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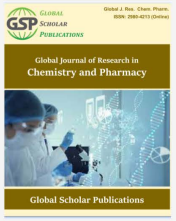

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# PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) DESTRUCTION AND MINERALIZATION: SCALABLE, ENERGY-EFFICIENT STRATEGIES FOR WATER AND ENVIRONMENTAL REMEDIATION

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## ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are a diverse group of synthetic chemicals used in industrial processes and consumer products because of their chemical, thermal and surface-active properties. Their environmental persistence is associated with the strength of carbon–fluorine bonds, resistance to conventional biological and chemical treatment, mobility of many compounds, and the formation of transformation products. Treatment technologies such as activated carbon, ion exchange and membrane separation can transfer PFAS from water to a concentrated residual stream but do not necessarily destroy the contaminant. This manuscript evaluates destructive approaches that seek to transform PFAS and, ideally, release fluorine as inorganic fluoride while reducing organic carbon to inorganic products. The principal methods considered are electrochemical oxidation, advanced reduction processes, non-thermal plasma, sonochemical treatment, photocatalysis and photoelectrocatalysis, supercritical water oxidation, and thermal or hydrothermal methods. Their mechanisms, strengths, limitations, energy considerations, matrix sensitivity, by-product risks and technology maturity are compared. Evidence indicates that no single process is universally optimal: long-chain compounds, short-chain PFAS, precursor molecules and mixed matrices respond differently, while reported parent-compound disappearance can overstate destruction when defluorination and product formation are not measured. A practical pathway is therefore to combine selective concentration with a validated destructive process, supported by fluorine mass balance, targeted and non-target analysis, toxicity assessment and life-cycle evaluation. Priority research needs include standardized performance metrics, realistic water and soil matrices, reactor scale-up, energy benchmarking, management of fluoride and secondary wastes, and demonstration of sustained operation at pilot and field scale.

**Keywords:** PFAS; Forever Chemicals; Defluorination; Mineralization; Electrochemical Oxidation; Plasma; Sonolysis; Advanced Reduction; Supercritical Water Oxidation; Energy Efficiency; Concentrate-and-Destroy.

## 1 INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) comprise a large and structurally diverse family of fluorinated compounds. Their use in aqueous film-forming foams, textiles, coatings, food-contact materials, electronics, lubricants and other applications has resulted in releases to air, soil, surface water, groundwater and wastewater. The properties that made many PFAS commercially useful including chemical stability, hydrophobicity or hydrophilicity, low surface tension and resistance to heat also complicate environmental remediation. Many PFAS are persistent, and some are mobile, bioaccumulative or associated with adverse health effects. The scale and diversity of PFAS contamination make treatment a major environmental engineering challenge. [1,2,6–8,16–18,23,24,29] [10,14,15]

Conventional water-treatment methods generally focus on separation rather than destruction. Granular activated carbon, powdered activated carbon, ion-exchange resins, foam fractionation and membrane processes can reduce PFAS concentrations in treated water, but spent media, brines, foams or membrane concentrates retain the contaminant burden. The environmental problem is therefore displaced unless the residual is securely managed or subjected to a destructive process. The emerging treatment paradigm is to separate PFAS from large volumes of dilute water and then destroy the concentrated stream, potentially lowering the energy and cost associated with destruction. [1,2,16–18,22–24,29]. The Conceptual pathway from PFAS release and environmental transport to separation, concentration, destructive treatment and verified mineralization has shown in Figure 1.

