Combining electrochemistry and ultraviolet radiation for the degradation of per- and poly-fluoroalkyl substances in contaminated groundwater and wastewater

Jean Noel Uwayezu a,*, Ivan Carabante b, Patrick van Hees b, Patrik Karlsson b, Jurate Kumpiene a

a Waste Science and Technology, Luleå University of Technology, Luleå, Sweden
b Environment Testing, Eurofins, Sweden

ARTICLE INFO

Keywords:
Electrochemical oxidation
Synergistic effect
Persulfate
PFAS
Vacuum ultraviolet irradiation

ABSTRACT

Electrochemical and ultraviolet-based methods are advanced oxidation processes emerging as viable water and wastewater treatment options. In this study, a combination of these two methods (EO-UV) using boron-doped diamond (BDD) electrodes and ultraviolet radiation at both 185 and 254 nm was assessed for the degradation of poly-fluoroalkyl substances (PFAS). Sodium persulfate (Na2S2O8) and sodium sulfate (Na2SO4) were used as electrolytes. The method was investigated on model solutions containing perfluorooctanoic acid (PFOA) and perfluorosulfonic acid (PFOS). The method’s effectiveness was assessed by comparing PFAS removal efficiencies and energy demands associated with the use of separate and combined treatments. The results showed that the highest removal of PFOA and PFOS was 96% and 85% respectively, which was achieved using EO-UV and persulfate electrolytes. Average removal efficiencies were 1.5–2 times higher in EO-UV than in EO and 4–6 times higher than in UV treatment. The degradation of PFAS under EO-UV and persulfate applied to PFAS-contaminated groundwater and wastewater reached 94% PFOA and 88% PFOS in groundwater and 51% and 63% in wastewater. The removal of the sum of eleven PFAS was 86% and 66% in groundwater and wastewater, respectively. The combination of EO, UV and persulfate was the most effective option for PFAS treatment at lower energy consumption.

1. Introduction

The widespread of per- and poly-fluoroalkyl substances (PFAS) in the environment causes significant threats against globally given their persistence and proven adverse effects on wildlife and human beings [1–3]. Considering the high concentration of PFAS in polluted areas [4,5], a clean-up is considerably needed to prevent their discharges to both surface and potable groundwater that serve as a source of drinking water [6]. Separation techniques such as filtration using activated carbon, resins and semi-permeable membrane have been developed for PFAS treatment in water [7–9]. However, these techniques present limitations of not being effective to remove all PFAS compounds and the need to treat spent materials [10]. Advanced oxidative processes (AOPs) namely chemical oxidation, photo-oxidation, Fenton-and sulfate-based AOPs, sonolysis, and electrochemical degradation were also proven to be promising for the complete removal of PFAS on small scales [7,8]. However, none of them enables an easy breakdown of PFAS on an industrial scale due to high treatment costs and challenges to achieve high removal efficiencies in solutions containing interfering substances [11].

Nowadays, ultraviolet (UV)-based AOPs are considered effective options for removing organic contaminants in drinking water and wastewater treatments [12–15]. In regard to PFAS treatment, UV radiation at 254 nm cannot break down PFAS unless mediated with chemicals (e.g., H2O2, SO4 2−, persulfate) [16–18]. On the other hand, UV radiation at 185 nm has the ability to destroy PFAS by itself, although it is often used in combination with other oxidative chemicals [19,20]. Activated sulfate radicals (SO4•−) have the ability to considerably enhance the photochemical degradation of PFAS [20–23]. Our recent work has demonstrated that UV radiation at 185 and 254 nm assisted with persulfate could degrade PFAS in spiked solution and groundwater, whereas the matrix effect decreased the performance of the method for PFAS degradation in landfill leachate and industrial samples [24].

Electrochemical degradation is another AOP method that can destroy
PFAS in samples with various matrices [25,26]. Boron-doped diamond electrodes (BDD) are commonly used in electron-oxidation processes due to their stability as well as the absence of release of hazardous by-products [27]. Our previous study showed that the electrochemical oxidation using the BDD anode reached 99.5% degradation of PFOA in model solutions [28]. However, the presence of dissolved organic matter and chloride significantly decreased PFAS removal in industrial wastewater samples [28]. Sodium sulfate and persulfate have been reported as two supporting electrolytes needed to form SO₄²⁻ radicals during electrochemical treatment [29–31], which play an important role in the degradation of PFAS.

