Chapter 2

Electrochemical Oxidation of Perfluorooctanoic Acid (PFOA) from Aqueous Solution using Non-Active Ti/SnO₂-Sb₂O₅/PbO₂ Anodes

Seema Singh^{1,2}, Kinjal J. Shah³, Nidhi Mehta^{1,4}, Vimal Chandra Srivastava⁵, Shang-Lien Lo^{1,6,*}

¹Graduate Institute of Environmental Engineering, National Taiwan University, 71 Chou-Shan Rd., Taipei, Taiwan, ROC

²Omvati Devi Degree College Bhalaswagaj, Haridwar, Uttarakhand, India

³College of Urban Construction, Nanjing Tech University, Fuzhu, Nanjing, China

⁴Department of Biochemistry, University of Washington, Seattle, WA, 98195, USA

⁵Department of Chemical Engineering, Indian Institute of Technology, Roorkee, Roorkee 247667, Uttarakhand, India

⁶Water Innovation, Low Carbon and Environmental Sustainability Research Center, National Taiwan University, Taipei 10617, Taiwan

* sllo@ntu.edu.tw (S.-L. Lo)

Abstract

In this study, electrochemical oxidation of perfluorooctanoic acid (PFOA, C₇H₁₅CO₂H) from aqueous solution was examined in terms of PFOA and total organic carbon (TOC) removal by using Ti/SnO₂-Sb₂O₅/PbO₂ non-active electrodes. The effects of operating parameters: initial pH (pH₀), current density (j), and electrolyte concentration (m) at different time intervals were examined. Specific energy consumption (SEC) was used to determine the process proficiency. The C-C bond between C₇F₁₅ was first cleaved and then degraded into fluoride ions (F⁻) and short carbon-chain per-fluorinated carboxylic acids (PFCAs) ((~C2–C7) such as perfluoroethanoic acid (PFEA: C₂F₅CO₂H), perfluoropropanoic acid (PFPA: C₃F₇CO₂H), perfluorobutanoic acid (PFBA: C₄F₉CO₂H), perfluoropentanoic acid (PFPeA: C₅F₁₁CO₂H), perfluorohexanoic acid (PFHxA: C₆F₁₃CO₂H), perfluoroheptanoic acid (PFHpA: C₇F₁₄CO₂H). These intermediates by-products were determined using the gas chromatograph-mass spectrometry (GC/MS) analysis. The rate of PFOA decomposition was followed the pseudo-first-order kinetics. About 82% TOC and 94% PFOA removals were formed at the optimal condition of pH₀ = 3.58, j = 168.34 Am⁻², and m = 250 mgL⁻¹ at 120 min of electrolysis with SEC = 593 kWh/kg

TOC. A plausible degradation mechanism was also proposed at the optimal treatment condition.

Keywords

Perfluorooctanoic Acid, Electrochemical Oxidation, Specific Energy Consumption, Reaction Kinetics, Degradation Mechanism

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1. Introduction

Polyfluoroalkyl substances (PFASs) and perfluorooctanoic acid (PFOA) are a group of chemicals that possess a complete fluorinated alkyl chain of various lengths which consists of an acidic head group i.e. carboxylic acid, phosphoric acid and sulfonic acid. These are extremely stable chemicals with higher C-F bond energy ((531.5 kJ mol⁻¹), which gives them higher thermal resistance and surface activity [1]. Along with PFASs, PFOA is broadly used in various industrial products such as sports clothing, lubricants, extreme weather military uniforms, firefighting foams, waterproof breathable fabrics, motor oil

additives and medical activities as metal coatings, surfactants, fire retardants, and surface treatments [2,3]. Owing to their synthesis and wide use of applications, PFOA has been regularly identified in the natural environment, air, water, wildlife, human serum, and solid waste [4,5]. After discharge, it can simply be transported into the water system. Environmental monitoring has exposed their persistence, bioaccumulation, and acute toxicity to aquatic organisms [5-8].