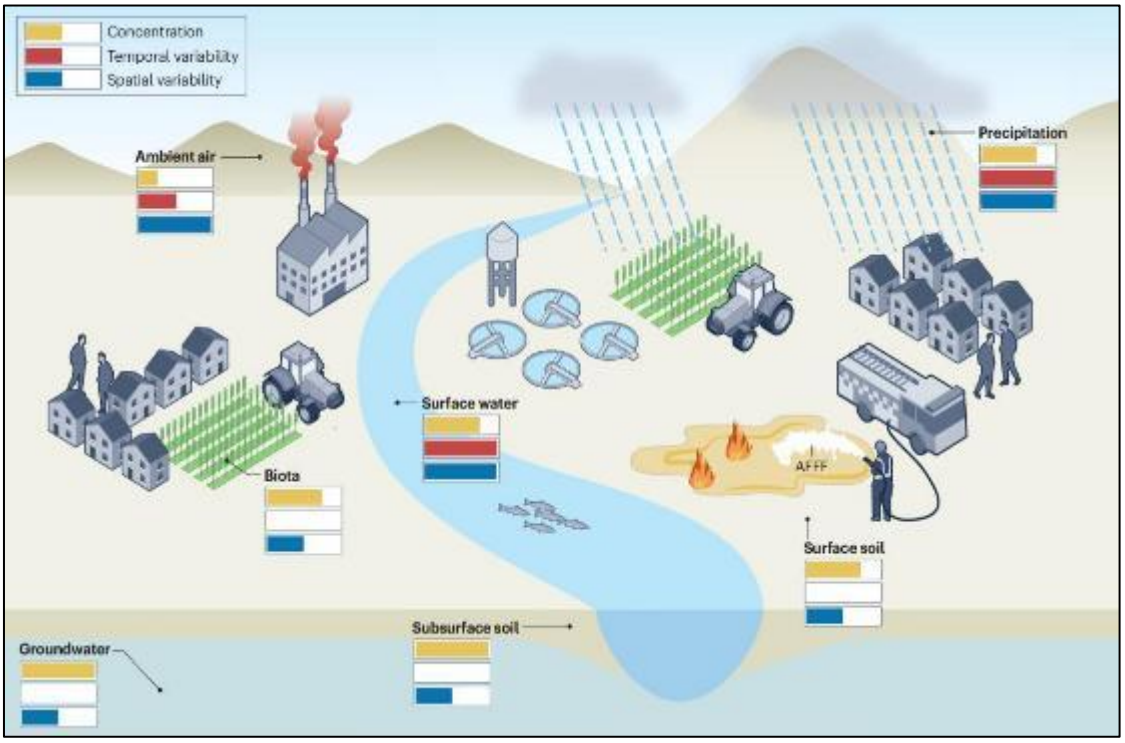


**Figure 1: Conceptual pathway from PFAS release and environmental transport to separation, concentration, destructive treatment and verified mineralization.**

## 2 PFAS CHEMISTRY AND THE CHALLENGE OF DESTRUCTION

PFAS definitions and inventories continue to evolve, and the group includes thousands of compounds with different functional groups, chain lengths and degrees of fluorination. Perfluoroalkyl acids such as perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) are frequently used as model contaminants. Polyfluorinated precursors may transform into terminal perfluoroalkyl acids, while fluorotelomer compounds and other precursor classes can produce mixtures of intermediates during treatment. [6,7,16–18,23,29]

## 3 ESSENTIAL PERFORMANCE DEFINITIONS AND ANALYTICAL EVIDENCE

Comparisons should use consistent definitions. Removal is a decrease in the measured aqueous concentration and may reflect adsorption, partitioning, precipitation or destruction. Degradation is chemical transformation of the parent compound. Defluorination is the conversion of organically bound fluorine to inorganic fluoride. Mineralization is the conversion of organic matter toward inorganic end products; for PFAS, complete mineralization requires evidence

beyond parent disappearance, including fluorine release and carbon transformation. [11,12,16,18,21,26]. The Recommended reporting metrics for PFAS destruction studies has shown in Table 1.

**Table 1: Recommended reporting metrics for PFAS destruction studies [11,12,16,18,21,26]**

| Metric | What it indicates | Recommended reporting |
|---|---|---|
| Parent PFAS removal (%) | Loss of parent analyte | Specify whether removal includes adsorption or phase transfer |
| Defluorination (%) | Organic fluorine converted to fluoride | Include initial fluorine, fluoride background and uncertainty |
| Mineralization / carbon balance | Extent of conversion toward inorganic carbon | TOC, inorganic carbon and relevant products |
| Transformation products | Potential residual hazard | Targeted and non-target analysis; time-course if possible |
| Energy | Process energy intensity | $kWh/m^3$, EE/O and kWh/g PFAS or fluorine destroyed |
| Chemical consumption | Reagent burden and secondary waste | Mass per volume or mass PFAS treated |
| Matrix tolerance | Real-world robustness | Water composition, organic matter, salts and competing species |
| Technology readiness | Deployment maturity | Continuous pilot duration, throughput, maintenance and cost |