Moreover, previous research where several destructive techniques were combined showed improvement in PFAS degradation due to the existence of synergistic effects between techniques [32,33]. Compared with the results achieved by ultrasound alone, Yang et al. (2013) reported an average increase of 11.5% PFOS defluorination whereas Sekiguchi et al. (2017) found an increase of 2% PFOA defluorination after combining ultrasound and UV radiation. Other studies reported an increased degradation of PFAS after using electrochemical and ultrasound methods [34,35]. Electrochemical and ultraviolet methods are oxidation processes emerging as viable options for water and wastewater treatment [10,11]. Further to that, these methods present a few advantages over other AOPs methods in terms of energy efficiency and good scalability [10,36,37]. Studies that investigated the degradation of organic pollutants in the EO-UV combined system showed that the removal efficiencies were higher in the EO-UV than using electrochemical oxidation or UV radiation alone [38–40]. However, little data on the synergistic effect between electrochemical and UV-based degradation exists for PFAS degradation [41]. Li et al. (2022) showed that the synergistic effect in a photoelectrochemical system (electrodes integrated into the UV reactor) occurred due to PFOS molecules changing from a ground state to an excited state under the UV radiation, which subsequently caused easier oxidation on a ceramic plate anode. Nevertheless, the EO treatments result in an increase in solution pH and temperature [28,42,43], which could be advantageous if the system is connected to another treatment step notably UV, favored by an increase in pH or temperature conditions. During the photochemical processes, an increase in pH increased the formation of hydrated electrons which initiates the degradation of PFAS [44]. Additionally, the quantum yield of hydrated electrons greatly decreases in acidic conditions (pH < 4) due to the scavenging of protons [45]. An increase in temperature is advantageous for the photodegradation of PFAS and the activation of persulfate which in turn enhances the degradation of PFAS [46,47]. Likewise, the coupling of two systems (EO and UV) could lower the solution pH, which favors the degradation of PFAS at the anode surface [48–52]. In alkaline conditions, electro-generated hydroxyl radicals (OH) have a low effect on the degradation of PFAS because of a decreased redox potential (E°OH/H₂O = 1.8 V) [29,53–55]. Thus, further studies of the synergistic effects of the electro-photochemical treatment are needed, especially in complex solutions such as wastewater, considering the stability and versatility of both BDD and UV systems for the removal of organic pollutants.

The aim of the present study was to evaluate the synergistic effects of the combined electrochemical oxidation and ultraviolet radiation (EO-UV) on PFAS degradation in spiked solutions and validate the method on PFAS-contaminated groundwater and industrial wastewater. Effects of electrolytes, time and levels of applied current densities were assessed.

2. Materials and methods

2.1. Materials

Two perfluorinated substances namely perfluorooctanoic acid (PFOA; 96%) and perfluorosulfonic acid (PFOS; 96%) were purchased from Sigma Aldrich (USA). Pure water with electrical conductivity of 0.055 μs cm⁻¹ was used to prepare spiked solutions. Sodium persulfate (Na₂S₂O₅, 99%) and sodium sulfate (Na₂SO₄, 99%) used as electrolytes were purchased from Merck (Germany). Sodium fluoride (NaF, 99%), sodium chloride (NaCl, ≥99.5), sodium hydroxide (NaOH, >99%), 1,2-diamino cyclohexane N, N, N,N-tetra acetic acid (CDTA, pro analysis) and glacial acetic acid (100%) used to make a buffer were obtained from Merck (Germany).

PFAS-contaminated industrial wastewater and groundwater samples were used to validate the method. Industrial wastewater was obtained from a Swedish waste management company. The groundwater sample was collected from an operating well in the vicinity of a former firefighting training site which became contaminated after the application of aqueous film-forming foams containing PFAS. The characteristics of the samples, including the concentrations of major detected PFAS, are summarized in Table 1.

2.2. Electro-photochemical experiment

The experimental setup consisted of electrochemical and photochemical reactors. The electrochemical cell was made of eight boron-doped diamond (BDD) electrodes, coated on a niobium substrate, with a surface area of 70 cm² per electrode. Electrodes were connected in series. Electrochemical experiments were performed at a constant electrical current of 350 or 700 A to provide a fixed current density (j) of 5 or 10 mA cm⁻², respectively. A required voltage output of 22–45 V was provided by a PHL120 DC power supply. The same photochemical reactor used in our recent work was used in the current investigation of PFAS degradation in EO and UV combined systems [24]. The treatment systems will be referred hereafter as UV for the treatment that used only radiations at combined 185 nm and 254 nm, EO for the treatment that used electrochemical oxidation and EO-UV for the treatment that used UV radiation at 185 nm and 254 nm combined with electrochemical oxidation. To facilitate easy operations at a full scale, the reactors in the combined EO and UV systems were connected in series. Furthermore, the sequential exposure of the contaminated solution to electrolysis and UV radiation allows for transformation to occur after each step, potentially offering advantages in the subsequent stage of the treatment.

