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Electrochemical degradation of per- and poly-fluoroalkyl substances in the presence of natural organic matter

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Abstract

Per- and poly-fluoroalkyl substances (PFAS), a contentious group of highly fluorinated, persistent, and potentially toxic chemicals, have been associated with human health risks. Currently, treatment processes that destroy PFAS are challenged by transforming these contaminants into additional toxic substances that may have unknown impacts on human health and the environment. Electrochemical oxidation (EO) is a promising method for scissoring long-chain PFAS, especially in the presence of natural organic matter (NOM), which interferes with most other treatment approaches used to degrade PFAS. The EO method can break the long-chain PFAS compound into short-chain analogs. The underlying mechanisms that govern the degradation of PFAS by electrochemical processes are presented in this review. The state-of-the-art anode and cathode materials used in electrochemical cells for PFAS degradation are overviewed. Furthermore, the reactor design to achieve high PFAS destruction is discussed. The challenge of treating PFAS in water containing NOM is elucidated, followed by EO implementation to minimize the influence of NOM on PFAS degradation. Finally, perspectives related to maximizing the readiness of EO technology and optimizing process parameters for the degradation of PFAS are briefly discussed.

Keywords

Water treatment; Electrochemical oxidation; Natural organic matter; Per-fluoroalkyl substances; Boron-doped diamond electrode

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Declaration of Competing Interest

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

1. Introduction

The ever-increasing volumes of wastewater generated by industries and the stringent regulatory policies governing its disposal have accelerated the need to develop innovative technologies to treat them efficiently and economically. Per- and poly-fluoroalkyl substances (collectively, PFAS) are anthropogenic compounds extensively employed in various industrial and commercial applications and pose potential environmental and health risks [1–3]. The six most studied PFAS compounds are perfluorooctane sulfonic acid (PFOS); perfluorooctanoic acid (PFOA); perfluorodecanoic acid (PFDA); perfluorononanoic acid (PFNA); perfluorohexane sulfonic acid (PFHxS); and perfluoroheptanoic acid (PFHpA). These 'forever chemicals' usually do not degrade naturally; they steadily cycle through and accumulate in the environment. Certain PFAS are also bioaccumulative [4], and several PFAS have been found at detectable levels in human blood [5]. PFAS toxicity is currently being studied, and there is sufficient evidence to inspire efforts to control environmental release and human exposure [6–8]. Also, the varying quantity and quality of organic matter (OM) significantly influence the selection, design, and operation of water treatment processes.

There are numerous barriers when attempting to treat PFAS-laden wastewater, particularly in the presence of other pollutants. Natural organic matter (NOM) is ubiquitous in the different compartments of the aquatic environment [1]. The unique structure of PFAS combines a hydrophilic ionic head ($-\text{COOH}$, $-\text{SO}_3\text{H}$) with a fluorinated carbon tail, giving them biphasic or surfactant properties [1,9]. NOM may engage in electrostatic or hydrophobic interactions with PFAS [1]. Organic matter, primarily composed of anionic species, can produce repulsive electrostatic interactions when it adheres to materials (e.g., adsorbents) [10]. Reduced long-chain retention caused by a more hydrophilic NOM emphasizes the significance of electrostatic and hydrophobic forces as well as the range that can be achieved depending on the overall net charge and PFAS hydrophobicity/hydrophilicity [11]. Through a hydrophobic interaction between the perfluoroalkyl tail and NOM adsorbed on the adsorbent surface, NOM may also promote the adsorption of PFAS [12]. It is currently unclear how these effects interact and which is dominant. When PFAS are released into the environment, the chemical characteristics that make them useful from an industrial standpoint also make them mobile and recalcitrant [13].

Conventional wastewater treatment methods (i.e., activated sludge) have proved ineffective in the biodegradation of PFAS [1,14–18]. It is attributed to the powerful and stable C-F bond (bond dissociation energy > 500 kJ/mol) [19,20] and the high electronegativity of fluorine in those compounds [21]. PFAS require specialized enzymes for their degradation. The microorganisms in activated sludge treatment systems are typically not equipped with the specific enzymes necessary to break down these compounds. Also, PFAS can inhibit the growth and activity of microorganisms responsible for biodegradation in conventional treatment processes. However, under harsh treatment conditions—high temperature and high pressure—PFAS can be efficiently degraded [22,23]. Most technologies utilize robust oxidizing species such as hydroxyl radicals ($\cdot\text{OH}$) $E^0 = 1.8\text{--}2.7$ V vs. normal hydrogen electron (NHE), semiconductor holes, sulfate radical ($\text{SO}_4^{\cdot-}$) $E^0 = \sim 2.4$ V vs. NHE, and reductive species like hydrated electrons (e_{aq}^-) $E^0 = \sim -2.9$ V vs. NHE [24]. The $\cdot\text{OH}$ reacts

fast with PFOA with rate constants (k) in the order of 10^8 - $10^{10} \text{ M}^{-1}\text{s}^{-1}$, while $\text{SO}_4^{\bullet -}$ reacts slowly, $k \approx 10^4 \text{ M}^{-1}\text{s}^{-1}$ [25,26]. It is known that $\bullet\text{OH}$ radical generated from conventional advanced oxidation processes has a limited capacity to break down PFAS [27]. During the decomposition processes, toxic byproducts may be formed, and it is difficult to achieve complete mineralization and defluorination of PFAS. More importantly, the presence of organic matter reduces the overall efficiency of most processes. The underlying problem in the entire defluorination process (completely transforming all the C-F bonds into F^- ions) is still debatable, particularly in the presence of organic matter. Therefore, there is still a need to develop an environmentally friendly and cost-effective method to effectively eliminate PFAS in the presence of organic matter to decrease their harmful impact.

Environmental Protection Agency (EPA) health advisory levels of PFOA and PFOS in drinking water previously established at 70 parts per trillion (ppt) have been lowered to 0.004 ppt and 0.02 ppt, respectively [28,29]. It has led to a global quest for effective PFAS degradation technologies. Various technologies have been proposed to remove PFAS from the environment, but complete degradation remains elusive. Advanced electrochemical [30], photochemical [31], plasma [32], electron beam irradiation [33,34], and chemical oxidation [35] techniques are suggested for PFAS destruction. Ongoing research is understanding the effectiveness of these techniques in creating a breakthrough in PFAS degradation.

There are limitations in both oxidative and reductive PFAS degradation. For example, fluorine can be effectively removed by e_{aq}^- via H/F exchange, but the chemical stability of the resulting fluorotelomer carboxylic acids (FTCAs, $\text{C}_n\text{F}_{2n+1}(\text{CH}_2)_m\text{-COO}^-$) increases dramatically with the further exchange of H/F [24]. On the other hand, while the oxidation process using h^+ , $\bullet\text{OH}$, and $\text{SO}_4^{\bullet -}$ can convert the PFAS of long-chain carboxylic acid into small chains [36,37], the strong shielding effect from the dense electron cloud surrounding the fluorine atoms significantly hinders defluorination. Herein, we present a comprehensive review of the electrochemical oxidation (EO) of PFAS in real water matrices. The content of this review is timely because it sheds light on the recent progress made in electrochemical strategies for PFAS degradation. The study delves into various aspects of the electrochemical approach, such as the degradation mechanism employed and the choice of electrode material, which are crucial factors in achieving efficient PFAS degradation. The main objective of this review is to draw attention to how NOM interferes with the EO process. By looking at these factors, we seek to understand better how to decompose PFAS utilizing the EO approach successfully. Finally, to significantly increase the destruction efficiency and result in complete PFAS degradation, we recommend the simultaneous participation or integrated oxidation and reduction process.

