Electrochemical Approaches for PFAS Removal and Destruction

THOMAS K.S. IGOU, Ph.D.
WaterTectonics
Everett, Washington

DORA CHIANG, Ph.D., P.E.
Jacobs
Atlanta, Georgia

QINGGUO (JACK) HUANG, Ph.D.
University of Georgia
Griffin, Georgia

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ABSTRACT

Electrochemical approaches for PFAS removal and destruction continue to offer advantages over traditional techniques, including *in-situ* generation of treatment chemicals, compact footprint, simple controls, and less sludge. Recent findings demonstrate electrochemical coagulation (EC) can achieve removal of PFAS via two primary pathways - (a) foam fractionation, and, (b) adsorption to EC-generated metal hydroxide flocs. Here, we update and contextualize the existing body of literature surrounding EC in standalone and integrated electrochemical treatment trains for PFAS removal in industrial wastewater treatment applications.

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a class of > 14,000 synthetic "forever chemicals" characterized by the presence of fully or partially (per- or poly-) fluorinated alkyl chains known for their toxicity at ultra-dilute concentrations (e.g., ng/L, parts per trillion), and extreme persistence and resistance to environmental degradation (Sigmund, 2025). PFAS were widely used in firefighting foams, coatings, and industrial processes for decades, leading to global water contamination. PFAS have been detected virtually everywhere on Earth, including drinking water (Domingo, 2019; Tymoorian, 2023; Wang, 2022), wastewater (Kim, 2022; Kim, 2023), rainwater (Kim, 2023), groundwater (Xu, 2021), Antarctic ice cores (Garnett, 2022), vegetables (Ghisi, 2019), livestock and game (Death, 2021), and of course, in human blood, milk and organs (Jian, 2018). To put the dilute nature of environmental PFAS contamination and human risk in perspective, the 4 ng/L US Environmental Protection Agency (EPA) maximum contaminant limit (MCL) for the 8-carbon PFOA and PFOS species is equivalent to 4 seconds in 126,839 years – further, there is no known "safe" concentration for PFAS exposure, and PFAS has been linked to prostate/breast/thyroid cancers and developmental complications in children. EPA recently pulled back proposed MCLs on PFOS, PFOA, PFHxS, PFNA, PFBS and HFPO-DA (also known as GenX) in drinking water, pushing out compliance dates for PFOA and PFOS to 2031 and intends to rescind regulations for the other four compounds. Contrary to recent actions by EPA, PFAS contamination continues to threaten virtually all water supplies globally.

Electrochemical water treatment approaches continue to offer advantages over traditional chemical- and biological-based techniques, including *in-situ* generation of coagulants, oxidants, reductant chemistries, compact treatment footprint, tunable process control, and reduced generation of sludge. Further, the relatively stable inflation-adjusted cost of electricity and increasing share of renewables within the domestic energy grid have advanced the value proposition for electrified treatment trains both in terms of economics and sustainability. As the grid becomes greener and more sustainable, any improvements in power generation will immediately be realized in water treatment. Although electrochemical oxidation (EO) has been investigated thoroughly for PFAS destruction, less information is available within the scientific literature describing electrochemical coagulation (EC) for PFAS removal - either as a standalone process or as pretreatment prior to EO within integrated EC-EO treatment trains.

PFAS SEPARATIONS - PFAS are notoriously resistant to traditional water/wastewater treatment methods. Due to their low/negative pKa values, amphiphilic nature and C-F bond strength PFAS are resistant to physical separations and chemical and biological transformations (**Table 1**). As such, PFAS concentrations can actually increase throughout water/wastewater treatment trains, resulting in the same or even higher PFAS concentrations found in effluents compared to influents due to the high extent of solids-solids contact in water treatment separations and transformations of short- and ultra-short chain compounds, precursors and uncharacterized PFAS to longer chain, definitively characterized compounds (Kim, 2022) (**Figure 1**).