The feed solutions consisted of PFAS spiked water, contaminated wastewater or groundwater samples. Before each experiment, solution chemistry was modified by separate additions of Na₂SO₄ and Na₂S₂O₅. The selection of supporting electrolytes was made based on previous study which showed that Na₂SO₄ is a safe electrolyte in the electrochemical treatment of organic pollutants whereas Na₂S₂O₅ improves the electrochemical and UV degradation of organic pollutants [30,31,36]. Experiments were carried out using separate and connected reactors (Fig. S1). A 600 mL of feed solution was continually recirculated at 42 mL min⁻¹ flow rate through the reactors using a Watson Marlow pump (026.3001.00E model, supply Watson-Marlow limited). In the EO-UV combined systems, the sample firstly passed through the UV reactor and the outlet solution passed into the EO reactor before recirculating back to the feed tank (Fig. S1). Experiments were run at room temperature. For each set of experiments carried out using PFAS spiked solutions, a 20 mL sample was taken in a polypropylene bottle from the feed tank after 1, 2, 3, and 4 h. The sampling for real samples (contaminated wastewater and groundwater) was done after 4 h. The pH and temperature were directly measured using a pH electrode before storing the sample at 4 °C for further analysis.

2.3. PFAS quantification and other analysis

The measurement of PFAS concentration in solutions was performed using a liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) following available standard methods (DIN 38407-42, UNEP Chemicals Branch 2015 mod; W-PFCLMS02). Eleven PFAS compounds namely perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDoA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA), perfluoropentadecanoic acid (PFPeDA), perfluorooctadecanoic acid (PFODA), and perfluoroundecanoic acid (PFUnA).
(PFNAs), perfluorodecanoic acid (PFDA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS) and 6-2 fluorotelomer sulfonic (6:2 FTS) were measured. The fluoride concentration resulting from PFAS degradation was quantified using a fluoride ion-selective electrode, following the method described by Uwayezu et al. (2021, 2022). Wastewater was characterized by measuring the TOC using a TOC-V CSH analyzer (Shimadzu) (limit of detection = 4 µg L⁻¹), and inorganic ions (chloride, nitrate, and sulfate) were measured using a colorimetric analyzer (QUATTRO PLUS, BRAN+LÜEBBE). A rapid spectrophotometric method was used to determine the concentration of persulfate as described in a previous study [56]. Briefly, in 10 mL polypropylene tubes containing 2.5 mL of NaHCO₃ (10 g L⁻¹ stock solution) and 5 mL of KI (200 g L⁻¹ stock solution) were added different volumes of sodium persulfate (2 g L⁻¹ stock solution) to make a series of calibration standards with a concentration ranging between 10 and 150 mg L⁻¹. Samples were prepared similarly to the calibration standards. After 15 min of equilibration time, absorbance was measured using Lambda 25 UV/Vis spectrophotometer (PerkinElmer) at 352 nm wavelength.

2.4. Data analysis

As an indication of PFAS degradation, the percentage of PFAS removal was calculated using an expression in Eq. (1).

\[
\% \text{PFAS removal} = \left( \frac{\text{PFAS}_t - \text{PFAS}_i}{\text{PFAS}_i} \right) \times 100
\]

where \(\text{PFAS}_t\) and \(\text{PFAS}_i\) are PFAS concentrations in untreated and treated, respectively. The initial concentration of PFAS was considered as the PFAS concentration in original solution that was recirculated in EO and UV reactors before applying any power or UV radiation.

A mass balance (MB) approach was used to estimate inorganic (fluoride), organic (bonded with PFOS and PFOS) and undetected fluoride following the same procedure described in our previous study [28].

The energy required for each treatment was calculated based on the applied voltage (V), current (A) and the treatment time. The inventory of energy normalized per log average removal of PFOA and PFOS was calculated based on prior work as shown in Eq. (2) [57].

\[
E = \frac{P \times t}{V \left( \log \left( \frac{\text{PFOS} \times 10^{P \times t}}{\text{PFOS}_i} \right) \right) \times 100}
\]

where E represents electrical energy (kWh m⁻³), P stands for electrical power in watts (P=V*I), t stands for the treatment time (hours) and V for sample volume (in dm³). PFOX (i) and (t) represent the average mass concentration of PFOA and PFOS before and after the treatment.