2. Advanced oxidation processes (AOPs)

Advanced oxidation processes (AOPs) have received increasing attention for wastewater treatment, particularly in the presence of NOM. NOM plays the dual role of enhancement and inhibition in AOPs [12]. AOPs use $\bullet\text{OH}$ to attack persistent organic pollutants and degrade them into smaller components or inorganic ions/molecules [38]. In some instances, NOM can enhance the removal of micropollutants during AOPs by complexing with PFAS via hydrophobic interactions [39,40]. Because of the larger diffusive flux of high-

concentration NOM to the electrode in the presence of PFOS-NOM hydrophobic contacts, the transport of PFOS to the site of oxidation at the electrode surface may be enhanced [39]. In contrast, NOM can also exhibit inhibitory effects on AOPs and organic pollutant removal [40]. This inhibition is primarily attributed to the competition for the available radicals between NOM and PFAS [41,42]. Due to their high concentrations in natural waters and complex structure, NOM compounds can readily react with the generated radicals, leading to their consumption [42]. This competition for radicals reduces the available reactive species crucial for micropollutant degradation. Consequently, the presence of NOM can hinder the removal efficiency of AOPs by decreasing the contact time between radicals and target micropollutants.

The production of aggressive oxidant ($\bullet\text{OH}$) radical requires a catalyst to react with ozone (O_3), hydrogen peroxide (H_2O_2), or UV light. In addition, $\text{SO}_4^{\bullet-}$ -based AOPs have been proven to possess preferable oxidation ability due to the high electrophilic property ($+2.437 \pm 0.019 \text{ V vs. NHE, } 25 \text{ }^\circ\text{C}$) and longer lifetime [43]. For example, Waclawek et al. reported PFOA degradation with slow reaction kinetics $\approx 10^4 \text{ M}^{-1} \text{ s}^{-1}$ [44]. The process requirements (e.g., chemicals, UV, and catalysis) to generate radicals mean harsh conditions and low environmental compatibility. However, electrochemical processes may have advantages in this aspect, as radicals can be generated in situ via electrochemical reactions.

The primary benefit of electrochemical processes is the simultaneous occurrence of numerous electrochemical reactions at anodes and cathodes (Fig. 1). The oxidation/reduction process can be driven by electricity rather than by chemicals to produce radicals. The lower consumption of chemicals, low energy demand (e.g., an opportunity to be integrated with renewable energy sources, including solar or wind power and fuel cells), operation in ambient conditions, and ability to be in a mobile unit makes the process more adaptable, sustainable, and environmentally friendly. Additionally, the electrochemical process can directly oxidize the targeted contaminants or produce other radicals besides $\bullet\text{OH}$ (e.g., superoxide radicals ($\bullet\text{O}_2^-$) and hydroperoxyl radicals ($\bullet\text{HO}_2$)), which can potentially degrade the persistent contaminants that cannot be degraded by $\bullet\text{HO}$ alone due to the stable fluoro-carbon skeleton [45]. Electrochemical treatment has shown removal rates of $>99\%$ for long-chain PFAS [9]. The processes also have the advantage of oxidizing most organic matter and completely mineralizing them to generate carbon dioxide and water [46]. The *in-situ* generated $\bullet\text{OH}$ is adsorbed by the metal oxide electrode in the oxygen potential zone forming ($\text{MO}_x(\bullet\text{OH})$) to oxidize the targeted pollutants.

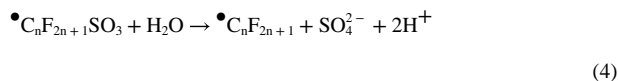
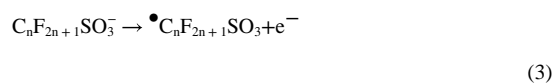
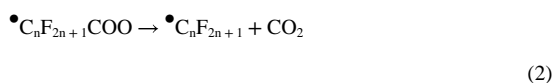
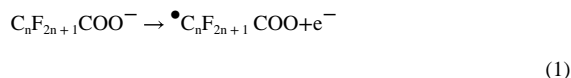
Electrochemical processes have some limitations, including the possibility of hazardous byproducts (e.g., hydrogen fluoride (HF), perchlorate, and halogenated organics), [47,48] the partial elimination of certain PFAS, efficiency loss owing to mineral contamination build-up on the anode, high cost of electrodes, and possible volatilization of contaminants (mainly HF vapor, which is highly corrosive) [48]. Even though long-chain PFAS have shown to be highly effective at being removed, short-chain PFAS are typically harder for the EO method to degrade. Due to the conversion of precursors, the concentration of short-chain PFAS may even increase after treatment. Despite such challenges, EO can be a promising 'green' technology for PFAS destruction as it is less energy intensive compared

to thermal incineration (>1100 °C) with a possibility of converting hazardous byproducts to high value-added compounds (contributing to the circular economy) [49]. Additionally, compared to single-solute PFAS systems, this technique can effectively degrade multi-solute solutions containing a mixture of PFAS [50]. Other notable benefits include the dual function of PFAS degradation and organic matter removal.

In the following sections, we present the mechanisms that govern the electrochemical processes and the role of electrode materials and reactor design in the degradation of PFAS in water.

3. Electrochemical oxidation (EO) of PFAS

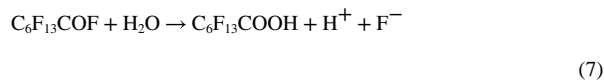
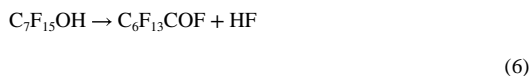
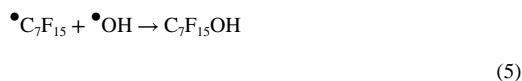
For EO, the applied electrical current densities are in the range of 20–350 A/m² to optimize the kinetics rates of PFAS degradation [51]. Results showed better removal efficiency at 50 mA/cm² compared to 10 and 20 mA/cm², and the removal efficiencies of PFBA and perfluoroalkyl acids (PFAA) were > 95% and 99%, respectively, within 8 h of treating synthetic PFAS samples [52]. Several factors, including electrode properties and surface area, initial PFAS concentration, coexisting contaminants, efficiency target, and voltage, directly influenced the contact time needed to treat PFAS. The degradation of PFAS on the surface of the electrodes was closely related to electron transfer reactions [53]. PFAS can be decomposed via direct and indirect oxidation. In the direct oxidation pathway (also known as anodic oxidation), an electron is transferred from the PFAS compound to the anode. In contrast, the indirect route involves electrochemically created, powerful oxidants—hydroxyl radicals. The following chemical reactions (Eqs 1–4) briefly describe the PFAS degradation mechanism involved in anodes.



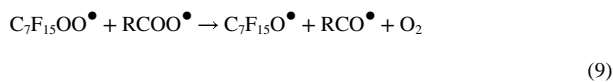
An electron is transported from the head group of PFAS to the anode under the influence of an electric field to create PFAS radicals (Eq (1), which are then decomposed into $\bullet\text{C}_n\text{F}_{2n+1}$

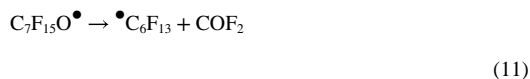
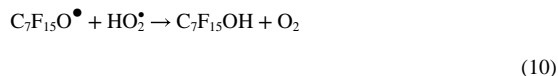
(Eq (2)). The formed radical $\bullet C_n F_{2n+1}$ would combine with $\bullet OH$ to undergo the subsequent step-by-step removal of $-CF_2-$ [54,55]. PFAS are expected to degrade through C–C chain cleavage rather than the C-F bond, especially the CF_2-COOH bond in PFOA and the CF_2-SO_3H bond in PFOS, given the bond strength/energy. In other words, defluorination is more challenging than degradation of the C–C chain via oxidation unless the catalysis is selective to the C-F bond.

The electrochemical degradation of PFOA involves two routes. The first route converts PFOA to perfluoroheptanoic acid (PFHpA having a lesser $-CF_2-$ than PFOA) [56,57]. The steps involved are given in Eqs 5–7.