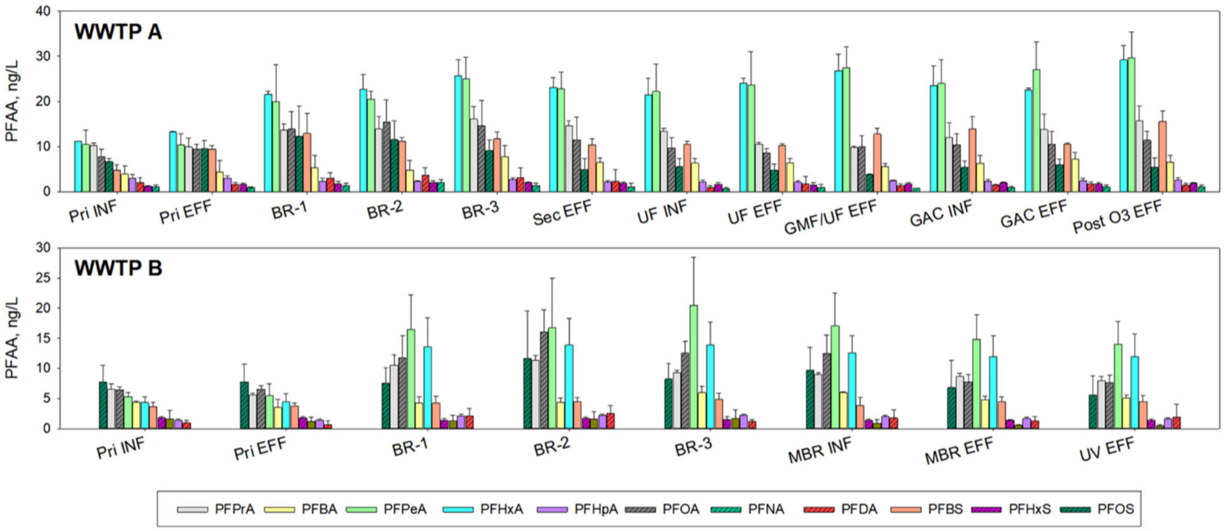


Figure 1: PFAS Transformations Across Wastewater Treatment Unit Processes.
WWTP A: Influent (INF), Effluent (EFF), Bioreactor (BR), Ultrafiltration (UF), Granular Media Filtration (GMF), Granular Activated Carbon (GAC), Ozone (O3); WWTP B: Influent (INF), Effluent (EFF), Bioreactor (BR), Ultrafiltration Membrane Bioreactor (MBR), Ultraviolet Disinfection (UV).

Table 1: PFAS Properties and Physicochemical Implications

PFAS Properties	**Physicochemical Implications**
Low or negative pKa	Highly water soluble at pH 0-14; strong acid dissociation; non-volatile
Amphiphilic	Hydrophilic head group and hydrophobic carbon chain lend surfactant properties but complicate removal strategies due to strong reliance on chemical structure/function, which varies by PFAS chain length
Bond strength	C-F bond dissociation energy (485 kJ/mol); strongest bond in organic chemistry; highly resistant to thermal, chemical, biological degradation

Several technologies have emerged as attractive PFAS concentration methods, including activated carbon (granular activated carbon, GAC; powder activated carbon, PAC), ion exchange (anion exchange resins, organoclays, composites) and foam fractionation. These technologies take advantage of long-chain PFAS hydrophobicity (activated carbons), ionic activity (ion exchange), and the surfactant properties of PFAS that encourage partitioning to air-water and water-solid interfaces due to hydrophilic/phobic interactions (e.g., foam fractionation) (Reid, 2023; Reid, 2025; Maroli, 2024).

However, performance of these technologies tends to suffer in the presence of co-occurring constituents that are fairly ubiquitous in the water matrix, including suspended solids, organics, and soluble ions (Kothawala, 2017). Further, these technologies do not destroy the removed PFAS compounds and are less effective for short- and ultra-short chain variants, in which electrostatic effects tend to dominate over hydrophobic effects due to comparatively less contribution from the hydrophobic carbon chain as chain length decreases.

PFAS DESTRUCTION - Beyond concentration, traditional oxidation-based methods such as ozone, UV/H_2O_2, and chlorination are largely ineffective against PFAS at ambient conditions, and even specialized methods (e.g., supercritical water oxidation, plasma, hydrothermal alkaline treatment, UV-sulfite, sonolysis) demand high energy inputs to achieve destruction. This has created urgent demand for novel technologies that can both separate and destroy PFAS in water. Further, the intensive nature of PFAS destruction reinforces the significance of effective pre-concentration to achieve maximum volume reduction prior to implementation of destructive technologies (Ryan, 2021a; Ryan, 2021b).