3. Results and discussions

3.1. PFAS removal in spiked solutions

3.1.1. Electrochemical degradation

The degradation of PFOA and PFOS in spiked solutions using the EO method was evaluated in sulfate and persulfate electrolytes. The magnitude of removals is illustrated in Fig. 1a. The results showed that at 5 mA cm⁻² and using \(\text{SO}_4^{2-}\) electrolyte, the removal of 41 % PFOA and 24 % PFOS were achieved after 2 h and up to 65 % PFOA and 42 % PFOS in 4 h treatment time. After doubling the current density (10 mA cm⁻²), the removal efficiencies increased by 14 % PFOA and 15 % PFOS during 2 h and then 18 % PFOA and 16 % PFOS after 4 h. The degradation of PFOA and PFOS increased by increasing both time and current densities in \(\text{SO}_4^{2-}\) solutions (Fig. 1a). In all experiments performed using the EO method, the removal was higher for PFOA than PFOS, which was consistent with previous studies conducted using the same electrode materials (Ni/BDD) [28,49,58,59]. The degradation was higher in persulfate solutions, than it was in sulfate solutions, probably due to the electro-generation of sulfate radicals which improve oxidation processes [30].

3.1.2. Degradation using UV radiation

The removal of PFOA and PFOS upon the UV treatment using 185 and 254 nm radiation is shown in Fig. 1b. The extent of degradation of both PFOA and PFOS was much lower than that found using electrochemical oxidation. However, like in the EO treatment, the degradation of PFOA was higher than that of PFOS in the UV system. This could happen because PFOA and PFOS have different absorption coefficients toward UV radiation. Particularly, PFOS has a poor molar absorption coefficient of 57.2 ± 6.4 M⁻¹ cm⁻¹ upon 185 nm photons [19]. The removal efficiencies during 4 h were 14 % PFOA and 12 % PFOS using \(\text{SO}_4^{2-}\) and 24 % PFOA and 16 % PFOS using \(\text{SO}_4^{2-}\), which indicated that sulfate radicals and increased the amount of UV photons, by increasing exposure time, increased the degradation of the two compounds, which were consistent with our previous study [24].

3.1.3. Combination of EO and UV

The treatment of PFOA and PFOS using a combined system (EO-UV) resulted in an increase of removal efficiencies compared to the results obtained in separated systems (Fig. 1a, b, c). For instance, by looking at the results obtained during 4 h, the average PFOA and PFOS removal in persulfate solutions were respectively increased by 13 % and 23 % at 10 mA cm⁻² compared to the results obtained using EO alone. The corresponding increases in sulfate solutions were 21 % and 23 %.

To examine the possible occurrence of synergistic effect in the EO-UV system, mathematical addition of PFOA and PFOS removal rates obtained under separated treatments were made, and calculated results are displayed in Fig. 1c. Interestingly, experimental results were slightly higher than the calculated ones, which could indicate a synergistic effect in the combined system. The analysis of results indicated the synergistic effect were higher during 2 h compared to 4 h and again higher at 10 mA cm⁻² compared to 5 mA cm⁻². In next subchapters, possible origins of synergies are discussed.
3.2. Evaluation of defluorination and mass balance analysis

The degradation of PFOA and PFOS using electrochemical oxidation and UV radiation is associated with a release of fluoride ions in solutions [24,28,60,61]. The measurement of fluoride indicates the extent of the cleavage of the C–F bond making the carbon skeleton chain. The fluoride generated under different treatment systems is shown in Fig. 2a, b and c.

The defluorination was higher for tests carried out using EO-UV than it was when individual methods were applied separately, which resembled the degradation behavior of PFOA and PFOS. In general, the pattern of fluoride generation was similar to that of PFOA and PFOS removal (i.e., the concentration of fluoride released into the solutions increased with increasing degradation). However, as can be seen in Fig. 2a and c, the electrochemical defluorination (EO and EO-UV) in the presence of persulfate was lower than that observed in the presence of sulfate, which resembled the removal pattern (i.e., the highest removal was found in the presence of persulfate). The reason for the defluorination behavior in sulfate and persulfate solutions was not well understood. However, an increase in sulfate concentration resulting from the stoichiometric production of two moles of sulfate from persulfate, could decrease the concentration of fluoride in the solution as shown in a previous study [28]. This tendency might be linked to an increase of solution ionic strength, which decrease activity of fluoride [62]. In addition, electrochemical activation of $\text{SO}_4^{2-}$ at the BDD anodes could suppress the electro-oxidation of PFAS, resulting in low defluorination [63].

The mass balance demonstrated that PFOA and PFOS were not completely transformed into their corresponding inorganic substances, which agreed with previous studies [20,28]. The electrochemical and photochemical degradation of PFOA and PFOS are accompanied by the generation of fluoride and the formation of short-chain PFAS including PFBA, PFHpA, PFHxA, and PFPeA [20,28]. The current results showed that the concentration of shorter-chain PFAS was relatively lower for the treatments carried out at low current densities and under UV radiation. The sum of decomposition products identified after the treatments is found in Fig. S2.