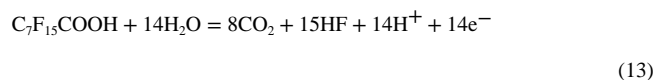


The degradation mechanism is initiated by abundant $\bullet OH$, resulting in strong chemical reactivity in the electrolysis process [58]. Then, the elimination of HF from $C_7 F_{15} OH$ to produce acyl fluoride $C_6 F_{13} COF$ takes place. In the final step, $C_6 F_{13} COF$ reacts with $H_2 O$ through hydrolysis to yield $C_6 F_{13} COOH$ [57]. However, another route may also be possible in which the $\bullet C_7 F_{15}$ radicals react with oxygen from water electrolysis to create the $C_7 F_{15} OO\bullet$ radicals (Eq (8)). Subsequently, the $C_7 F_{15} OO\bullet$ radical would combine with another $RCOO\bullet$ radical (Eq (9)), forming a $C_7 F_{15} O\bullet$ radical [57]. The $C_7 F_{15} O\bullet$ radical has two potential reaction routes: (i) $C_7 F_{15} OH\bullet$ formation as a result of a reaction with $HO_2\bullet$ and (ii) further decomposition to form perfluoroalkyl radicals ($\bullet C_6 F_{13}$) and carbonyl fluoride (COF_2). In the final step, the produced COF_2 decomposes entirely to CO_2 and HF (Eqs 10–12).

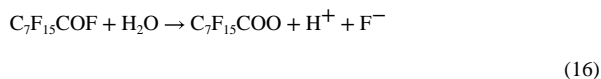
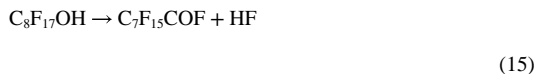
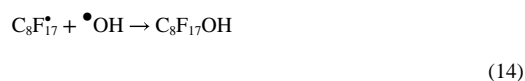




The complete mineralization of PFOA to CO_2 , HF, and H^+ involves 14 electrons, where the initial step must undergo a series of subsequent steps (Eq (13) [49]). A schematic of the mechanisms that govern PFAS degradation is provided in Fig. 2. The formed HF and the change in pH can affect EO.

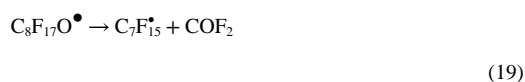
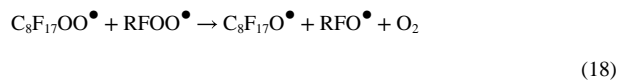


The electrochemical decomposition mechanisms of PFOS also follow two pathways. One decomposition pathway involves $\text{C}_8\text{F}_{17}\text{SO}_3^-$ transferring an electron from its head group to the anode material to be converted into $\text{C}_8\text{F}_{17}^\bullet$ [57]. The subsequent electrolysis of $\text{C}_8\text{F}_{17}^\bullet$ by H_2O produces $\text{C}_8\text{F}_{17}\text{OH}$, which quickly undergoes hydrolysis to form $\text{C}_7\text{F}_{15}\text{COO}^-$ [59]. Next, $\text{C}_7\text{F}_{15}\text{COO}^-$ undergoes a stepwise decarboxylation cycle, eliminating the CF_2 units until complete mineralization occurs (Eqs 14–16).



The first step is similar to the previously described mechanism. With a considerable amount of oxygen produced by water hydrolysis, the formed $\text{C}_8\text{F}_{17}^\bullet$ can undergo a reaction that transforms it into $\text{C}_8\text{F}_{17}\text{OO}^\bullet$ (Eq17), which would then combine with RFOO^\bullet to create

$C_8F_{17}O^\bullet$ (Eq (18) [56]. Due to the instability, $C_8F_{17}O^\bullet$ then breaks down into $C_7F_{15}^\bullet$ and COF_2 (Eq19). The formed COF_2 later reacts with water to produce CO_2 and HF. The reprocessing cycle allows for the breakdown of PFOS into CO_2 and F^- .



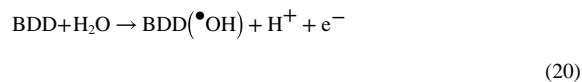
4. Electrode materials and reactor design

4.1. Anode material

Electrodes for electrochemical oxidation/reduction play a significant role in PFAS degradation. Anode material determines whether the system can operate stably and efficiently. For anodes with high oxidation power, a high current efficiency for organic oxidation and a low electrochemical activity for oxygen evolution are typically observed [60]. This is due to the weak interactions between these anodes' electrodes and hydroxyl radicals [60]. The direct electron transfer at the anode typically restricts the rate of PFAS oxidation electrochemically (i.e., the rate-limiting step for PFAS oxidation on an electrode). The resulting perfluoroalkyl radical can then react with $^\bullet OH$, O_2 , or H_2O to degrade the one-carbon shorter perfluoroheptanecarboxylate by severing the head group ($-COOH$ vs. $-SO_3H$) (i.e., perfluoro alkyl carbonate). The newly formed carboxylate, one carbon shorter, then undergoes the same decomposition as the original PFOA, which converts the carboxylic acid head to carbon dioxide, the fluorine atoms to hydrogen fluoride, and the CF_2 to another carboxylic acid group in that order. The electrode materials mentioned in the literature include platinum (Pt), carbon or graphite (C), iridium dioxide (IrO_2), ruthenium dioxide (RUO_2), tin dioxide (SnO_2), boron-doped diamond (BDD), lead dioxide ($PbCO_2$), Ti_4O_7 (Ebonex), as well as TiO_2 nanotube array. These electrode materials can boost the productivity of radicals and inhibit the emission of O_2 . However, BDD is a more promising anode material to carry out EO for the degradation of PFAS.

BDD anodes offer a 'chemical-free' treatment for PFAS-contaminated water by effectively initiating the electron removal from PFOA and PFOS-like ionic heads. The reason for choosing BDD electrodes as anode material compared to other anodes is the greater overpotential required to oxidize water to oxygen [60,61]. For anodes such as platinum, gold, or glassy carbon, the oxygen overpotential falls within the 1.7 to 2.2 V range [61]. This enables the boron-doped material to act as an anode with better efficacy. The surface of the

BDD electrode can produce enough concentration of quasi-free state hydroxyl radical ($\bullet\text{OH}$), and its high redox potential can oxidize almost all refractory pollutants to CO_2 , H_2O , and inorganic ions without selectivity (Eq (20)).



Other advantages of BDDs include the ability to generate $\bullet\text{OH}$ at a low electrical current, stability at high current densities [62], chemical inertness, long life span, mechanical durability, and less fouling tendency compared to other anodes. In a bench-scale laboratory experiment, BDD was used as the electrode material, and it was found that under ideal circumstances, the degradation efficiency of PFAS was over 90% [63]. This study also showed that current density and treatment time are crucial to achieving the optimum degradation results. Due to cost issues (approximately $\$7125/\text{m}^2$) [64,65], the BDD anode is often substituted with other anode materials like mixed metal oxide (MMO)— SnO_2 , MnO_2 , and PbO_2 [66]. MMOs are considered good alternatives but aren't commercialized due to their short life span and metal leaching issues [67]. The potential surface damage to the MMO electrode caused by fluorination is also a problem. However, F^- doping may sometimes prove beneficial in the degradation process. For instance, it was found that PbO_2 doped with F^- inhibited O_2 emission and expedited oxidation, improving the degradation efficiency [68]. The reason is that incorporating F^- into the bulk structure reduces the extent of adsorbed water at $\alpha\text{-PbO}_2$ or $\beta\text{-PbO}_2$ [69]. Similarly, SnO_2 doped with F^- has been shown to be promising for highly effective PFOA wastewater treatment [70]. The Magneli-phase (Ti_4O_7) has recently gained popularity as advantageous electrode material due to its superior electrical activity, conductivity (1000 S/cm), chemical stability, and cost-effectiveness [71,72].