## 4 DESTRUCTIVE TREATMENT TECHNOLOGIES

### 4.1 Electrochemical oxidation

Electrochemical oxidation uses an applied potential to drive direct oxidation at the electrode surface or generate reactive species that participate in degradation. Anodes such as boron-doped diamond (BDD), Magnéli-phase titanium suboxides and other high-oxygen-overpotential materials have been investigated. PFAS may be adsorbed or concentrated near the electrode, where electron transfer, decarboxylation or other pathways initiate chain transformation. Electrochemical systems are modular and can be integrated with concentrate streams, but electrode cost, fouling, competing reactions, conductivity requirements and energy consumption are important constraints. [3,20,27,28]

Performance depends on electrode material, current density, cell configuration, electrolyte, pH, PFAS structure and matrix. High current may increase throughput but can also promote oxygen evolution, chlorinated oxidants or other unwanted chemistry in chloride-containing waters. Scale-up requires attention to electrode spacing, hydraulic distribution, mass transfer, voltage losses, durability and maintenance. Reported degradation should be accompanied by fluoride and product measurements rather than relying only on parent removal. [3,20,27,28]

### 4.2 Advanced reduction processes (ARPs)

Advanced reduction processes generate highly reducing species, particularly hydrated electrons, capable of initiating reductive cleavage of carbon–fluorine bonds in selected PFAS. UV/sulfite systems are commonly studied, with other electron-donor, photocatalytic or radiolytic approaches under development. Reduction can be advantageous for compounds that resist oxidative pathways, and some systems have shown substantial defluorination under controlled conditions. [4,21]

The main limitations include photon or energy demand, donor consumption, oxygen scavenging of reducing species, sensitivity to natural organic matter and salts, and the need to manage residual chemicals. Because treatment can be most practical for low-flow, concentrated streams, ARPs may be paired with ion exchange, foam fractionation or membrane concentration. The field needs more comparative studies under real-water conditions and transparent energy accounting that includes UV, chemical preparation and residual treatment. [4,21]

### 4.3 Non-thermal plasma

Non-thermal plasma generates energetic electrons, reactive oxygen and nitrogen species, ultraviolet emission, electric fields and interfacial phenomena without necessarily heating the bulk liquid to high temperatures. PFAS can accumulate at gas–liquid interfaces, which may improve contact with plasma-generated reactive species. Plasma reactors have attracted interest for treatment of PFAS-containing concentrates and for coupling with gas, foam or bubble-based processes. [1,2,11,12,16,30]

Potential advantages include rapid treatment, modular reactor designs and the possibility of targeting interfacial PFAS. Challenges include energy efficiency, gas transfer, reactor geometry, electrode erosion, scaling, matrix effects and incomplete fluorine recovery. A plasma system should be evaluated using electrical energy per order of removal and, preferably, energy per mass of fluorine mineralized, with accounting for off-gas and secondary products. [1,2,11,12,30]

### 4.4 Sono chemical treatment

High-frequency ultrasound produces acoustic cavitation: bubbles form, grow and collapse, creating localized extreme conditions and reactive species. PFAS can be enriched at cavitation interfaces, and degradation may proceed through interfacial reactions and radical pathways. Sonolysis has demonstrated activity against several PFAS and is often investigated for concentrated solutions or as part of hybrid treatment. [19,21]

The principal barriers to deployment are energy demand, acoustic-field nonuniformity, scale-up of cavitation, reactor throughput, temperature control and sensitivity to dissolved gases and matrix constituents. The energy cost of sonication can be high for dilute water, strengthening the case for preconcentration and process intensification. Large-scale reactors must demonstrate reproducible cavitation distribution and sustained operation rather than extrapolating from small laboratory vessels. [19,21]