As a result, it is necessary to develop a systematic process to eliminate the PFOA from the wastewater. Some treatment methods including adsorption, coagulation, UV irradiation, ultrasonic irradiation, electrochemical oxidation, and zero-valent iron (ZVI) reduction were employed [5,7-12]. Although some of these processes need acute conditions of treatment because of comparatively unsuccessful PFOA removal and limit to their large-scale application [11-15]. Therefore, it is a great challenge to develop an environmentally friendly and cost-effective technology such as high mineralization and complete degradation of PFOA.

In contrast of the above processes, the electrochemical oxidation of pollutants removal from aqueous medium has become a promising technology because of its higher oxygen evolution potential (OEP) towards anode materials, excellent oxidation ability, electron transfer capacity, mild treatment conditions, hydroxyl radical ($\cdot\text{OH}$) formation, and environmental compatibility. Recently, some studies have been performed on PFOA degradation with electrochemical oxidation [1,16,17] and it could be effectively degraded with “non-active” anodes, such as niobium (Nb), tungsten (W), and tantalum (Ta) doped boron-doped diamond (BDD), lead dioxide (PbO_2) electrodes, and tin oxide (SnO_2) even at higher concentrations [18] than “active anodes” including Ti/RuO_2 , Ti/IrO_2 , Ti/IrO_2 , Pt and graphite electrodes due to higher OEP, higher electron transfer ability, and higher $\cdot\text{OH}$ generation rate [1,19,20]. Previous reports have examined the EO performance for PFOA with non-active anodes and generally followed in the following order: $\text{BDD} > \text{SnO}_2\text{-Sb} > \text{PbO}_2\text{-Ce}$ [21].

Although BDD has superior performance due to its long life, higher OEP, and excellent chemical and electrochemical stability but higher cost and particularly hard to find the suitable substrate for the deposition limit large-scale uses of BDD electrode. Nb, Ta, and W substrates are too costly; silicon (Si) is extremely fragile and have lesser conductivity; Ta (Ti/BDD) is a choice as a substrate, however service life is comparatively small [1,16,17]. Thus, in search of a low-cost industrialized electrode for the PFOA degradation shows a very significant. Potential electrodes, particularly Sb doped $\text{Ti/SnO}_2\text{-Sb/PbO}_2$ anodes, have various benefits such as high OEP (~ 1.9 V versus SHE), long life time, easy preparation, cost efficiency, and high chemical stability [1,19,20] confirmed the 73.9% defluorination and 98.8% degradation of PFOA were formed over $\text{Ti/SnO}_2\text{-Sb}$ anode at

the optimum treatment conditions of $j = 40 \text{ mA cm}^{-2}$, $\text{pH} = 5$, electrolyte concentration of 10 mM NaClO_4 and keeping the distance between the electrode plate about 1.0 cm for 100 mg L^{-1} PFOA initial concentration after 90 min electrolysis. But, Zhao et al. [20] have confirmed that 20% PFOA removal efficiency decrease at $\text{Ti/SnO}_2\text{-Sb}$ anode in presence of Na_2SO_4 electrolyte because SO_4^{2-} ions adsorbed at the surface of anode and its active sites was occupied which results decrease in the concentration of $\cdot\text{OH}$ generation.

This study aimed to examine the electrochemical oxidation (EO) of PFOA using $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5/\text{PbO}_2$ anodes in aqueous solution. We carried out the experiments to determine the effect of various influencing factors such as solution pH (pH_0), current density (j), and sodium chloride (NaCl) as an electrolyte concentration (m) for PFOA and TOC removal. Specific energy consumption (SEC) during each parameter optimization was used to detect the process performance of EO. To evaluate the PFOA degradation rate constant, kinetic studies of PFOA removal was determine. In addition, intermediate by-products such as organic and inorganic byproducts were identified during PFOA electrolysis, and finally, a plausible degradation mechanism of PFOA removal during EO was suggested with the help of intermediates byproducts identification.