Various other strategies are also developed to produce better anode material for the efficient destruction of PFAS. An effective Ti_4O_7 electrode loaded with amorphous Pd clusters has been developed [72], outperforming Ti_4O_7 electrodes loaded with crystalline Pd particles, which have been widely considered as a benchmark to enable the electrode's catalytic function. This can be explained by the enhanced electron transfer through predominate Pd-O bonds in an amorphous Pd-loaded catalyst. These amorphous Pd clusters were distinguished by their noncrystalline, disordered arrangement of Pd single atoms in close proximity. They also showed that the anodic PFOA oxidation process does not involve any radical formation, which is particularly advantageous for electrocatalytic systems in the water treatment process [72]. This may minimize the quenching of radical species by background species like NOM and subsequent decrease in contaminant removal. Few other techniques (e.g., defect engineering (by doping)) have the potential to improve the catalytic activity and stability significantly by modifying the surface properties and electronic structures [73]. In a different study, the PFOS oxidation rate increased 2.4 times when 3 at. % of Ce^{3+} dopant was added to the Ti_4O_7 electrode [73]. The introduction of a minor amount (0.1–2.0% wt%) of carbon materials to the Ti_4O_7 electrode surface create a heterojunction structure which could significantly enhance the interfacial electron-transfer process because the presence of

–C–O(H) on the carbon material surface decreases the electron-transfer resistance [74]. The presence of 0.1 wt% of carbon content resulted in a 13-fold increase of the oxalic oxidation kinetics compared to those of the pure Ti_4O_7 electrode. Reactive sites of heterogeneous catalysts usually lie on the surface and subsurface, which allow the improvement of the catalytic property via engineering the surface atoms [75]. Sb-doped SnO_2 electrodes can also be an appealing electrode material for the anodic oxidation of organic pollutants like PFOA because they have good conductivity and a high overpotential for oxygen evolution of about 1.9 V vs. SHE (i.e., 600 mV higher than Pt). An additional approach is creating 3D porous anodic material, such as BDD, that can be an alternative to the conventional 2D-BDD anode. The reason for choosing 3D anodic materials is their high electrochemical active surface area (ECSA) and higher mass transfer coefficient (PFOA towards PP-BDD is $2.6 \times 10^{-5} \text{ m s}^{-1}$, which is about 6.1 times higher than that of 2D-BDD with $0.42 \times 10^{-5} \text{ m s}^{-1}$), thus achieving PFOA degradation even at high applied current, compared to the 2D anode material [76]. Ti powders with > 99.9% purity were chosen as the original material for 3D printing fabrication and used as the electrode substrate for PFOA removal [76]. The different anode materials used in the electrochemical oxidation of PFAS are listed in Table 1.

4.2. Cathode material

In the electrochemical processes to degrade PFAS, consideration should also be given to the cathode and the reactions occurring at the electrode to recover energy by producing and utilizing the electrical currents. As a required component of an electrochemical cell, the cathodic reaction should be designed to maximize the activity and reduce the energy requirement in PFOA electro-oxidation. The four major roles of cathodic material involve i) H_2 evolution, ii) direct reduction of pollutants and intermediates, (iii) metal electrodeposition, and (iv) indirect production of oxidizing agents [80]. O_2 and H_2O_2 are produced during the EO treatment of organic pollutants using a BDD anode [81]. Therefore, it is reasonable to anticipate that these species will undergo cathodic reduction and may even produce $\cdot\text{OH}$, which may aid in global decontamination. The contribution of cathodic hydroxyl radical generation to the enhancement of the electrooxidation process for water treatment is shown in Fig. 3. The defluorination trends are the following: Pt > BDD > Zr > Steel [82]. The hydrogen produced at the surface of the Pt electrode is responsible for the PFOA hydrodefluorination.

As discussed earlier, the direct electron transfer happens at the anode surface, where the PFOA is inert to the hydroxyl radicals. The alcohol is produced after the reaction of $\cdot\text{OH}$ with the adsorbed hydrogen produced by the water electro-reduction at the cathode, releasing 2F^- [36]. After the defluorination process from the cathode, the $\cdot\text{OH}$ can possibly reattack, forming $\text{C}_6\text{F}_{13}\text{COOH}$. It is important to note that the specific reaction steps depend on the cathode material. The feasibility of electrochemical reductive decomposition of PFOA using an Rh/Ni cathode has been reported [83], in which the cathode material was modified by coating Rh^{3+} on Ni foil via an electrodeposition process. Hydrodefluorination occurs using DMF as the solvent (medium with a wide electrochemical window where the target pollutant can migrate to the cathode) at a cathodic potential of -1.25 V , and the Rh coating assisted in the adsorption of PFOA through $\text{Rh}\cdots\text{F}$ interactions and facilitated C-F

bond activation. The C-F bond eventually dissociated and transformed into the C-H bond via H* substitution due to the continuous interaction of cathode-supplied electrons [83].

4.3. Reactor design

The energy consumption for the PFAS degradation process is a significant issue, and the reactor design is an important parameter that can enhance the overall performance. The optimal cell can reduce energy loss and increase efficacy. In the electrochemical destruction of PFAS, the anodic part is given more attention for EO, whereas the energy utilized in the cathodic part is often overlooked. The bubbles in the electrochemical cell have a significant role in enhancing the activity by concentrating the PFAS. It has been shown that the air bubbles produced on the surface of hydrophobic carbonaceous adsorbents have a substantial role in PFOS adsorption. Using cathodic-produced bubbles during the electrochemical reaction can improve PFAS degradation efficiency [84]. By simply changing the orientation of the cathode by 90°, and when the anode is placed at the top (AO/rotation), as shown in Fig. 4, the PFOA gets concentrated by the cathodic-generated hydrogen bubble and moves towards the anode for further oxidation. In this approach, the PFOA concentration near the anode can be increased more than three times, achieving 50% more PFOA removal at 4.5 V vs. standard hydrogen electrode (SHE) in AO/Rotation system. In another work, the extent of PFOS removal by the pristine carbon nanotubes and graphite decreased by 79% and 74%, respectively, after vacuum degassing for 36 h, indicating that air bubbles are primarily responsible for PFOS adsorption [85]. This reveals that designing a better electrochemical reactor could achieve enhanced removal of PFAS degradation with less energy consumption, making this technology economically viable in practical application.

The mass transfer of PFAS from the bulk solution to the anode surface, which only occurs at or near the anode surface, limits EOP degradation [86]. Reactive electrochemical membrane (REM) operation, which improves interphase mass transfer by filtering polluted samples using porous material that serves as both a membrane and anode, was proposed as a solution to the mass transfer constraint [87]. Therefore, even a single water flow through the membrane may help to improve the overall effectiveness of electrochemical oxidation for removing PFAS. The REM system has been examined to degrade PFOS by utilizing a ceramic membrane with a Magneli phase titanium suboxide [88]. The REM reactor was operated at a 40.0 mL/min flow rate with the target pollutant PFOS (2.0 M) and electrolyte Na₂SO₄ (100.0 mM). With different current densities, the change in linear PFOS concentration was investigated. Since there was no application of electric current during the first 40 min, there was no difference in the concentration of PFOS in the permeate, which was the same as in the retentate, indicating only modest adsorption of PFOS onto the membrane electrode. Immediately after applying electric current, the concentration of PFOS in the permeate decreased. During 120 min of current supply, the PFOS concentration remained low, but the elimination increased to 98% when the current density climbed to 4.0 mAcm⁻². After 120 min, the current flow was cut off, and the concentration of PFOS in the permeate recovered to being similar to that of the retentate. These findings demonstrate that electrochemical degradation is the only mechanism by which PFOS was removed from the permeate stream. A batch reactor-based direct electrochemical oxidation method using a titanium suboxide tubular anode was used to compare the performance of the REM system.

PFOS consistently degraded in the batch electrochemical oxidation system, except when the current density was below 0.5 mAcm^{-2} . Similar to the REM system, as the applied current density grew, so did the rate of PFOS degradation in the batch system.