### 4.5 Photocatalysis and photo electrocatalysis

Photocatalysts absorb photons to generate electron–hole pairs. Charge carriers may participate in direct oxidation or reduction, while surface-bound species and reactive oxygen species contribute to transformation. Materials explored include titanium dioxide, modified semiconductors, carbon-based materials, metal oxides, heterojunctions and defect-engineered catalysts. Adsorption and interfacial charge transfer are often decisive because PFAS are difficult to attack in the bulk solution. [5,12,21]

Photocatalysis offers the possibility of solar-driven treatment, but practical efficiency is constrained by light absorption, charge recombination, catalyst recovery, fouling, competing ions and the limited reactivity of some generated species toward fully fluorinated compounds. Photoelectrocatalysis may improve charge separation and enable controlled electrode reactions, yet reactor design, light penetration and energy accounting remain critical. Research should prioritize visible-light response, immobilized catalysts, realistic matrices, catalyst stability and fluorine mass balance. [5,12,21]

### 4.6 Supercritical water oxidation (SCWO) and hydrothermal processes

Supercritical water oxidation operates above water's critical point, where water exhibits properties that support rapid oxidation of organic compounds in the presence of an oxidant. The process can potentially destroy PFAS in concentrated aqueous wastes and may achieve high conversion under suitable conditions. Hydrothermal and related high-temperature, high-pressure approaches are also being investigated. [9,11,13,16,30]

SCWO is potentially powerful but has substantial engineering requirements: high pressure and temperature, corrosion-resistant materials, salt precipitation and plugging, heat recovery, oxidant demand, and safe handling of feed and products. Fluoride-containing products can create corrosion and materials challenges. Energy efficiency depends strongly on feed concentration, heat integration, reactor design and the ability to recover useful energy. The technology is therefore more plausibly applied to concentrated residual streams than to large volumes of dilute water. [9,11,13,16,30]

### 4.7 Thermal, hydrothermal and mechanochemical routes

Thermal approaches include incineration, pyrolysis, thermal desorption followed by destruction, microwave-assisted treatment and hydrothermal processing. High temperatures can break down PFAS, but removal from a matrix does not establish complete mineralization. Products of incomplete destruction (PIDs), including volatile fluorinated compounds, may form if temperature, residence time, mixing and oxygen availability are inadequate. [9,13,16,30]. The Comparative overview of PFAS destructive technologies and Qualitative matching of PFAS destructive technologies to treatment contexts has shown in tables 2 and 3.

Thermal technologies require rigorous off-gas treatment, fluoride capture, corrosion control and product monitoring. Mechanochemical approaches use mechanical energy, often with reactive additives, to induce chemical transformation in solids or concentrated residues. They may avoid large water volumes and could be relevant to soils, adsorbents or waste media, but energy consumption, reagent use, reactor throughput and evidence of complete fluorine conversion need further evaluation. [9,13,16,30]. Mechanistic comparison of electrochemical oxidation, advanced reduction, plasma, sonolysis, photocatalysis, supercritical water oxidation and thermal treatment has shown in Figure 2.

