3 (Schaefer et al., 2020). Water treatment facilities bear the responsibility of treating the total mass of PFAS in the bulk water treated; accordingly, if ion exchange (or other nondestructive technology) is used to concentrate and separate PFAS from the bulk water, volume normalization may be effective for reflecting the energy costs for the facility with respect to treating all of the influent water containing PFAS. Based on these results, ion exchange may be a promising technology for concentrating PFAS from treated water to provide efficient side-stream destructive PFAS treatment using electrooxidation.

3.2.2 | Electrooxidation for membrane filtration concentrates

Nanofiltration and reverse osmosis concentrates (i.e., membrane concentrates) may be amenable to

electrooxidation, due to effective PFAS separation from drinking water. Of note, low-pressure membranes such as microfiltration and ultrafiltration poorly remove PFAS and are not discussed in this review (Glover et al., 2018; Rahman et al., 2014). Membrane concentrates have different water quality conditions than ion exchange regenerants, where membrane concentrates contain the raw water constituents that are removed from the treated drinking water stream (i.e., ions, NOM, and metals) and do not contain solvent alcohols (such as methanol). Moreover, differences between nanofiltration and reverse osmosis concentrates will impact treatment. For example, nanofiltration membranes allow monovalent ions (e.g., chloride) to pass through the membrane into the drinking water stream and retain divalent ions (e.g., sulfate) and other contaminants in the concentrate (Urtiaga, 2021). Alternately, reverse osmosis systems reject both monovalent and divalent ions, so chloride will enter reverse osmosis concentrate streams (Crittenden et al., 2012). The chloride in reverse osmosis concentrate streams can transform into secondary oxidants and perchlorate during electrooxidation, and also potentially form regulated disinfection byproducts (Bagastyo et al., 2012; Urtiaga, 2021).

As summarized in Table 3, early nanofiltration-electrooxidation studies focused on treating PFAS in industrial process water (Soriano et al., 2017), while other studies focused on membrane preconcentration for groundwater treatment (Pica et al., 2019; Soriano et al., 2020; Urtiaga, 2021). Pica et al. (2019) used electrooxidation to treat nanofiltration concentrates containing the fluorinated compound hexafluoropropylene oxide dimer (HFPO-DA, otherwise known as GenX), which is a substitute for PFOS and PFOA found in some environmental waters (Xiao, 2017). Preconcentration via nanofiltration decreased the E_{EO} for electrooxidation treatment of GenX from 1470 to 237 kWh/m^3 (Pica et al., 2019). Additionally, the removal kinetics improved by a factor of two, likely due to the higher GenX levels in the nanofiltration concentrate (Pica et al., 2019).

During electrooxidation of groundwater reverse osmosis concentrates containing spiked PFAS (PFOS, PFHxS, and PFBS), more than 80% degradation of parent PFAS compound was achieved after 18 h of electrolysis, and short-chain PFAS were produced with 42% defluorination (Trautmann et al., 2015). However, these concentrates were spiked with PFAS levels that may exceed the actual PFAS levels in concentrates (i.e., PFHxS = 10 mg/L, PFBS = 4 mg/L, PFOS = 19 mg/L) (Table 3) (Trautmann et al., 2015). Soriano et al. (2020) compared the electrooxidation of PFAS compounds in reverse osmosis-concentrated samples versus nonconcentrated samples at PFAS levels more representative of reverse osmosis

concentrates from groundwater treatment (e.g., 10–230 μg/L, as shown in Table 3). Electrooxidation of the nonconcentrated samples degraded PFAS more quickly than the concentrated samples (Soriano et al., 2020). This difference may be attributed to the lower conductivity in the nonconcentrated samples that require higher voltages and potentials that subsequently enhanced direct electron transfer reactions (Soriano et al., 2020). However, the voltage required for the nonconcentrated samples was nearly double the voltage required for concentrated samples (43.3 V for nonconcentrated vs. 23.8 V for concentrated). This difference may result in higher electrical energy demands and higher costs that do not compensate for improved kinetics in nonconcentrated conditions (Soriano et al., 2020). The shorter chain PFAS were most resistant to degradation, and concentrations of PFBA increased during the first 20–40 min of electrolysis due to short chain production. After 60 min of electrolysis, >90% PFAS removal was achieved in the reverse osmosis-concentrated and nonconcentrated samples, with the exception of PFBA, which required 80–120 min for >90% removal (Table 3) (Soriano et al., 2020).