The analysis showed that the sum of organofluorine (fluorine bound to PFAS) and fluoride in treated solutions was not equivalent to the total fluorine initially bonded to PFOA and PFOS, indicating that there was another fraction of fluoride that was not detected (undetected fluorine). This could likely happen due to the adsorption of bioproducts radicals on the BDD surface or the formation of volatile products including CF$_4$ and C$_2$F$_6$ [64,65]. In general, no distinction in undetected fluorine was found after using UV treatment (Fig. 2e) whereas in the EO and EO-UV treatments, the undetected fluoride increased when the treatment time was increased from 2 to 4 h under the same treatment conditions (Fig. 2d and f), a pattern similar to that found in other studies [28,55,66]. However, an increase in the current density was advantageous in the conversion of PFAS into inorganic substances (release of fluoride) and the decrease of undetectable fluorine species.

3.3. Change in solution pH and temperature during treatment systems and their effect on PFAS degradation

The pH varied depending on the method and the used electrolyte. In the sulfate solution, the pH became acidic in UV treatment (pH = 3.9), close to neutral (pH = 6.8) in the EO system and pH of 5.1 in the EO-UV (Fig. 3a). This implied that the EO-UV lowered the pH by about two units compared to the solution pH in EO system alone and increased the pH by about two units compared to the solution pH in UV system alone. The UV radiations took part in lowering the solution pH under the EO-UV
Based on PFAS degradation pattern and change in solution pH, the observed synergy in the degradation of PFOA and PFOS during the EO-UV treatment could be linked to a decrease in pH which facilitates the electro-oxidation processes [48,51,52]. Furthermore, an increase in pH could enhance the photochemical degradation of PFOA and PFOS (in the EO-UV treatment) due to an increased quantum yield of hydrated electrons resulting from a decreased scavenging of protons [44,45]. However, dissimilar to the change in pH observed using sulfate solutions, the pH in Na₂SO₄ solutions was always acidic (pH ≤ 2.2) in all treatment systems, implying that the synergy observed using...
persulfate could not be explained by the pH factor.

The treatment using single or combined treatments changed solution temperature, as shown in Fig. 3b. Under the EO and the EO-UV treatments, solution temperature increased from 20 °C to 28 °C and 34 °C in persulfate and sulfate solutions respectively, due to resistive heating [65]. The temperature remained constant in the UV treatment system. Although the change in temperature does not affect the electro-oxidation of PFAS [55], this temperature increase is advantageous for the activation of persulfate [46,47]. Furthermore, an increase in solution temperature was reported to enhance the photochemical degradation of PFOA [67]. Thus, the synergy that occurred in the EO-UV system could also be explained by an increased amount of sulfate radicals and temperature, which enhanced the degradation of PFAS.

3.4. Effect of current density for PFOA and PFOS degradation in different treatment systems

One of the major factors that affect the electrochemical degradation of PFAS is the current density [28]. The effect of applied current density was investigated in EO and EO-UV systems by evaluating the degradation efficiencies of PFOA and PFOS under 5 and 10 mA cm⁻². In both systems, increasing current density improved the degradation of both PFOA and PFOS via increased electron transfer from these molecules to the anode [52,58]. The proportionality between PFAS degradation and the current density in both EO and EO-UV systems was consistent with various previous studies [52,55]. However, it was noticed that an increase in current density did not result in a linear increase in PFAS degradation, i.e., doubling the current density from 5 to 10 mA cm⁻² did not increase twice the removal of PFOA and PFOS (Fig. 1a and c). The most probable reason could be that a low flow rate (42 mL min⁻¹) employed in the current study reduced the mass transfer and reaction rate at the increased current density, which in turn did not result in equivalent degradation. Prior studies have shown that the efficiency of the electrochemical oxidation of organic pollutants is proportional to the flow rate due to the change from a laminar to a turbulent flow, which leads to an improved mass transfer coefficient [55,68,69]. This suggests optimization of both current density and a flow rate to simultaneously maximize method efficiency at low power consumption. It is worth noting that the effect of current density was pronounced after increasing time from 2 to 4 h, implying that degradation time was also an important parameter in the electrochemical oxidation of PFAS as described in our previous study [28].

It is of great importance to evaluate the degradation behavior of PFOA and PFOS under electrochemical oxidation as these pollutants coexist in contaminated waters. The current results indicated that the degradation of PFOA was higher than that of PFOS at lower and higher current densities in both EO and EO-UV processes. For instance, a calculation of the difference between PFOA and PFOS removal in the EO showed that the average difference at 5 mA cm⁻² was about 15 % whereas it was about 17 % at 10 mA cm⁻². The difference in degradation behavior of PFOA and PFOS is linked to the competition of these compounds; PFOA suppresses the removal of PFOS by reducing the contact of PFOS on reactive sites of the anode [54]. Furthermore, an increase in current density is associated with an improved formation of hydroxyl radicals which are able to achieve partial degradation of PFOA but not PFOS [53-55].