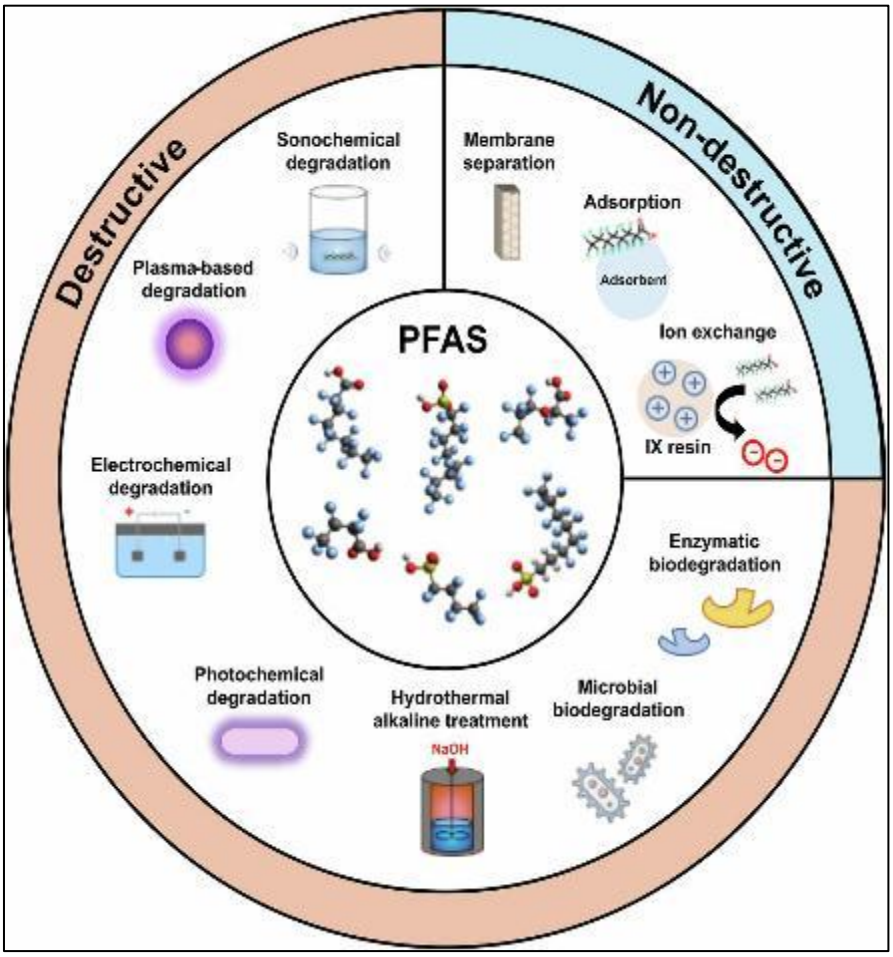


**Figure 2: Mechanistic comparison of electrochemical oxidation, advanced reduction, plasma, sonolysis, photocatalysis, supercritical water oxidation and thermal treatment.**

**Table 2: Comparative overview of PFAS destructive technologies [1–4,9,11,16,19–21,27–30]**

| Technology | Primary mechanism | Potential strengths | Main limitations | Scale-up focus |
|---|---|---|---|---|
| Electrochemical oxidation | Direct electron transfer / reactive species at electrodes | Modular; suitable for concentrates; controllable | Electrode cost, fouling, competing reactions, energy | Electrode durability, mass transfer, continuous flow |
| Advanced reduction | Hydrated electrons and reductive pathways | Can target resistant PFAS; potential high defluorination | UV/energy and donor demand; matrix scavenging | Low-flow concentrate treatment, donor recovery |
| Non-thermal plasma | Energetic electrons, radicals and interface reactions | Rapid; interfacial enrichment; modular potential | Electrical efficiency, reactor scale, by-products | Gas transfer, energy metrics, off-gas controls |
| Sonolysis | Acoustic cavitation and interfacial reactions | Broad applicability; useful hybrid option | High energy demand; scale-up difficulty | Cavitation uniformity, concentrated feed |

| | | | | |
|---|---|---|---|---|
| Photocatalysis / PEC | Photogenerated charges and surface reactions | Potential solar input; catalyst engineering | Charge recombination, light penetration, fouling | Immobilized catalysts, real matrices, stability |
| SCWO / hydrothermal | High-temperature-pressure oxidation | Potential rapid destruction of concentrated waste | Pressure, corrosion, salts, heat demand | Heat recovery, materials, plugging prevention |
| Thermal / pyrolysis | Thermal decomposition | Applicable to solids and residuals | PIDs, off-gas, high temperatures | Verified mineralization, emissions control |
| Mechanochemical | Mechanical activation with reactive additives | Potential for solids and spent media | Energy, reagent and throughput uncertainty | Continuous processing, mass balance |