Systems engineering can be used to quantify the benefits of treating PFAS in different water matrices as technologies are scaled up for implementation. Soriano et al. (2020) used this approach to determine the optimal reverse osmosis–electrooxidation treatment conditions for a treatment goal of <70 ng/L (sum of PFOA and PFOS). The optimized system consisted of four stages of reverse osmosis followed by electrooxidation of the concentrate, where preconcentration prior to electrooxidation reduced the total costs of treatment by up to 75% relative to treatment costs for electrooxidation alone. The highest costs for electrooxidation were reportedly the capital costs for the reactors and the replacement costs for boron-doped diamond electrodes (Schaefer et al., 2020). The total specific cost of PFAS mitigation was $13.10/m^3. For context, the costs for water treatment of nonexplicit treatment goals (e. g. disinfection, total suspended solids reduction, general operation) in advanced direct or indirect potable reuse facilities (among the most energy intensive treatment trains) generally range from $0.16/m^3 to $1.70/m^3 (US Environmental Protection Agency, 2018).

4 | BARRIERS TO IMPLEMENTATION

4.1 | Barriers to electrocoagulation implementation

Although electrocoagulation can be advantageous for PFAS mitigation, potential barriers to implementation need to be considered, including sludge generation and management,

long-term electrode quality and electrode passivation, and secondary contamination due to metal release from the electrode alloys (Garcia-Segura et al., 2017). Existing electro-coagulation studies for PFAS utilized long electrolysis times that may result in sludge generation exceeding typical sludge generation during coagulation processes. Additionally, electrocoagulation uses sacrificial electrode materials that deteriorate over time, and the efficiency of coagulant generation may be inhibited by electrode passivation. Electrode passivation may be minimized by using polarity reversal, mechanical cleaning, and other techniques summarized by Ingelsson et al. (2020). Lastly, the electrodes used during electrocoagulation may potentially be a secondary source of metal contamination depending on the alloys used. For example, manganese is common in steel alloys, causing it to co-dissolve with iron during electrocoagulation (manganese is regulated at 50 μg/L in the U.S. EPA.'s National Secondary Drinking Water Regulations) (Zhang & Cheng, 2007). Aqueous zinc may similarly impede zinc-electrocoagulation. However, Lin et al. (2015) found that the final aqueous zinc concentration in electrocoagulation-treated samples was 0.88 mg/L, which falls below the 5.0 mg/L U.S. EPA secondary standard.

While electrocoagulation can serve as an effective drinking water treatment process for PFAS, more research is needed to assess electrocoagulation performance in environmental source waters containing NOM, low conductivity, and lower PFAS concentrations (i.e., ng/L–μg/L) to better simulate real drinking water treatment conditions. For example, high concentrations may add bias in experimental design by causing sorption-based processes to proceed at faster rates, resulting in higher removal than would occur in drinking water scenarios with lower PFAS concentrations (Lin et al., 2015). Micelle/hemi-micelle formation (i.e., the aggregation of surfactants [including PFAS]) may also lead to enhanced sorption. The critical micelle concentration for PFAS has been reported in g/L conditions; however, hemi-micelles have been speculated to form at lower concentrations that are factors of 0.01 to 0.001 of the critical micelle concentrations (e.g., mg/L PFAS levels, which is similar to concentrations used in studies discussed in this review (Johnson et al., 2007; Yu et al., 2009)). The initial PFAS concentration may also govern the contribution of physical removal (nondestructive) versus redox removal (destructive removal) during electrocoagulation. For example, using a lower initial PFAS concentration than other electrocoagulation studies (i.e., 10 mg/L vs. 100–200 mg/L; Table 1), Kim et al. (2020) observed oxidation-based PFAS removal rather than the sorption-based removal observed in the nondestructive electrocoagulation studies discussed in this review.

4.2 | Barriers to electrooxidation implementation

The capital costs associated with boron-doped diamond fabrication and manufacturing serve as a major barrier to electrooxidation implementation (Chaplin, 2019; Radjenovic et al., 2020). A techno-economic analysis determined that decreasing the costs of electrooxidation electrodes is critical for improving the cost effectiveness of electrooxidation for water treatment (Stirling et al., 2020). Accordingly, interdisciplinary research focused on bridging materials science and environmental engineering is needed to develop cost-effective electrodes capable of meeting treatment targets. For example, electrode materials can be modified with nanotechnology to enhance contaminant mitigation, increase electrode longevity, and decrease material fouling (Garcia-Segura, Qu, et al., 2020). While Ti_4O_7 electrodes may serve as an alternative to boron-doped diamond electrodes based on similar PFAS degradation and cheaper fabrication costs, additional research is needed to evaluate the impact of matrix constituents and byproduct production via Ti_4O_7 (Lin et al., 2018; Wang et al., 2020). Industry and manufacturing learning curves (e.g., scaling up manufacturing processes for mass production, conducting cost analyses, and training workforces for new technology) impart high initial costs for electrooxidation implementation in the water sector, posing a hurdle to rapid adoption (Garcia-Segura, Qu, et al., 2020). However, as units are produced and skilled labor gains familiarity with new technology, the production efficiency will increase in accordance with economy of scale (Garcia-Segura, Qu, et al., 2020).