2. Materials and methods

2.1 Materials

All chemicals of analytical grade were used in this study. Hydrochloric acid (HCl), sodium bi-carbonate (NaHCO_3), sodium carbonate (Na_2CO_3), and sodium hydroxide (NaOH) were purchased from Nacalai Tesque. The synthetic solution of PFOA (Sigma Aldrich Chemical, USA) was prepared by dissolving its suitable amount of deionized/ultrapure water. NaOH and HCl were used to adjust the solution's pH.

2.2 Electrode preparation and characterization

Rectangular shape of Ti plates with a dimension of $2.5 \text{ cm} \times 2.0 \text{ cm}$ and 1 mm thickness were prepared by immersed it into a freshly prepared $40 \text{ wt\% NaOH}$ solution at 333K for 2h to remove the grease, and then plates were etched for 2h by boiling with $10\text{wt\%}$ oxalic acid to generate a grey black surface with regular roughness. Later, $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5$ interlayer was prepared by thermal decomposition method. In brief, the precursor solution was prepared by mixing the mole ratio $9:1$ of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and SbCl_3 in butanol and hydrochloric acid. After that, paint solution was applied on pretreated Ti plates with a brush, which was dried at 393K for 10min in the oven, and then sintered in the muffle furnace for the coating at 773K for 10 min . This process was revised ten times to generate the $\text{Ti/SnO}_2\text{-Sb}$ electrodes, and the final baking was kept at 773K for 1h . At the end,

various interlayers were attained. Afterwards, β -PbO₂ films were electrodeposited on the as-prepared interlayers of Ti/SnO₂-Sb. For this purpose the β -PbO₂ was produced from 0.1M HNO₃ acidic medium containing 0.5M Pb(NO₃)₂ and 40 mM NaF. The Ti plate and interlayer were employed as an anode and cathode, respectively. Both anode and cathode were perpendicularly put in the electrodeposition solution with a fixed distance of 1.0 cm. The β -PbO₂ films were electrodeposited after 2h with a constant j of 200 A cm⁻² at 333K. At last, the different interlayers of β -PbO₂ electrodes were formed.

2.3 Electrochemical experiments

The EO experiments of PFOA were conducted in a double layered cylindrical batch reactor having 1.5 L capacity of wastewater treatment. Each experiment was conducted with a constant direct current (DC) power supply (GPR-30H10D) connected with two Ti/SnO₂-Sb₂O₃/ β -PbO₂ electrodes and the distance between each electrodes was maintained about 1 cm. The base of electrodes was kept 5 cm above from EC reactor bottom for the trouble-free stirring of solution at 400–500 rpm. The batch tests were carried out at room temperature and the voltage varied between the ranges of 1–15 V. All experiments were conducted with 1 L PFOA solution in a batch reactor. The conductivity of solution was maintained by using the NaCl electrolyte and the dilute solution of NaOH and HCl were used to adjust the solution pH. The EO experiments were conducted to optimize the various operating parameters within the various ranges such as initial pH (pH_o) of solution 3.8–10, current density (j): 56.31–225.25 Am⁻², electrolyte concentration (m): 150–300 mgL⁻¹ and treatment time of 180 min. The treated solution was collected at different time intervals of each experiment and centrifuged then filtered prior to know the residual TOC and PFOA concentration.

2.4 Instrumental analysis

The initial and final concentration of PFOA was determined with a UV- spectrophotometer (UV-1800, Shimadzu) and TOC of the solution was measured in a TOC analyzer (1030 TOC analyzer, USA) equipped with OI Analytical model. Before TOC detection, all samples were acidified, filtered with 0.22- μ m syringe filter and then nitrogen gas spurge in the solution to remove the inorganic carbon before the analysis. Gas chromatograph-mass spectra (GC-MS) analysis was used to detect the intermediate by-products. For GC-MS analysis, GC and mass spectrometer (MS, Saturn 2100T) equipped with a capillary column and electron spray source respectively to extract the intermediate by-products of PFOA by using the 1:1 ratio of 10mL of di-chloro-methane (DCM) mixed with 10 mL sample of treated PFOA solution. This procedure was repeated thrice, and then anhydrous sodium sulfate (dehydrating agent) was used to dehydrate the sample. The complete range of mass spectra was obtained between the 100 to 450 m/z by using the following program.