ELECTROCHEMICAL COAGULATION

Electrochemical coagulation (EC) typically uses iron, aluminum or zinc sacrificial electrodes – when an electrical potential is applied across the electrodes, several processes occur simultaneously including, (a) *in-situ* dissolution of metal cations (anode), (b) evolution of hydrogen gas (cathode), and (c) generation of hydroxide ions (cathode) (**Figure 2**).

Dissolved metals then react with hydroxide ions via hydrolysis, creating metal hydroxides that entrain and adsorb contaminants such as dissolved metals, suspended solids, nutrients, oil and grease, and others. Hydrogen gas evolution then enables contaminant removal by floatation in addition to gravity settling or media filtration of EC flocs. Although protons are generated during EC, they are rapidly consumed resulting in net-zero pH throughout the overall reaction. EC, in contrast with chemical coagulation, does not require addition of salts and their counterions (e.g., Cl^- in $FeCl_3$, K and SO_4^{2-} in $KAl(SO_4)_2$) which meaningfully reduces the amount of sludge generated during treatment. Chemical methods for water treatment often involve the procurement, transport and storage of hazardous chemicals which can be avoided by electrifying the coagulation process. This is beneficial in low-resource or off-grid settings where chemicals can be costly, but electricity is ubiquitous.

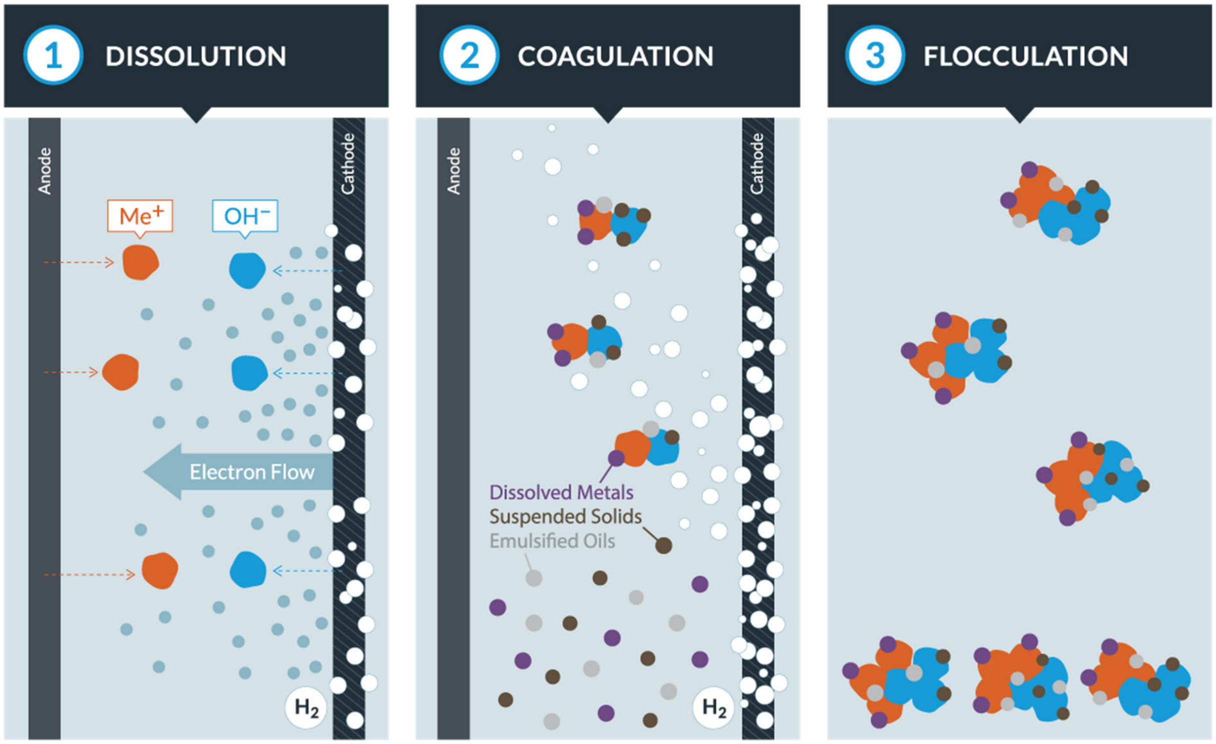


Figure 2: Electrochemical Coagulation Process.