**Table 3: Qualitative matching of PFAS destructive technologies to treatment contexts [1,2,8,11,16,22–24]**

| **Treatment context** | **Potentially relevant technology families** | **Key design and verification considerations** |
|---|---|---|
| Dilute water after selective concentration | Electrochemical oxidation; plasma; sonolysis; photocatalysis/photoelectrocatalysis; advanced reduction | Concentration factor; residual composition; energy per fluorine destroyed; product and fluoride mass balance |
| PFAS-rich brines, foams, or regeneration liquids | Electrochemical oxidation; plasma; SCWO/hydrothermal; selected thermal routes | Salt, corrosion and plugging risks; reagent demand; off-gas and secondary-residual management |
| Spent sorbents and solid residues | Thermal treatment; mechanochemical approaches; desorption followed by destruction | Volatile products; fluoride capture; reagent use; proof of destruction; secondary waste |
| Mixed PFAS and precursor-containing streams | Hybrid concentration–destruction trains; combinations selected for stream profile | Targeted/non-target analysis; precursor conversion; short-chain PFAS monitoring; toxicity screening |

## 5 CONCENTRATE-THEN-DESTROY TREATMENT TRAINS

A practical remediation strategy may combine separation and destruction. The first stage—activated carbon, ion exchange, foam fractionation or membrane concentration—reduces the volume requiring intensive treatment. The second stage applies a destructive process selected for the residual's composition and concentration. This configuration can improve energy efficiency because the destruction unit treats a smaller volume with a higher PFAS loading. [1,2,8,22–24]

The concentrate is not automatically benign: spent media, brines, foams and regeneration liquids may contain mixtures of PFAS and co-contaminants. Treatment-train design should consider PFAS recovery or concentration factor, residual composition, destruction capacity, energy use, transport, secondary waste and overall fluorine balance. The most appropriate train may differ for drinking-water treatment, landfill leachate, industrial wastewater, firefighting-foam impacts, groundwater and contaminated soil. [1,2,8,22–24]. The Concentrate-then-destroy treatment train showing influent characterization, selective concentration, destructive reactor, fluoride/product monitoring and residual management has shown in Figure 3.




**Figure 3: Concentrate-then-destroy treatment train showing influent characterization, selective concentration, destructive reactor, fluoride/product monitoring and residual management.**