The desolvation and source temperature were kept at 550°C and 120°C. The capillary potential and cone voltage were 4.5 kV and 35 V, respectively. N₂ gas pressure was 0.8 MPa at 1.0 s scan time and an average of 90 scans were used to obtain the mass spectra. NIST library was used to determine the intermediate by-products. Fluoride ions concentration (F⁻) was measured by using an ion chromatograph system (ICS-3000, Dionex, USA) with a separation column (150 × 4.0 mm) couple with conductivity detector. A mixture of NaHCO₃ (1.0 mM) and Na₂CO₃ (3.2 mM) was used as a mobile phase at 2 mL min⁻¹ flow rate for anion measurement, and 50 µL was kept the sample injection volume.

The TOC and PFOA removal efficiencies were determined by using the following relationships (Eqs. 1-4):

$$\text{TOC removal (\%)} = \frac{(TOC_o - TOC_f)}{TOC_o} \times 100 \quad (1)$$

$$\text{PFOA removal (\%)} = \frac{PFOA_o - PFOA_f}{PFOA_o} \times 100 \quad (2)$$

where TOC_o/TOC_f and PFOA_o/PFOA_f are the TOC and PFOA concentrations (mgL⁻¹) at t=0 and after t=t.

The amount of energy absorbed (in kWh) per kg TOC removed in terms of specific energy consumption (SEC) was measured by using the following expression:

$$\text{SEC} = \frac{V_{ap} I \Delta t}{(TOC_i - TOC_f) V_r} \times 100 \quad (3)$$

where TOC_i/TOC_f are the initial and final TOC (mg L⁻¹), V_{ap}, I and t are the applied voltage (V), applied current (A) and electrolysis time (h), respectively.

During electro-oxidation, the removal efficiency is directly proportional to the oxidants produced during electrolysis and initial PFOA concentration. Therefore, the kinetics of PFOA and TOC removal can describe via the pseudo first-order kinetic mode

$$\frac{d}{dt}[C] = k[C] \quad (4)$$

The value of k rate constant (min^{-1}) for TOC reduction (mg L^{-1}) was determined by plotting the graph between $\ln(C_0/C_t)$ versus treatment time t (min).

3. Results and discussion

3.1 Effect of pH

Solution pH greatly affected the PFOA and TOC removal efficiencies because it influences the concentration of OH production, life span of anodes, and OER which consequently affects the EO efficiency of PFCs removal [1,22]. Fig. 1a and b shows the pH effect from 3.8-9 at $j=166.67 \text{ Am}^{-2}$, initial PFOA concentration 100 mg L^{-1} and NaCl concentration of 250 mg L^{-1} . PFOA and TOC removal efficiencies were found to be higher in the acidic range of solution pH because higher OER and OH radicals' production rate increased [19,23]. In acidic medium, the low range the solution pH restricts the O_2 evolution reaction which increases the degradation of PFOA to some degree. Fig. 1a and b shows the maximum PFOA and TOC reduction at $\text{pH}=3.58$, but the removal efficiencies were decreased from the pH of 5 to 9. This is because the active sites of an electrodes adsorbed more OH radicals in the alkaline medium, these radicals progressively react with $\text{CF}_3(\text{CF}_2)_6\text{CO}_2^-$ anion via the decarboxylation reaction, whereas the acidic pH range helps in PFOA removal. [19] These results confirm that the acidic pH promote the PFOA degradation with Ti/SnO₂-Sb electrode than alkaline pH. The PFOA degradation rate was found 2 times higher at initial pH of 5 than that of $\text{pH}=11$. Similarly, Zhao et al. [23] was observed that the PFOA degradation rate decreased with Si/BDD anode with increasing the pH conditions in the following sequence of $\text{pH } 3 > \text{pH } 9 > \text{pH } 12$. Fig. 1c shows the pH effect on SEC. The SEC values were found maximum for $\text{pH}=3.8$ after 180 min of electrolysis, while the value of SEC increased from 660-743.24 kWh/kg TOC with increasing the solution pH from 3.8 to 9. Fig. 1d shows the values of k and R^2 decrease from 14×10^{-3} to 9×10^{-3} when solution pH was increased from $\text{pH}=3.8$ to $\text{pH}=9$, signifying that acidic pH more favorable to increasing the PFOA degradation and higher OH radicals generation.