An energy-efficient Magneli phase Ti_4O_7 REM has also been utilized to oxidize PFOA and PFOS [71]. In one run through the REM, these chemicals were removed around 5-log, with residence durations of 11 s at 3.3 V/SHE for PFOA and 3.6 V/SHE for PFOS. From starting concentrations of 4.14 and 5 mg/L, the permeate concentrations of PFOA and PFOS were 86 and 35 ng/L, respectively. At a permeate flux of $720 \text{ L m}^{-2}\text{h}^{-1}$ (residence durations of 3.8 s), the maximum removal rates for PFOS and PFOA were 2436 and $3415 \text{ mol m}^{-2}\text{h}^{-1}$, respectively. Energy requirements (per log removal) were 5.1 and 6.7 kWh m^{-3} , respectively, to remove PFOA and PFOS to levels below detection limits. Interestingly these values are the lowest reported for electrochemical oxidation and roughly an order of magnitude lower than those reported for other technologies (such as ultrasonication, photocatalysis, vacuum ultraviolet photolysis, and microwave-hydrothermal decomposition), showing that electrochemical oxidation is not as efficient as other processes.

The following section will discuss the impact of the co-existence of PFAS and NOM in contaminated groundwater and wastewater on EO performance. We aim to highlight that most lab-tested technologies have been tested with synthetic solutions and tend to perform inefficiently in the natural environment due to the interference of NOMs.

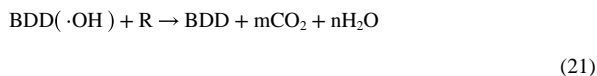
5. Electrochemical treatment in the presence of natural organic matter

One of the primary sources of water supply is surface water, which contains NOM—a mixture of organic matter from biological and terrestrial sources [89]. Humic acid, polysaccharides, proteins, and lipids comprise most of its structure. Additionally, it may be aggregated with contaminants such as antibiotics or pesticides. Since lipids and aliphatic proteins include organic materials or monomers with carboxyl groups, these substances are oxidized by electrochemically produced free radicals to acids with lower molecular weight and are then mineralized to produce CO_2 and H_2O . NOM has the advantage of acting as an electron donor or acceptor with various other redox-active species, mediating reactions between species with varying redox potentials. Due to the extensive coupling of redox-active moieties in NOM via intramolecular conduction, the sample potential sometimes reflects a continuum of electrode response, similar to the NOM redox properties [90]. Also, due to poor contact between the redox-active moieties in NOM and the working electrode surface, conventional electrochemical voltammograms typically produce poor results (with more broad and average features). Advanced techniques like the sequential use of cyclic and square-wave voltammetry (SCV and SWV) can be valuable in interpreting peaks and other features regarding NOM redox processes.

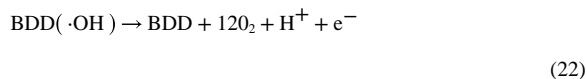
NOM significantly impacts the effectiveness of electrochemical oxidation during wastewater treatment. Therefore, it is crucial to investigate molecules' specific interactions and oxidation reactions in the electrochemical process and which parts of NOM may preferentially react with free radicals in the electrolyte solution [89]. It is feasible to oxidize the specific saturated functional groups of NOM electrochemically. Electro-oxidation of

NOM itself may lead to the formation $\cdot\text{OH}$, indirectly contributing to the degradation of targeted contaminants by participating in secondary reactions and generating additional oxidizing agents. Although many of the unsaturated hydrocarbons in NOM are polycyclic aromatic hydrocarbons, theoretically, unsaturated bonds are more accessible to oxidize than saturated bonds. However, there is a potential for some unstable chemical bonds to be oxidized into intermediate products that are challenging to degrade when complex unsaturated compounds are reduced to small molecules and combined with other free radicals. Previous results show that NOM contains the main functional groups C = C, C = O, and C–O–C [89]. From Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS), the H/C ratio of most molecules in NOM was found to be between 0.3 and 1.8. The H/C ratio of NOM molecules decreases significantly after electrochemical oxidation, primarily between 0.3 and 1.7. It indicates that the extent of NOM unsaturation decreases following the electrochemical oxidation processes. The O/C ratio of most NOM molecules is between 0.05 and 0.8, and the O/C ratio of NOM molecules increases between 0.1 and 0.8, demonstrating that most NOM molecules are oxidized [91]. NOM can form a passivating layer on the electrode surface, which acts as a physical barrier and inhibits the direct contact of contaminants with the electrode. This layer can reduce the electrode's reactivity and impede targeted contaminant oxidation, making the process less effective. NOM can occupy active sites on the electrode, reducing the availability of these sites for the targeted contaminants. This can hinder the electrooxidation process and decrease the overall efficiency of contaminant removal. Overall, it is crucial to investigate the influence of NOM on the mechanism of the electrochemical oxidation process to degrade PFAS. The effect of NOM on the electrochemical degradation of PFAS is depicted in Fig. 5.

A wide variety of electrode materials have often obtained different organic matter efficiencies; however, no comparative benchmark between electrode materials exists for NOM removal. BDD 'nonactive' anode, a promising anode material for PFAS degradation, is also proven excellent for NOM oxidation [93]. The diamonds in BDD electrodes act as magnetic isolating material, facilitating anodic oxidation in electrochemical water treatment. The hydroxyl radical physically adsorbed on the surface site reacts with organics in the following manner (Eq (21) [81,93],



Additionally, oxygen evolution on inactive electrodes occurs between H_2O and $\text{BDD}(\cdot\text{OH})$ to form O_2 (Eq (22) [94].



For cost-effectiveness, BDD can be replaced by MMO (active anode), as suggested earlier, for the degradation of PFAS [20]. Electrooxidation by BDD and MMO electrodes relies heavily on current density, which is proportional to the number of reactions on the electrode

surface. BDD has more active sites than MMO; thus, BDD electrodes showcased a more effective breakdown of NOM [93]. Recently, the EO was used to treat standardized Suwannee River NOM at two different current densities (10 and 20 mA cm⁻²) and pHs (6.5 and 8.5) [93]. This study showed that BDD electrodes demonstrated higher oxidation of the NOM under a broader range of operating conditions (duration, current, pH). Additionally, BDD-based electrodes had the lowest energy consumption and outperformed MMO electrodes at higher pH and current. On the contrary, the MMO electrode system exhibited improved performance at pH 6.5 and lower current (10 mA cm⁻²) from 0 to 30 min [93].

6. Challenges in the electro-oxidation approach

The rapid advancement of electrochemical oxidation technology for PFAS degradation is hampered by several essential but commonly disregarded issues. First, this method is ineffective for treating low concentrations (parts per billion) of both long and short chains of PFAS. Second, additional research is needed to understand the synergistic or antagonistic removal mechanism of PFAS in the presence of mixtures of PFAS (i.e., the simultaneous presence of shorter and longer chain PFAS). The proposed technique has been proven for the rapid destruction of high concentration of long-chain PFAS and the profound destruction of organic matter. Still, it faces the challenge of treating short-chain PFAS, where the degradation process is much slower (0.004 mM/h of PFBS vs. 0.0123 mM/h of PFOS in terms of Zeroth order) [95]. Hydrophilicity can be the reason for this [61]. Shorter chain PFAS are generally more concerning from health and environmental perspectives than longer chain PFAS. They are more water-soluble and have higher bioavailability, meaning living organisms absorb them more easily. Shorter-chain PFAS have been found to bioaccumulate more in organisms than longer-chain PFAS—implying that they can build up in the tissues of living organisms at higher concentrations, increasing the risk of adverse effects. Third, there is a lack of research demonstrating the removal of high PFAS concentration in complex real water matrices, where both organic and inorganic scavengers are present. The fourth issue involves a lack of information on the process's long-term operation, including lifecycle electrode costs, analyzing process constraints caused by minerals build-up. Fifth possible toxicity concerns (e.g., perchlorate production (ClO₄⁻) during the process). Other anodic materials like PbO₂, IrO₂, and Ti₄O₇ also report the formation of ClO₄⁻ during the EO process. This indicates that perchlorate formation is a critical issue in the EO process and is highly challenging. Field demonstration is needed to demonstrate scale-up and optimize process parameters effectively. Finally, the sixth issue is a lack of information on potential PFAS byproducts. It is often seen that incomplete defluorination with PFAS degradation results in fluorinated product formation, which are as persistent or more persistent than parent PFAS. Thus, the transformation product identification and mechanism study during the remediation of PFAS contamination holds special attention.