## 6 ENERGY EFFICIENCY, SCALABILITY AND TECHNOLOGY READINESS

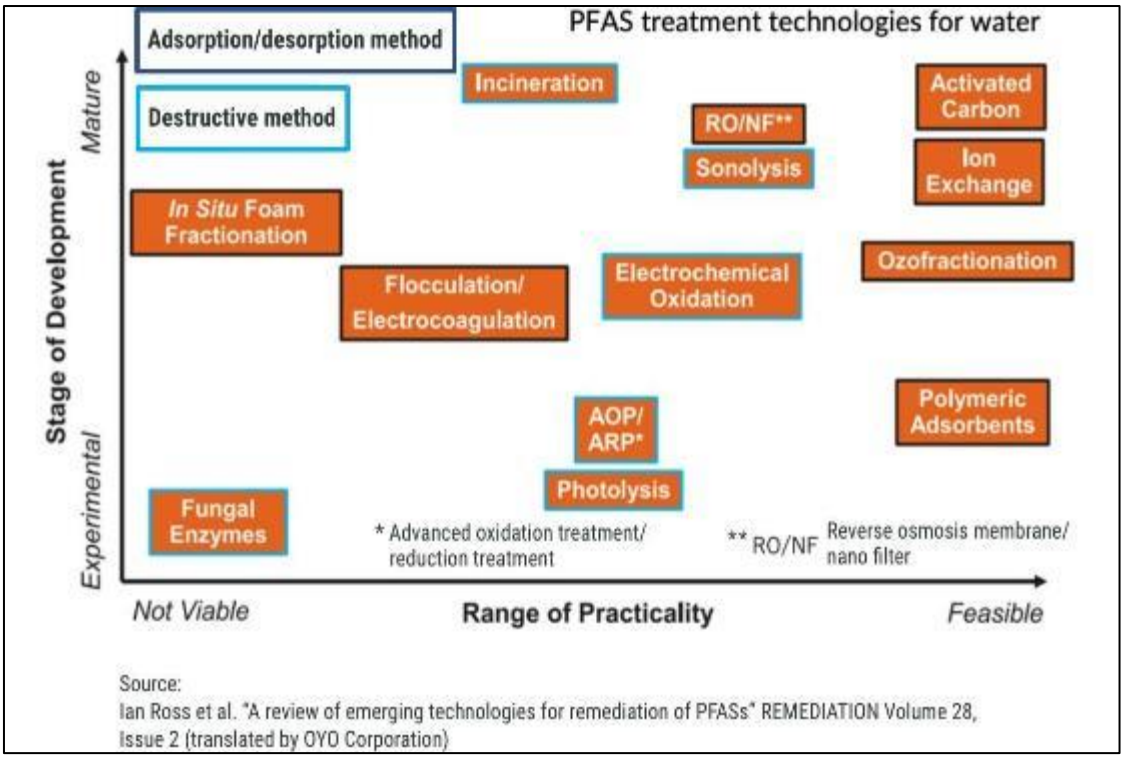


**Figure 4: Proposed multi-criteria decision framework for selecting PFAS destruction technologies based on matrix, concentration, PFAS profile, energy, by-products, cost and technology readiness.**

Energy comparisons are difficult because studies report different units, initial concentrations, target compounds, matrices, reactor scales and endpoints. Energy per volume treated can favor high-throughput processes even when destruction is incomplete; energy per mass PFAS removed can be misleading when removal reflects adsorption; and energy per mass fluorine mineralized is more chemically meaningful but is not yet routinely reported. A standardized set of metrics should include electrical energy per order (EE/O), kWh per cubic metre, kWh per gram of PFAS, kWh per gram of fluorine released as fluoride, chemical consumption, and life-cycle greenhouse-gas emissions. Proposed multi-

criteria decision framework for selecting PFAS destruction technologies based on matrix, concentration, PFAS profile, energy, by-products, cost and technology readiness has shown in Figure 4. [8,11,12,16,24]. Proposed multi-criteria decision framework for selecting PFAS destruction technologies based on matrix, concentration, PFAS profile, energy, by-products, cost and technology readiness has shown in Figure 4.

## 7 BY-PRODUCTS, ENVIRONMENTAL SAFETY AND VERIFICATION

Incomplete transformation can produce shorter-chain PFAS that may be more mobile and difficult to capture, as well as other fluorinated intermediates. Thermal systems may generate volatile products, while electrochemical and plasma systems can form oxidants or other matrix-derived species. Residual streams may contain elevated fluoride, salts, metals, spent catalysts or unreacted chemicals. Environmental safety therefore requires evaluation of treated water, off-gas, sludge, spent media and concentrates. A minimum verification package should combine targeted PFAS analysis, precursor or total-organic-fluorine methods where feasible, fluoride measurement, transformation-product analysis, carbon balance and toxicity screening. Analytical blanks, recovery controls, replicate measurements and treatment-specific sampling are essential; claims of complete destruction should be reserved for studies with adequate mass-balance evidence and transparent uncertainty. [9,11,13,21,26,30]

## 8 CONCLUSIONS

PFAS remediation is moving from the goal of aqueous removal toward verified chemical destruction. Electrochemical oxidation, advanced reduction, non-thermal plasma, sonolysis, photocatalysis, supercritical water oxidation, and thermal, hydrothermal or mechanochemical treatment each offer potential pathways, but performance depends on PFAS structure, matrix composition, reactor conditions and the endpoint used to define success. No single technology currently combines universal applicability, low energy demand, complete mineralization, low cost and demonstrated full-scale reliability. A scalable strategy is likely to combine selective concentration with a destructive process matched to the residual stream. Progress will require standardized energy metrics, rigorous fluorine and carbon mass balances, transformation-product identification, toxicity evaluation and sustained pilot demonstrations. The central benchmark should be demonstrable reduction of organic fluorine and safe management of all products and residuals not simply disappearance of the parent PFAS.

## STATEMENTS ON COMPLIANCE WITH ETHICAL STANDARDS

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### *Disclosure of conflict of interest*

The authors declare no conflicts of interest.

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