In summary, an increase of current density in the EO-UV system improved the PFAS-degradation by (i) increasing the electron transfer during the oxidation reaction, (ii) increasing the formation of hydroxyl radicals, (iii) increasing the temperature, which activates persulfate and (iv) generating persulfate from sulfate, which further enhances the degradation in the UV system [7,29,30,46,49].

3.5. Effect of electrolyte on the degradation of PFOA and PFOS in different treatment systems

The SO₄²⁻ and S₂O₅²⁻ were measured during the electrochemical degradation of PFOA and PFOS in solutions containing Na₂SO₄ electrolyte (Fig. 4a). The analysis showed that the concentration of S₂O₅²⁻ was below detection limit, which was an indirect indication that SO₄²⁻ was not formed or formed in lesser quantities. This agrees with Chen et al. 2018, who showed that a noticeable transformation of sulfate into persulfate may occur only when a high concentration of sulfate is used (~14.2 g L⁻¹ SO₄²⁻).

The results showed that for all treatments carried out in the presence of sulfate, its concentration did not significantly change over time, which further provided evidence that the formation of persulfate was negligible. Thus, in agreement with Urtiaga et al. (2015), sodium sulfate was only involved in the electrolysis processes as a supporting electrolyte, it did not participate in the electrochemical oxidation of PFAS.

The current study also investigated the practicability of EO, UV radiation, and EO-UV methods for PFOA and PFOS degradation in solutions containing persulfate. The removal efficiencies of the two compounds were much improved in the presence of persulfate compared to the removal efficiencies obtained in the presence of sulfate. For instance, the EO removal at 10 mA cm⁻² and during 4 h was increased by 13 % PFOA and 9 % PFOS in the presence of persulfate compared to the use of sulfate. This indicated the involvement of other mechanisms associated with the use of persulfate.

As an indicator of persulfate transformation, SO₄²⁻ and S₂O₅²⁻ were measured during the PFOA and PFOS treatment in the presence of Na₂S₂O₈ (Fig. 4b). The analysis showed that <0.6 g L⁻¹ S₂O₅²⁻ (about 10 % of the initial electrolyte) remained after 1 h treatment time in both EO and EO-UV. After that, no more S₂O₅²⁻ was detected in the solutions. This implied that the enhancement of the electrochemical degradation of PFAS using persulfate occurred in the first minutes of the treatment, which resembled a previous study [31]. The analysis of SO₄²⁻ showed that the concentration of sulfate doubled that of the initial concentration of persulfate after 1 h, which confirmed that persulfate was electrochemically transformed into sulfate. The involvement of persulfate in PFOA and PFOS degradation in the first minutes could be explained by the electrolytically generated sulfate radicals on the BDD cathode [31]. Later on, the degradation in the EO and EO-UV systems would be similar in both Na₂S₂O₈ and Na₂SO₄ electrolytes. In the UV treatment, the concentration of persulfate ions gradually decreased over time, indicating the photochemical activation of the working electrolyte and its involvement in PFOA and PFOS degradation [20,47].

The pathways for PFOA and PFOS degradation in combined EO-UV systems using sulfate and persulfate could be summarized based on previous studies [20,31,52,70,71]. In the presence of sulfate, the degradation might happen via two steps: direct oxidation on the BDD anode and photolysis under the 185 nm radiation. In the presence of persulfate, degradation might happen via three stages: electron transfer at BDD anode, radical oxidation by electrochemically activated persulfate on BDD cathode and by UV radiation assisted with activated sulfate.

3.6. Operational cost

A consideration of cost associated with treatment technology is important given that this is one of the major factors that limit their practical use on an industrial scale. A comparison of the current methods in terms of energy and chemical demand as the main cost drivers is presented in Table 2. In general, energy consumption comprises the largest share of the total operational cost. In comparison to PFOA and PFOS treatment using sulfate electrolytes, the analysis of methods performance in terms of the PFAS removal efficiency and cost showed that the use of persulfate had double advantages, such as improved degradation and lowered energy consumption. The temporal activation of one mole of persulfate resulted in the stoichiometric production of two
moles of sulfate, which reduced the solution resistance and subsequently the electrical potential according to Ohm’s law (V=IR and P=VI).