Multiple processes can be combined to increase efficacy while reducing energy requirements to achieve complete PFAS destruction (including short and long carbon chains at low concentrations). One hybrid treatment system can integrate the electro-oxidation process with advanced reduction technologies that could pave the way for the complete destruction

and defluorination of PFAS. EO can effectively break down the long-chain PFAS and has the capability for the destruction of organic matter. In contrast, ARP destroys the residual short-chain PFAS with high efficacy in the absence of natural organic moieties that absorb light and scavenge the aqueous electrons. The potential use of such a hybrid system can be cost-effective for removing PFOS and PFOA with $< 20 \text{ kWh/m}^3$ to achieve $> 90\%$ destruction [96].

7. Conclusions and future perspective

One of the main challenges in predicting and improving treatment conditions is the variability in water composition (e.g., the presence of PFAS compounds in mixtures and at various concentrations). Significant research efforts have been devoted to developing technologies to treat industrial wastewater while considering the system's technical and financial aspects. Yet, each technique currently used has significant limitations. The EO process has shown to be promising in eliminating persistent contaminants. However, widespread implementation of EO is hampered by poor destruction of short-chain PFAS, its high cost, and electrode lifetimes due to surface fouling by natural water constituents, among other issues. However, EO works efficiently for scissoring the long-chain PFAS and causes profound destruction of organic matter.

Multiple treatment technologies may be needed to effectively treat a mixture of PFAS in complex natural water matrices. A combined system of EOP followed by ARP might work more effectively than an individual one. Advanced reduction processes (ARPs) can be used for the nonselective defluorination of PFAS to nonfluorinated small organics and the fluorine ion due to hydrated electrons (e_{aq}^-). However, since organic matter is more abundant than PFAS at trace concentrations, they act like scavengers for the e_{aq}^- generated through ARP. Consequently, the fraction of e_{aq}^- allocated for the PFAS degradation gets reduced, leading to low treatment efficiency. Therefore, destroying organic matter via EO can help improve the treatment efficiency of ARP. These two technologies working together will have a substantial outcome— high removal rates with minimal expenditure. The two obvious advantages of combining EOP with the ARP are improved radical generation efficiency and enhanced electrode self-cleaning function. Finally, future research should focus on gaining a mechanistic understanding of the role of NOM in the reduction/oxidation of PFAS in a real water system, which can lead to the development of a highly efficient destructive technology for PFAS in the natural environment.

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Data availability

Data will be made available on request.

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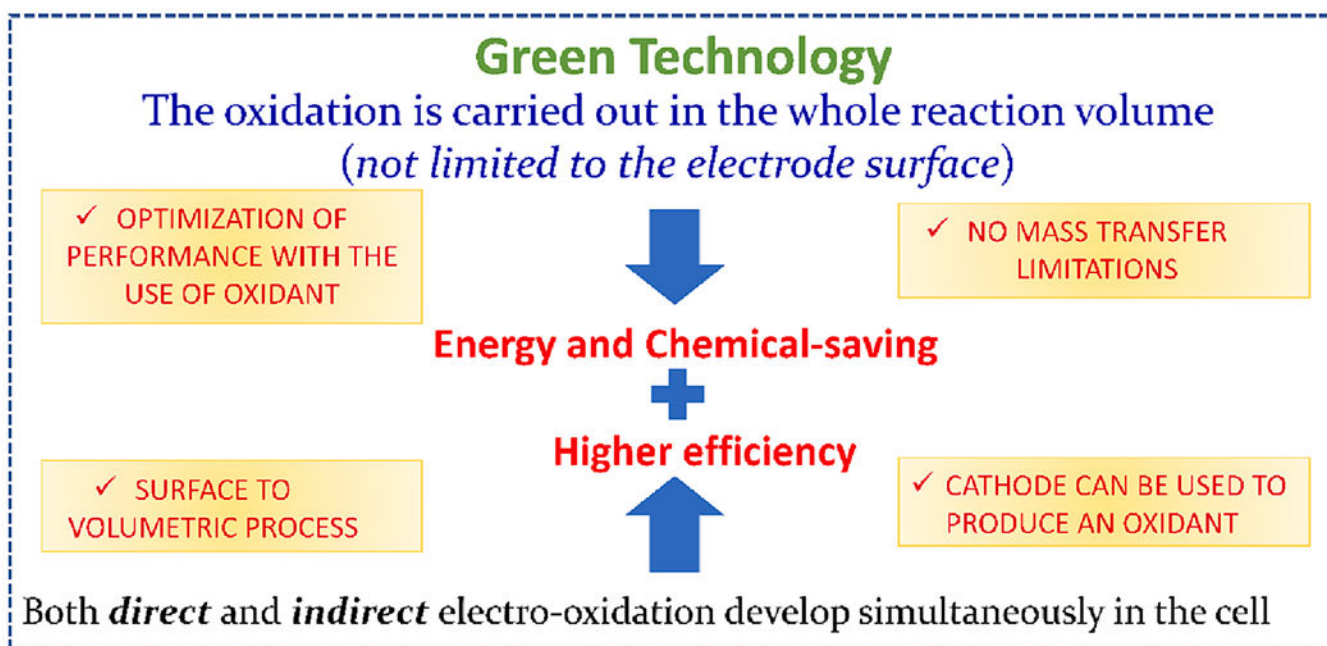


Fig. 1. Advantages of the electrochemical process for PFAS degradation.