High levels of perchlorate generation can also serve as a barrier to electrooxidation implementation as perchlorate has been reported to have negative health impacts (Radjenovic & Sedlak, 2015). The World Health Organization has a perchlorate guideline of 70 μg/L (World Health Organization, 2014). Several studies reported perchlorate concentrations near or in excess of this level (65–220 mg/L) following the extensive electrooxidation times required for PFAS mitigation (Trautmann et al., 2015; Wang et al., 2021, 2020). Perchlorate generation may be minimized by removing chloride prior to electrooxidation of concentrates (e.g., using nanofiltration to separate PFAS from waters containing chloride) or using free chlorine/chlorine radical quenching during treatment. Removing precursor chloride can be accomplished by nanofiltration pretreatment to concentrate trace organics (e.g., PFAS) while excluding ionic species like chloride (Urtiaga, 2021). Yang et al. (2019) determined that applying 50 mM H_2O_2 successfully inhibited perchlorate production without decreasing PFAS treatment performance. The presence of

100–1000 mM methanol in ion exchange regenerant also decreased perchlorate formation during electrooxidation without compromising PFAS treatment performance (Wang et al., 2021). Additionally, Ti_4O_7-electrooxidation generated less perchlorate than boron-doped diamond-electrooxidation. However, Ti_4O_7 electrodes generated more free chlorine than boron-doped diamond, which may raise concerns over regulated organic disinfection byproduct formation (Wang et al., 2020).

In addition to perchlorate, regulated organic disinfection byproduct (e.g., trihalomethanes and haloacetic acids) should also be monitored to ensure treatment compliance following PFAS electrooxidation. For example, electrooxidation of reverse osmosis concentrate using boron-doped diamond produced trihalomethanes and haloacetic acids in excess of U.S. EPA regulations (Bagastyo et al., 2012). However, few studies have monitored regulated disinfection byproduct production in the context of electrooxidation when treating waters containing lower levels of chloride and NOM relevant to typical drinking water sources. It is possible that EC and EO could be paired so that EC can remove bulk contaminants like NOM while concentrating PFAS and other micropollutants followed by EO that oxidizes the concentrated pollutants (Heffron et al., 2019; Shi et al., 2021; Maher et al., 2020).

5 | ROADMAP FOR FUTURE RESEARCH

The studies reviewed here demonstrate proof-of-concept that electrochemical water treatment may be effective for PFAS mitigation in drinking water and water treatment residuals. However, future research is needed to guide implementation of electrochemical treatment in the drinking water sector, as illustrated in Figure 4. Specific needs include: (1) Determining the impact of water quality parameters on treatment performance to understand PFAS treatability in real source waters, (2) evaluating the impact of environmentally relevant PFAS concentrations on treatment performance, (3) investigating the removal and transformation of PFAS and monitor total PFAS removal, and (4) conducting systems-level analysis to assess contributing factors for cost evaluation.

5.1 | Environmentally relevant water matrices in electrochemical research studies

Environmental source waters contain diverse constituents (e.g., NOM, ionic constituents, and pH conditions) that can

have major impacts on treatment process efficacy. For emerging treatment processes to translate to full-scale processes, research is needed to validate the performance of a technology in a range of environmental source water conditions, including variations in NOM and electrolyte species and concentrations. Few studies have accounted for the impact of environmental NOM on PFAS mitigation in electrochemical treatment. NOM is common in source water and can serve as an oxidation scavenger to impede treatment performance or it may co-dissolve PFAS and enhance mass transfer to the electrode, thereby improving removal during electrocoagulation or electrooxidation. For nondestructive treatment, studies have shown that NOM improved PFAS adsorption via granular activated carbon due to the formation of PFAS-NOM complexes that were more amenable to adsorption (Kothawala et al., 2017). Other studies reported that NOM inhibited PFAS removal via sorption due to competition for sorption sites (Gagliano et al., 2020; Yu et al., 2012). Accordingly, the impact of NOM on PFAS mitigation remains unclear and more research is needed to understand NOM characteristics that influence PFAS mitigation in electrochemical treatment processes.