The observed removal efficiencies and energy consumption of EO with respect to the use of persulfate and sulfate was in line with previous studies [70,72]. The order of average energy consumption for PFOA and PFOS degradation was as follows: UV (in persulfate) > UV (in sulfate) > EO (in sulfate) > EO-UV (in sulfate) > EO (in persulfate) > EO-UV (in persulfate). The energy requirement in the EO-UV (in persulfate) was in reasonable agreement for PFOA degradation using BDD electrodes, but lower than that reported for PFOS degradation [66]. It is also important to mention that the energy use in EO-UV method was much lower compared to the energy required for other methods including ultrasonic, microwave-hydrothermal, Fenton oxidation processes, and heat-based treatments [36,57,73].

3.7. PFAS degradation in contaminated water

The workflow of EO oxidation and combined EO-UV-based oxidation was applied to degrade PFAS in PFAS-contaminated groundwater and wastewater samples. The industrial wastewater contained high concentrations of TOC and Cl⁻, and predominantly 6-2 FTS, PFOS, PFHxS, PFHxA and PFBS, which accounted for 94 % of measured eleven PFAS (Table 1). The groundwater contained undetectable levels of TOC and Cl⁻, but higher concentrations of PFOA, PFOS, PFHxA and PFHxA than the wastewater. PFOS and PFHxS dominated, which accounted for 92 % of the measured eleven PFAS compounds. A comparison of PFAS concentration in untreated and treated samples was done to evaluate the effectiveness of the methods. The concentrations of eleven PFAS compounds measured after the treatment are provided in Table SI 1.

3.7.1. PFAS degradation in groundwater

The removal of PFAS in groundwater is shown in Fig. 5a. It was observed that the removal of PFAS was influenced by the type of electrolyte, a behavior similar to that observed during the treatment of spiked solutions. In comparison to PFAS treatment using sulfate electrolyte, the electrochemical oxidation yielded a slightly higher PFAS degradation in the presence of persulfate (an average increase by 6 % removal for the eleven PFAS compounds), due to the activation of persulfate.

In the EO-UV treatment, the removal was further improved by about 18 % for eleven PFAS under identical treatment conditions of current density and electrolyte, due to the 185 nm photons, which were shown to break down PFAS on its own [74,75]. The order of PFAS degradability was as follows: PFOA (86.5 %) > PFOS (83 %) > PFHxS (74 %), a tendency that is consistent with the degradation behavior of the three compounds reported using electrochemical oxidation [59,76]. The current findings indicated that the degradation of PFOA and PFOS under EO-UV in groundwater was much closer to the degradation of the same compounds in spiked solutions. The removal of eleven PFAS was 86 %. The remaining PFAS was composed of non-degraded PFAS and a part of generated byproducts including PFAS, such as PFBA, PFHxA, PFHxS and PFHpA, since their concentration was increased after the treatment. This indicated that the degradation of some PFAS (longer chain) generated other PFAS byproducts. These shorter-chain PFAS (i.e., PFBA, PFHpA, PFHxS and PFHpA) contributed to 33–47 % of the detected PFAS after the treatment.

3.7.2. PFAS degradation in wastewater

The removal of PFAS in wastewater is shown in Fig. 5b. The removal was lower than that in groundwater (i.e., the removal of eleven PFAS in wastewater was 66 % compared to 86 % in groundwater), which was not a surprise due to the high concentration of other anions in wastewater decreases the degradation of PFAS [28,71]. Wastewater sample contained other measurable oxidizable substances including organic carbon and chloride, which undergo electrochemical and UV-oxidation and could compete with the degradation of the target compounds [16,28]. Moreover, the sample had suspended particles, with a turbidity of 4400 NTU. These particles are a barrier to the passage of UV light through the solution [77] and could be another cause of low degradation of PFAS using photochemical processes. Increased treatment time might help to overcome the effect of sample matrices. The degradation of PFAS in wastewater was under the combined EO-UV method and in the presence of persulfate, which highlights the importance of combining treatment systems for achieving high PFAS removal. It is worth mentioning that the degradation of PFOA in wastewater was lower than that of PFHxS and PFOS, which was contrary to that observed in groundwater and previously reported in other studies [50,76]. However, the current

Table 2
Estimation of energy and chemical consumption for EO, UV and EO-UV during the treatment of PFOA and PFOS.