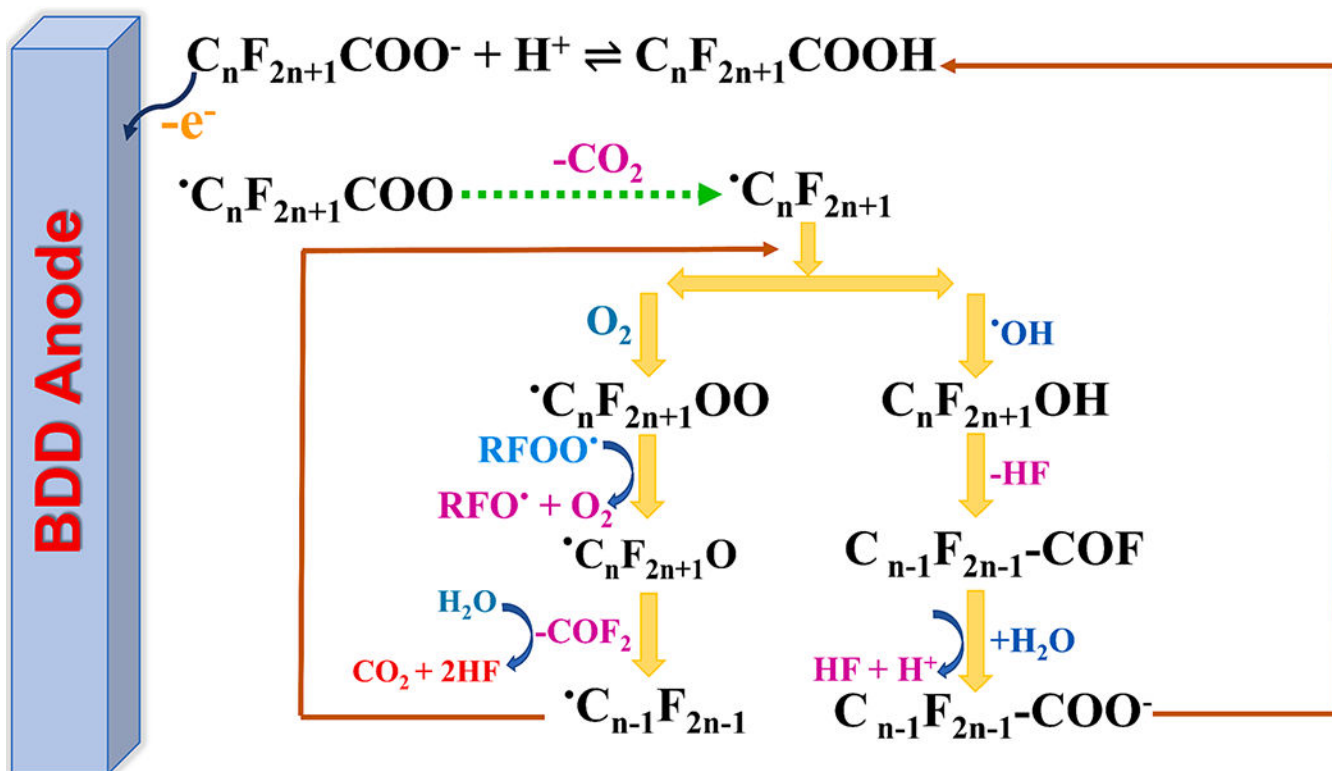


Fig. 2.
The proposed degradation mechanism of PFOA.

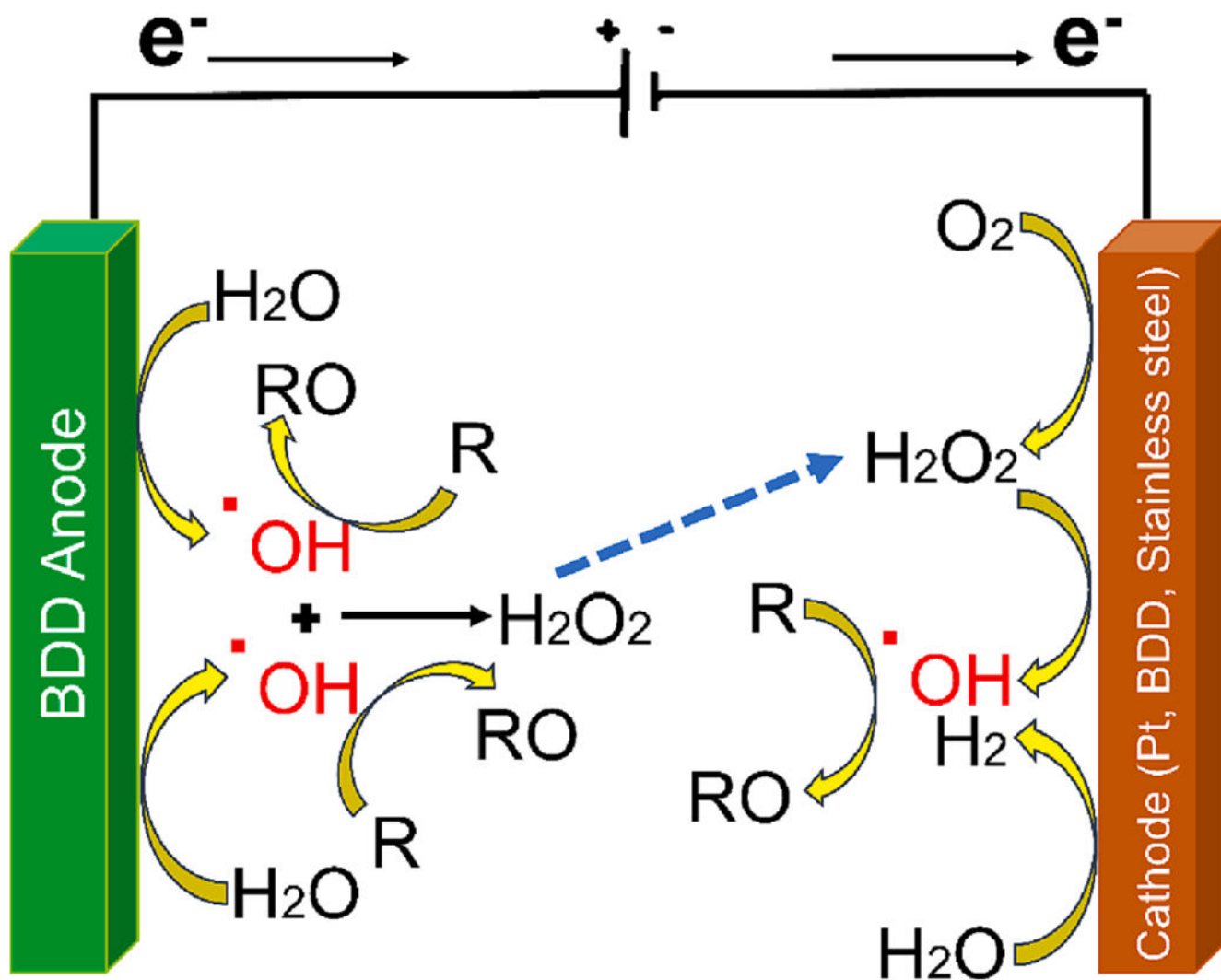


Fig. 3. Cathodic hydroxyl radical production during electro-oxidation (EO) enhances water decontamination (Adapted with permission from Medel et al. [80]Elsevier).

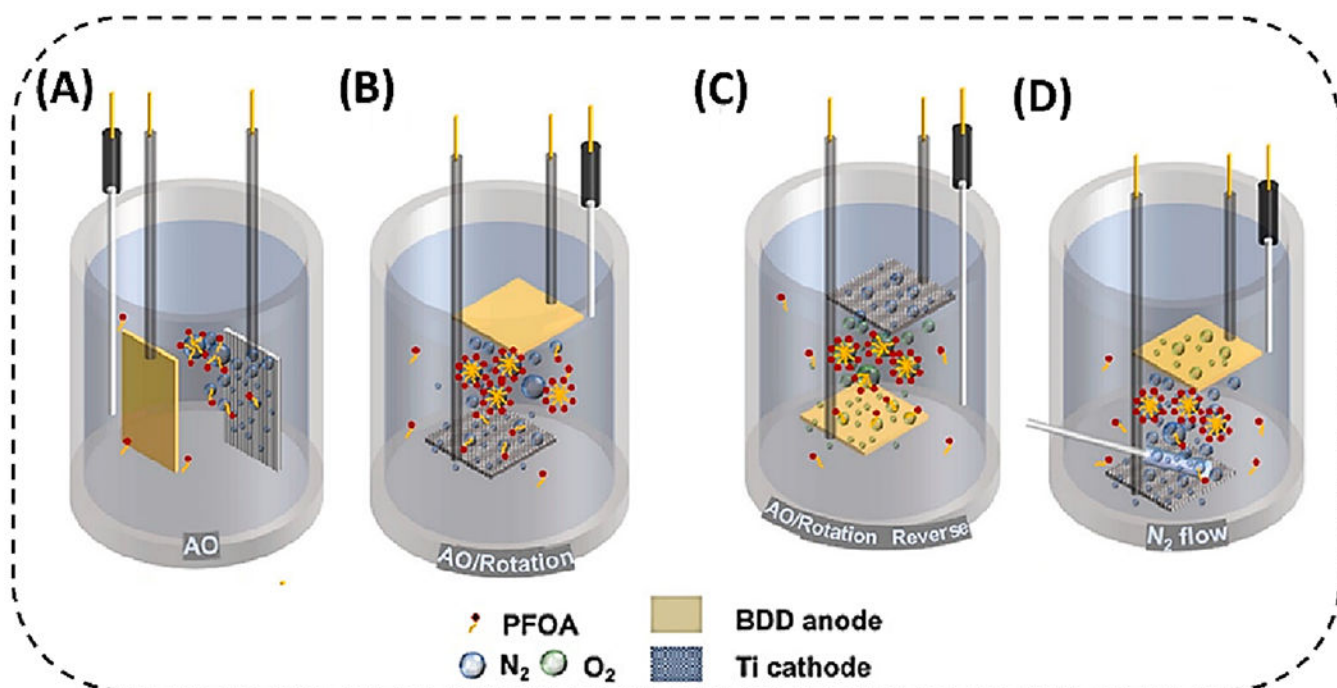


Fig. 4. Schematic diagram of (a) AO system, (b) AO/Rotation system, the experimental setup for (c) eliminating bubble interference from cathodic hydrogen evolution reaction, and (d) exploring the influence of bubble flow rate. (Adapted with permission from Wan et al. [84] American Chemical Society).