Additionally, the bulk of electrochemical studies have used high conductivity matrices to provide favorable electrochemical treatment conditions, whereas most drinking water sources have lower conductivity. These high electrolyte concentrations may be an issue for drinking water treatment by exceeding secondary standards for electrolytes like chloride and sulfate. High chloride conditions may also yield high perchlorate and disinfection byproducts which may compromise treated water quality (Jasper et al., 2017). Accordingly, electrolyte levels must be representative of the low conductivity in typical source water to assess drinking water treatment performance for real source waters. Real source waters with low conductivity may have excessive power demands that limit mainstream drinking water treatment application, making electrolyte or PFAS membrane preconcentration beneficial to offset power demands and operating costs. These data will be important for delineating which matrices are most applicable to electrochemical treatment (Garcia-Segura, Nienhauser, et al., 2020).

5.2 | Environmentally relevant PFAS concentrations

PFAS generally occur at ng/L to μg/L concentrations in drinking water sources, which are orders of magnitude lower than concentrations used in most electrochemical research (Tables 1–3). Contaminant concentrations impact removal efficacy and misrepresentative initial concentrations can limit translation of the data to real world treatment goals. Accordingly, future electrochemical PFAS

research should focus on environmentally relevant PFAS concentrations and demonstrate that the proposed processes can actually meet stringent proposed regulations (e.g., <70 ng/L) regulations (Garcia-Segura, Nienhauser, et al., 2020; Radjenovic et al., 2020).

5.3 | Research on transformation products following electrochemical treatment

The majority of existing treatment studies focus on PFOA and PFOS, which have been phased out and replaced by PFAS-related substitutes in manufacturing processes (Xiao, 2017). If treatment processes are designed for PFOA and PFOS removal, they will be under-designed with respect to short-chain compounds, which are more recalcitrant to destructive treatment due to their hydrophilic structure (relative to PFOA and PFOS) (Ateia et al., 2019). Extractable organofluorine can also serve as an effective monitoring parameter/research metric for nontarget PFAS analysis and evaluating the extent of total PFAS removal (Cousins et al., 2020). Nontarget PFAS analyses are important given that a 2016 sampling campaign showed that 60% of the PFAS (based on extractable organofluorine) present in tap water were not included in the targeted PFAS analysis, demonstrating the occurrence of unknown PFAS (Hu et al., 2019).

FIGURE 4 Summary of research needs for implementation of electrochemical treatment for per- and polyfluoroalkyl substances (PFAS) mitigation in drinking water. Each tier represents a different foundation of research that needs to be examined in order to progress to the goal of engineering application. Tier one research focuses on proof-of-concept research to verify that a technology can work for a specific contaminant. Tier two research focuses on assessing different applications of research and the influence of matrix factors, transformation products, and the costs associated with treatment. Tier three focuses on research explicitly focused on implementation for drinking water treatment and includes studying the impact of environmentally relevant conditions and is validated based on regulatory targets. Finally, the peak of the pyramid is "engineering application" which requires a stable foundation supported by the underlying tiers of research

5.4 | Systems-level analysis for cost-effective treatment goals

Systems-level analyses focus on the ranges of system parameters (e.g., energy costs, electrode costs, treatment times, materials cost, and treatment goals) to delineate the contribution of each component to the overall cost associated with implementation. Accordingly, systems-level analysis is needed to parameterize the costs associated with PFAS mitigation for meeting proposed treatment goals (e.g., lower than 70 ng/L). Cost analyses are useful to inform status quo and future projections related to electrode development, process scale-up, and environmental impacts (Soriano et al., 2020). These analyses can also be applied to evaluating the costs of different electrode materials (e.g., boron-doped diamond and Ti_4O_7 for electrooxidation, or iron, aluminum, and zinc for electrocoagulation) as a function of electrode longevity, lifespan, stability, and materials cost in order to understand what aspects of electrodes and system operation contribute to cost effectiveness, similar to the approach used by Soriano et al. (2020). Overall, systems-level analyses are an important first step for scaling up emerging technology to the pilot scale and transferring laboratory-scale treatment performance to full-scale drinking water treatment processes.

CONFLICT OF INTEREST

The authors declare no conflicts of interest that would otherwise impact or otherwise influence the production of this work.

DATA AVAILABILITY STATEMENT

This manuscript is a literature review that focuses on data presented in previously published studies and critical analysis for the proposed roadmap of research. Accordingly, this manuscript does not include original data.

AUTHOR CONTRIBUTIONS

Donald R. Ryan: Conceptualization; data curation; formal analysis; investigation; visualization; writing – original draft; project administration; writing – review and editing. **Brooke K. Mayer:** Conceptualization; supervision; funding acquisition; writing – original draft; project administration; writing – review and editing. **Claire Baldus:** Data curation; investigation; visualization; writing – original draft; writing – review and editing. **Sean T. McBeath:** Writing – review and editing. **Yin Wang:** Conceptualization; data curation; funding acquisition; visualization; writing – review and editing. **Patrick J. McNamara:** Conceptualization; supervision; funding acquisition; writing – original draft; project administration; writing – review and editing.

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