<table>
<thead>
<tr>
<th>Treatment conditions</th>
<th>Removal (%)</th>
<th>Electrical energy (kWh m⁻³)</th>
<th>Chemical (kg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PFOA</td>
<td>PFOS</td>
<td>PFOA</td>
</tr>
<tr>
<td>10 mA cm⁻², 5 g L⁻¹ Na₂S₂O₄ and 4 h</td>
<td>70</td>
<td>54</td>
<td>368</td>
</tr>
<tr>
<td>10 mA cm⁻², 5 g L⁻¹ Na₂S₂O₄ and 4 h</td>
<td>83</td>
<td>63</td>
<td>195</td>
</tr>
<tr>
<td>UV, 5 g L⁻¹ Na₂S₂O₄ and 4 h</td>
<td>14</td>
<td>12</td>
<td>1520</td>
</tr>
<tr>
<td>UV, 5 g L⁻¹ Na₂S₂O₄ and 4 h</td>
<td>24</td>
<td>16</td>
<td>1129</td>
</tr>
<tr>
<td>UV, 10 mA cm⁻², 5 g L⁻¹ Na₂S₂O₄ and 4 h</td>
<td>91</td>
<td>77</td>
<td>317</td>
</tr>
<tr>
<td>UV, 10 mA cm⁻², 5 g L⁻¹ Na₂S₂O₄ and 4 h</td>
<td>96</td>
<td>85</td>
<td>205</td>
</tr>
</tbody>
</table>

Fig. 4. Sulfate and persulfate concentration in PFAS spiked solutions treated using EO, UV and EO-UV methods in the initial concentration of (a) sulfate and (b) persulfate. The current density was 10 mA cm⁻², initial concentration of both Na₂S₂O₄ and Na₂SO₄ electrolytes was 5 g L⁻¹.
behavior of PFOA and PFOS degradation was consistent with the behavior reported in industrial wastewater [28]. One of the possible reasons for low PFOA removal in wastewater could be that the sample contained precursors which were not analyzed in our study. For instance, a previous study showed that 8-2 fluorotelomer carboxylic acid (8-2 FTCA) is transformed into PFOA via oxidation processes [78,79]. Similar to the behavior observed in groundwater, the degradation of PFAS bearing sulfonate functional group (i.e., PFOS, PFHxS and PFBS) in wastewater was higher for longer chain molecules (i.e., PFOS) and decreased as the carbon chain decreased, which was in accordance with a degradation pattern reported using BDD electrodes [50]. It was shown that the recalcitrant character of the PFAS toward the electrochemical oxidation increases as carbon chain length decreases [80].

In general, the EO-UV treatment of contaminated samples showed higher removal of PFAS than using EO alone. The degradation was more readily in groundwater than in wastewater sample and the removal was further improved in the presence of persulfate. However, the studied methods did not lead to complete degradation of PFAS in groundwater and wastewater solutions. Increasing the treatment time and current density might further improve PFAS degradation to the regulatory levels.

4. Conclusion

The current study where PFAS degradation using a combination of electrochemical oxidation with BDD electrodes and UV radiation at 185/254 nm were applied on PFOS and PFOA spiked solutions showed that this combination of the methods and the presence of persulfate improved PFAS removal compared to the use of separate methods. The order of method effectiveness based on PFOA and PFOS degradation was EO-UV (in persulfate) > EO-UV (in sulfate) > EO (in persulfate) > EO (in sulfate) > UV (in persulfate) > UV (in sulfate). The highest removal of 96 % PFOA and 85 % PFOS were found in the EO-UV treatment at the applied current density of 10 mA cm$^{-2}$ and in the presence of persulfate. All the treatments were more efficient for PFOA than for PFOS.

The energy consumption was the lowest in electrochemical oxidation using persulfate, while adding UV-step did not significantly change the energy demands. Thus, the most efficient method in terms of PFOA and PFOS degradation, was also the most energy efficient. Furthermore, this combination of methods was nearly equally efficient to treat PFAS contaminated groundwater as the spiked solutions. Nevertheless, the treatment efficiency of industrial wastewater, which contained other anionic oxidative species, such as TOC and Cl$^-$, decreased by ca 9–20 % for 11 PFAS, indicating a further need for method optimisation either by modifying the treatment factors or adding an additional pre-treatment step to remove the interfering species. The current study was performed at unoptimized conditions, which led to minor synergies after combining the EO and UV steps. Thus, a need to optimize the process, which would increase the synergistic effects, is important. This would not only improve the removal of the contaminants, but also prevent the formation of PFAS byproducts that were observed during the treatment.

Availability of data and materials

All relevant data and materials are included in the manuscript.

CRediT authorship contribution statement

Jean Noel Uwayezu: Conceptualization, investigation, methodology, writing - manuscript.
Ivan Carabante: Conceptualization, planning, methodology, manuscript editing & supervision.
Jurate Kumpiene: Conceptualization, planning, methodology, manuscript editing & supervision.
Patrik van Hees: Investigation & methodology.
Patrik Karlsson: Investigation & methodology.

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.

Data availability

Data will be made available on request.

Acknowledgments

The study is funded by the European Union and the European