The following reactions (Eq. 1-7) describe the EC process using iron electrodes in the presence of oxygen (Mollah, 2004).

Anode Reactions:

$Fe\ (s) \rightarrow Fe^{2+} + 2e^{-}$ (Eq. 1)

$2H_2O \rightarrow 4H^{+} + O_2\ (g) + 4e^{-}$ (Eq. 2)

$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$ (Eq. 3)

Cathode Reactions:

$2H_2O + 2e^{-} \rightarrow H_2\ (g) + 2OH^{-}$ (Eq. 4)

$Fe3+ + 3e- \rightarrow Fe\ (s)$ (Eq. 5)

Hydrolysis Reactions:

$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3\ (s) + 3H^{+}$ (Eq. 6)

$$Fe^{3+} + 2H_2O \rightarrow Fe(OH)_2\ (s) + 2H^+ \qquad \text{(Eq. 7)}$$

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2\ (s) + 2H^+ \qquad \text{(Eq. 8)}$$

Iron hydroxides and polymeric hydroxy complex speciation is highly dependent on pH. Depending on the influent pH, the generated species can include those seen in Eq. 6-8 above, as well as $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)_2^{+}$, $Fe_2(H_2O)_8(OH)_2^{4+}$, and $Fe_2(H_2O)_6(OH)_4^{4+}$.

Coagulant dosing can be calculated according to Faraday's Law (Eq. 9), enabling precise reaction automation and control according to applied potential and current.

<u>Faraday's Law:</u>

$$m = \frac{It}{ZF}(MW) \qquad \text{(Eq. 9)}$$

where m is the mass of dissolved coagulant, I is current, t is time, Z is coagulant charge, F is Faraday's constant (9.6485×10^4 C/mol), and MW is coagulant molecular weight.

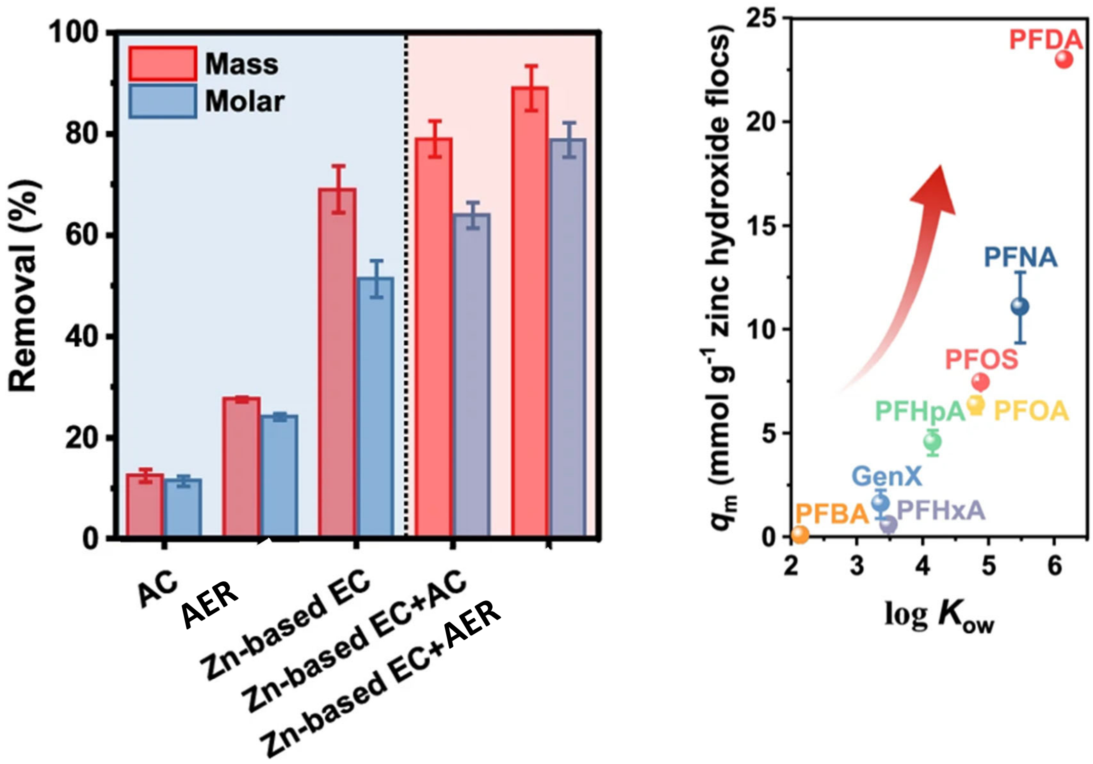
The primary mechanism for PFAS removal in EC is adsorption of PFAS onto the surface of *in-situ* generated metal hydroxide flocs. Metal hydroxides provide a high-surface area, positively charged surface that targets the hydrophilic head groups through electrostatic interactions and targets the hydrophobic carbon chain through van der Waals and hydrophobic interactions at the floc surface.