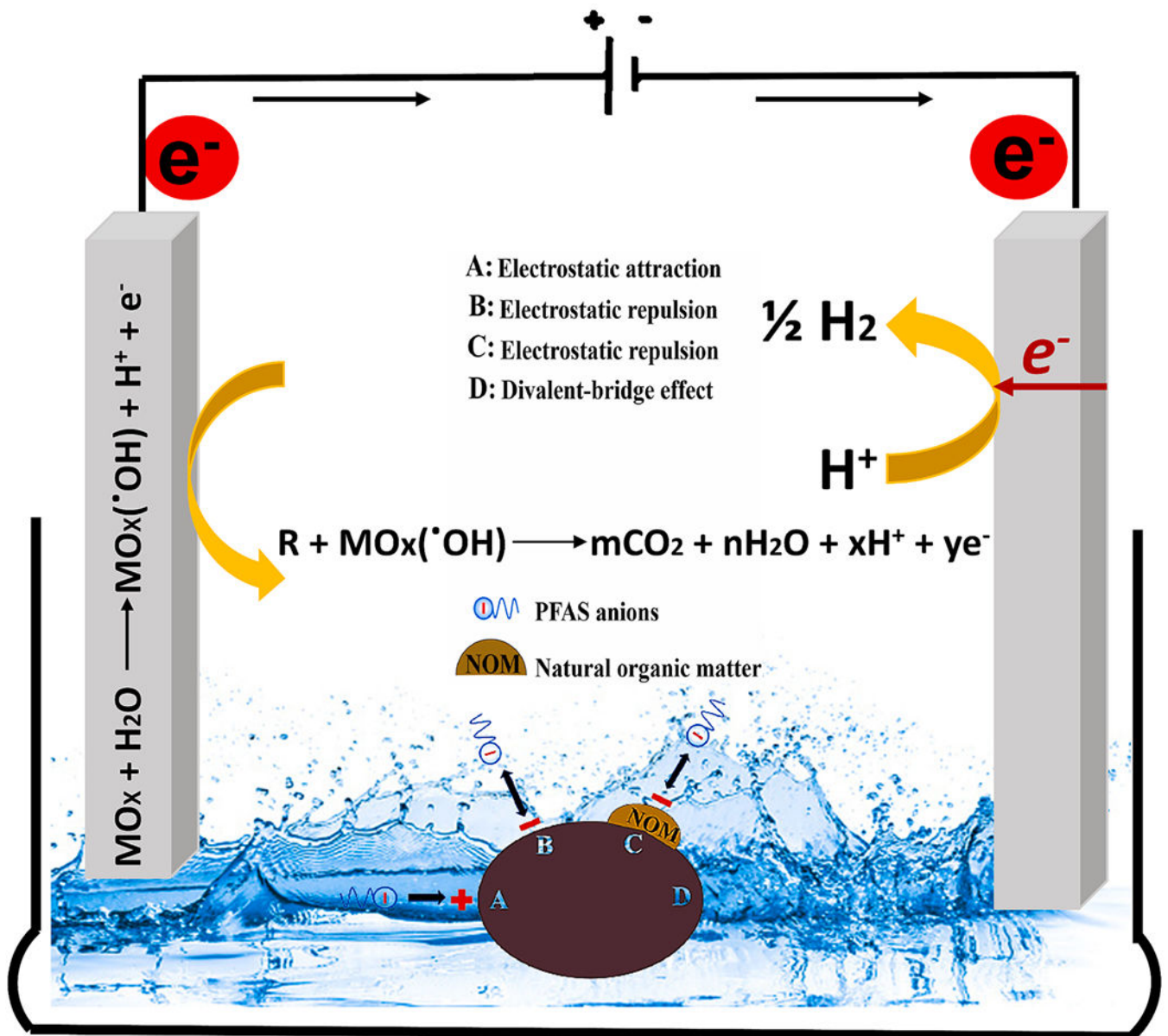


Fig. 5.
 Schematic diagram of the NOM effect in the PFAS electrochemical degradation process
 (Adapted with permission from Lei et al. [92]Elsevier).

Table 1

A summarized table of different anode materials used in the electrochemical oxidation of PFAS.

Anode	PFAS Type	Experimental Parameters	Initial Concentration	Time (mins)	Removal Efficiency	Ref
Zn-PbO ₂	PFOA	current density = 10 mAc ^{m-2} Temperature = 25 °C constant current density: 10 mA cm ⁻² Initial pH value: 4.8 10 mmol L ⁻¹ NaClO ₄ supporting electrolyte	100 ppm	90	97%	[77]
Ce-PbO ₂	PFOA	current density = 20 mAc ^{m-2} Temperature = 25 °C 10 mmol L ⁻¹ NaClO ₄ supporting electrolyte	100 ppm	90	96.7%	[67]
Ti ₄ O ₇	PFOA	current density = 5 mAc ^{m-2} Temperature = 25 °C, 20 mM NaClO ₄ supporting electrolyte.	50 ppm	180	93.1%	[78]
Ti/SnO ₂ -Sb/PbO ₂	PFOA	current density = 10 mAc ^{m-2} Temperature = 25 °C 10 mmol/L NaClO ₄ supporting electrolyte.	100 ppm	90	91.1%	[79]
Ti ₄ O ₇ anode	PFOS	current density = 5 mAc ^{m-2} Temperature = 25 °C 20 mmol/L NaClO ₄ supporting electrolyte.	50 ppm	180	93.1%	[78]
Ti ₄ O ₇ REM	PFOS	Temperature = 25 °C 100 mM K ₂ HPO ₄	5 ppm	NA	>99.9%	[71]
(Ti _{1-x} Ce _x) ₄ O ₇ (x = 3%)	PFOS	current density = 20 mAc ^{m-2} Temperature = 25 °C current density of 1 A/cm ² the solution pH value was not adjusted	10 ppm	240	>99%	[73]
Ti/SnO ₂ -Sb-Bi	PFOA	1.4 g/L NaClO ₄ electrolyte constant current = 0.25 A Temperature = 32 °C	50 ppm	120	99%	[56]
F doped Ti/SnO ₂	PFOA	current density = 20 mAc ^{m-2} 10 mM NaClO ₄ electrolyte	100 ppm	30	>99.9%	[70]
BDD	PFOA	1.4 g/L NaClO ₄ electrolyte Temperature = 32 °C pH = 3.0 current density = 23.24 mAc ^{m-2}	47 ppm	120	97.48	[61]
2D BDD	PFOA	current density = 20 mAc ^{m-2}	200 ppm	180	67	[76]

Anode	PEAS Type	Experimental Parameters	Initial Concentration	Time (mins)	Removal Efficiency	Ref
3D BDD	PFOA	Temperature = 24 °C 0.05 M Na ₂ SO ₄ electrolyte current density = 20 mAcm ⁻² Temperature = 24 °C 0.05 M Na ₂ SO ₄ electrolyte	200 ppm	150	100	[76]