Studies have demonstrated that hydrophobic interactions are the dominant force driving PFAS sorption to EC flocs (Lin, 2015). In the case of $Zn(OH)_2$ flocs, Lin *et al.* (2015) showed that even with a 10 mM NaCl background, PFOA and PFOS adsorption was very rapid, < 10 min to equilibrium, and showed a Langmuir-type isotherm with high capacities (max adsorption capacity 5.7 mmol/g for PFOA and 7.7 mmol/g for PFOS on Zn flocs). Hydrophobic interactions were assumed to be the primary driver since PFOS (which is more hydrophobic due to its sulfonate and longer perfluoro-chain) had higher uptake than PFOA, and adsorption was favorable even at high ionic strength where electrostatic effects are dampened by presence of background ions. Further, longer-chain PFAS and sulfonates generally exhibit greater sorption to flocs than shorter chains or carboxylates. For example, adsorption capacity on Zn flocs was observed in one study to follow the order: PFOS (C8) > PFNA (C9) > 8:2 FtS (C10) > PFOA (C8) > PFHxS (C6) > 6:2 FtS (C8) > PFHpA (C7) > PFHxA (C6) > PFBS (C4) (Huang, 2021). This trend correlates strongly with hydrophobic tail length and functional group, indicating longer perfluoroalkyl chains bind more strongly. PFOS (C8 sulfonate) topped the list, while PFBS (C4 sulfonate) was among the lowest, consistent with PFBS's much lower hydrophobicity.

However, electrostatic attraction still plays a role. PFAS are anions and most metal hydroxide flocs have point-of-zero-charge between pH 7 to 8meaning at neutral pH the floc surfaces likely carry a slight positive charge that can bind anions (Deng, 2011). Deng *et al.* (2011) speculated that PFOA removal by polyaluminum chloride involved both electrostatic attraction of the carboxylate to Al^{3+} sites and adsorption onto precipitated $Al(OH)_3$ surfaces. In EC, the continuous generation of fresh metal hydroxides ensures a steady supply of adsorption sites that can trap PFAS as water flows through the system.

Notably, PFAS sorption can exhibit hemimicellar or bilayer formation at high local concentrations, creating a positive feedback loop that encourages further PFAS sorption to PFAS already adsorbed to the surface (Reid, 2025) (Liang, 2023). Liang *et al.* (2025) exploited this phenomenon using EC with Zn electrodes and were able to achieve 92% removal of PFOA in a concentrated fluorochemical wastewater containing 36 mg/L characterized PFAS compounds (107 compounds, of which 49% was PFOA) and 23 mg/L uncharacterized PFAS (total organic fluorine = 49 mg/L). Other water quality parameters for this wastewater include pH 7.3, 36 mg/L total organic carbon, 26 mg/L total inorganic carbon, 388 mg/L chloride, 35 mg/L nitrate, 181 mg/L sulfate and 45 mg/L fluoride. This Zn-based EC pre-treatment was able to reduce effluent PFOA concentrations to just 0.3 mg/L with an anion exchange resin (AER) process implemented downstream, compared to an effluent concentration of 22.3 mg/L when using AER only, equating to an improvement of 12.3X more bed volume throughput until 80% breakthrough (e.g., BV_{80}). Similar to other studies, adsorption performance generally correlated positively with PFAS carbon chain length (Liang, 2025) (**Figure 2**).

Figure 2: Zn-based Electrochemical Coagulation Performance.



ELECTROCHEMICAL OXIDATION

In contrast to EC, electrochemical oxidation (EO) relies on dimensionally stable anodes typically characterized by very high oxygen evolution overpotential. Examples of widely used anode materials include boron-doped diamond (BDD), titanium suboxide (Ti_4O_7), PbO_2, SnO_2-Sb, or mixed metal coatings (Veciana, 2022). Due to high stability, these anode materials can generate hydroxyl radicals and other compounds with extremely high oxidation potential, or they can directly transfer electrons to species adsorbed at the electrode-water interface. At the anode surface, the primary reactions include water splitting or formation of chemisorbed active oxygen (MO·) on oxide anodes (Lin, 2015). PFAS anions are drawn to the positively charged anode surface, especially if supporting electrolyte increases the solution conductivity and provides a medium for current (common electrolytes like Na_2SO_4, NaCl can also yield secondary oxidants such as persulfate or chlorine).

Once transported to the anode, a PFAS anion can undergo direct oxidation to form a radical, initiating bond cleavage and degradation (Mirabediny, 2023) (Shi, 2021). In presence of water or oxygen, this perfluoroalkyl radical then transforms into shorter perfluorinated acids and fluoride. Long-chain PFAS are oxidatively sliced apart one or two carbons at a time, producing a sequence of shorter-chain perfluoroalkyl acids as the reaction continues. If conditions are sufficiently aggressive (e.g., long reaction time, high anode potential, addition of co-oxidants), this process ultimately converts PFAS to CO_2 and F^-, which is referred to as complete mineralization. Complete mineralization is challenging but achievable in EO.

Notably, the kinetics of PFAS EO are often pseudo-first-order but slow. Long-chain PFAS tend to degrade faster than short-chain ones in EO because longer chains adsorb more readily to the anode surface (more hydrophobic interaction) and have more C–F bonds that can be attacked (Trzcinski, 2024). Short-chain PFAS (e.g., PFBA, PFBS) often remain after prolonged EO, as observed in pilot studies where short-chain degradation was significantly lower than long-chain degradation. For example, a field pilot combining foam fractionation and EO saw up to 86% degradation of long-chain PFAS but only ~31% for short-chain in the same timeframe (Smith, 2023). This is because short chains (C4 and below) are highly soluble and less surface-active due to higher hydrophilicity and relatively more electrostatic contribution from head groups, so they spend less time at the anode surface and are harder to oxidize.

INTEGRATED EC-EO TREATMENT TRAINS

EO often requires a supporting electrolyte like Na_2SO_4 or NaCl if the water is low in ionic strength. In an integrated EC–EO process, the EC step can provide coagulant as electrolyte (Shi, 2021). For example, dissolving Zn flocs in acid yields Zn^{2+} and SO_4^{2-} (if H_2SO_4 is used), which can then improve performance of EO. In some cases, salts (e.g. NaOH, Na_2SO_4) are intentionally added following EC as a pretreatment for EO, to improve conductivity and also sometimes to create a favorable environment. High pH can enhance defluorination efficiency, whereas sulfate can generate persulfate ($S_2O_8^{2-}$) at the anode which is a strong oxidant that can assist PFAS breakdown. Choice of electrolyte can thus influence the oxidation pathways. Chloride, for example, can produce chlorine/hypochlorite which might help break PFAS via secondary reactions, though chlorine is not very effective on C–F bonds and can form undesired, kinetically favorable byproducts like perchlorate.

Figure 3: Integrated EC-EO Process Flow Diagram with Mechanistic Detail.

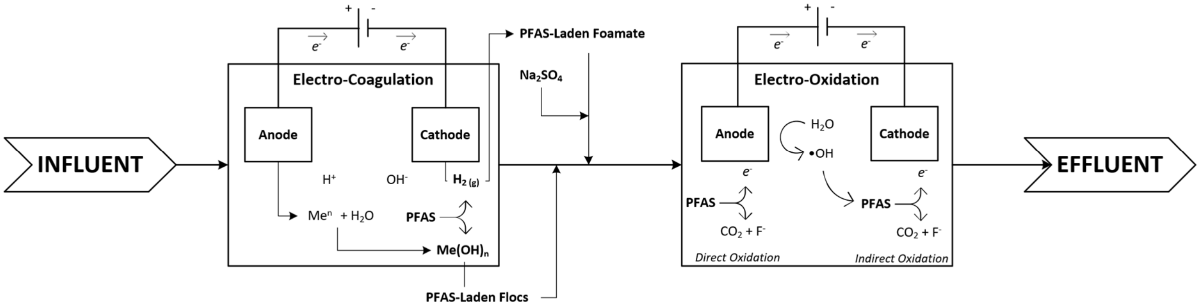


Figure X illustrates a conceptual block flow diagram for an integrated EC–EO process. The system begins with sacrificial metal electrodes (e.g., Me (s)) generating hydroxide flocs and hydrogen gas under applied current. These flocs adsorb PFAS through hydrophobic and electrostatic interactions, while hydrogen evolution can promote foam fractionation. In parallel, the EC process increases solution ionic strength by releasing metal cations, which can serve as supporting electrolyte for subsequent EO. Optional salt additions (e.g., Na_2SO_4, NaCl, NaOH) may be introduced depending on matrix requirements and targeted PFAS destruction pathways. The EO step then mineralizes the concentrated PFAS fraction by either direct or indirect oxidation, converting them to shorter chain PFAS and eventually CO_2 and F^- under high anodic potentials. Electrical inputs are supplied via a DC power source, with current density tuned to optimize floc generation versus foam fractionation.

Representative influent concentrations for industrial wastewaters reported in the literature range from tens of µg/L (Kim, 2022) to > 30 mg/L (Liang, 2025). Using Zn electrodes, Liang *et al.* (2025) demonstrated that EC pretreatment reduced PFOA from 36 mg/L to 0.3 mg/L prior to downstream anion exchange, a > 99% reduction. When paired with EO, this concentrated PFAS fraction can be further degraded, with long-chain compounds mineralized efficiently (>85% removal) and short-chain species partially degraded (~30–40%) under pilot-scale conditions (Smith, 2023). As stated before, when preceded by EC, settling, and acid dissolution of PFAS-laden EC flocs, EO did not require additional conductivity to achieve PFAS destruction (Shi, 2021).

Notably, Zn floc generation prior to EO is synergistic rather than redundant. Adsorption concentrates PFAS onto floc surfaces and reduces bulk solution concentrations, mitigating EO energy demands by improving mass transfer and reaction kinetics. At the same time, dissolution of Zn^{2+} increases electrolyte conductivity, enhancing EO kinetics.

In summary, the integrated EC–EO process marries the strengths of both EC's ability to quickly pre-treat and sequester PFAS from large volumes at low cost, EO's ability to destroy PFAS in small volumes with concentrated contamination, and EC's ability to generate supplemental electrolyte and/or oxidants for EO.

KEY CHALLENGES TO TECHNOLOGY SCALING

Although EC, EO, and integrated EC-EO have demonstrated promising results for PFAS removal and destruction in challenge wastewaters, several open issues remain that must be addressed to improve the cost, energy, and electrode performance necessary for robust full-scale implementation.

CURRENT DENSITY AND HYDRAULIC RETENTION TIME - Typical current densities for full-scale EC range from 0.5 – 5 mA/cm^2 (5 – 50 A/m^2). Current density controls the rate of cathode hydrogen gas evolution and anode metal dissolution, allowing the process to be steered towards floc adsorption (lower current density, longer retention time) or foam fractionation (higher current density, shorter retention time). Deeper understanding of the relationship between current density, hydraulic retention time, and PFAS removal is needed to support more advanced manipulations of EC parameters via control systems for on-the-fly performance optimization.

ENERGY INTENSITY - Laboratory studies report relatively high energy intensities for PFAS removal and destruction, on the order of 10 to 30 kWh/m^3 (Huang, 2021), although some studies have reported exceptionally low energy intensity e.g., < 0.2 kWh/ m^3 for 100 mg/L PFAS removal (Lin, 2015), and 0.14 kWh/m^3 for 100% PFOA removal with an air cathode EC (Mu, 2021). Commercial EC systems generally operate between 1 to 5 kWh/m^3, with lab studies sometimes surpassing 30 kWh/m^3. Although the results to-date appear promising, future studies should carefully consider the energy intensity implications of design, control and experimental parameters.

EC ELECTRODE CONSUMPTION – Sacrificial anodes are consumed according to Faraday's Law (with the exception of Al). Although a significant mass of coagulant may be consumed during the EC process, electrode degradation is offset by the low cost of electrode materials (e.g., iron, zinc plates) and the high adsorption capacity of metal hydroxide flocs. Using Zn electrodes and maximum adsorption capacity reported by Liang *et al.* (2025) as an example, 5.7 mmol PFOA (2,360.2 mg PFOA) and 7.7 mmol PFOS (3,851 mg PFOS) can be removed by a single gram of Zn floc generated by EC. Still, electrodes are sacrificial, and replacement is a guarantee over long deployments – as such, designers should take maintenance and replacement into account during scale up conceptualization.

SCALING AND FOULING – Precipitates formed by divalent cations like calcium and magnesium can create scaling in waters with moderate hardness. Further, floc itself can accumulate at the electrode, decreasing available electrode surface area and preventing dissolution. Both scaling and fouling can be mitigated by polarity switching, where the flow of current is periodically reversed, converting the anode to cathode and vise versa. Otherwise, maintaining sufficient flow past the electrodes can provide the advective flow and turbulence necessary to prevent stagnation at the surface and shear to dislodge flocs that may have opportunistically attached.

EO ELECTRODE STABILITY – BDD electrode coatings can deteriorate during aggressive EO, and titanium suboxide can oxidize to TiO_2 which is non-conductive. It is important to select electrode material according to application, expected EO conditions, and routine maintenance requirements. Similar to EC, polarity switching can be used to provide *in-situ* electrode cleaning. EO electrodes can also be washed in acid to remove deposits on the electrode surface.

RESIDUALS HANDLING – Integrated EC-EO aims to achieve a zero-PFAS-residual discharge. However, a designer may want to implement EC without EO in their process. Although EO is the preferred strategy for management of PFAS-laden EC flocs due to the performance improvement endowed by high electrolytic conductivity, this process is compatible with other destructive technologies. EC generates less residual sludge than chemical coagulation due to elimination of the requirement for chemical counterions to balance the coagulant. We have observed that PFAS associates tightly with EC flocs (Liang, 2025). Acid washing can liberate PFAS from floc, generating a concentrated PFAS solution ready for downstream destruction.

CONCLUSIONS

Electrochemical technologies present a compelling, modular toolkit for addressing the growing challenge of PFAS contamination in water and wastewater systems. Electrochemical coagulation (EC) offers an efficient and scalable method to concentrate PFAS by leveraging high surface area and reactive *in-situ* generated metal hydroxide flocs, with the added benefit of exploiting PFAS's surfactant behavior for foam fractionation. Electrochemical oxidation (EO), while more energy-intensive, provides a viable pathway for the mineralization of PFAS once concentrated, converting PFAS into benign products e.g., carbon dioxide and fluoride.

Together, integrated EC-EO treatment trains enable the strengths of both processes. EC can be used for broad-spectrum PFAS capture across chain lengths and wastewater matrices, and EO for targeted destruction of the most persistent, or most important compounds for regulatory compliance. The synergy between these two methods e.g., taking advantage of electrolyte, reactive intermediates, and operational flexibility/controls, provides a platform for developing sustainable, electrified water treatment systems with minimized chemical dependency and residual waste.

However, key challenges remain prior to cost-effective, full-scale deployment. These include optimization of energy use and electrode stability, management of scaling and fouling, and cost-effective strategies for handling PFAS-laden residuals. As the regulatory and public health pressures surrounding PFAS intensify, electrochemical treatment represents a promising frontier in achieving robust, resilient, sustainable outcomes to protect the environment and human health.

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