3.2 Effect of applied current density

The j value is an important operating parameter that influences the EO of PFOA in aqueous solution; it regulates the OH radical generation and electron transfer on the surface of electrode [19,22,23]. Fig. 2a and b illustrates the effect of j on PFOA degradation and TOC reduction in the range of 56.31-225.25 Am^{-2} .

Figure 1: Effect of j on PFOA degradation: (a) PFOA removal, (b) TOC removal efficiency, (c) kinetics studies, and (d) SEC (kWh/kg TOC) at pH 3.8, $m = 250 \text{ mgL}^{-1}$ and $C = 100 \text{ mgL}^{-1}$ at different time intervals.

Fig 2: Effect of solution pH on PFOA degradation: (a) PFOA removal, (b) TOC removal efficiency, (c) kinetics studies, and (d) SEC (kWh/kg TOC) at $j=168.9 \text{ Am}^{-2}$, $m = 250 \text{ mgL}^{-1}$ and $C = 100 \text{ mgL}^{-1}$ at different time intervals.

Table 1: TOC removal and kinetic characteristics of PFOA degradation after 150 min of electrolysis for different parameters.

Parameters	TOC removal (%)	Kinetic Study	
		K (min ⁻¹)	R ²
j (A m ⁻²) Other conditions: pH = 3.5, C _o = 100 mg L ⁻¹ , m = 1.5 g L ⁻¹			
56.31	62	7×10 ⁻³	0.963
112.62	75	12×10 ⁻³	0.995
168.94	82	14×10 ⁻³	0.996
225.25	87	15×10 ⁻³	0.997
Solution pH _o Other conditions: j = 168.94 A m ⁻² , C _o = 100 mg L ⁻¹ , m = 1.5 g L ⁻¹			
3.8	82	14×10 ⁻³	0.963
5	75	12×10 ⁻³	0.996
7	74	10×10 ⁻³	0.997
9	68	9×10 ⁻³	0.986
m (mgL ⁻¹) Other conditions: j = 168.94 A m ⁻² , C _o = 100 mg L ⁻¹ , pH _o = 3.8			
150	67	9×10 ⁻³	0.994
200	73	10×10 ⁻³	0.995
250	82	12×10 ⁻³	0.991
350	89	14×10 ⁻³	0.996

The low $j=56.31 \text{ A m}^{-2}$ could not sufficient to stimulate the PFOA degradation because low potential compared to oxidation potential of PFOA degradation and also a poor OH radicals concentration were produced by the anodes [22]. For example, 6.2% PFOA decomposition was attained at low $j= 1.42 \text{ mA cm}^{-2}$ with Ti/ $\text{SnO}_2\text{--Sb}_2\text{O}_5\text{--Bi}_2\text{O}_3$ electrode [22]. However, PFOA and TOC removal efficiencies were increased with increasing the j from 56.31-225.25 A m^{-2} . For $j=168.94 \text{ A m}^{-2}$, the PFOA and TOC removal were maximum about more than 90% and 82%, respectively (Fig. 2a and b) because rate of OH radical formation rate increased with increasing the j with t (Eqns. 5 and 6) that effectively participates in the oxidation reaction and PFOA mineralization (Eqn. 7). Similarly, H_2O_2 production rate also increased via the cathodic reaction of oxygen reduction (Eqns. 8 and 9) at higher j , which in turn raises the electron generation rate and helps in the PFOA degradation [19,23]. The PFOA decomposition rate considerably increased from 76.9% to 98.8% with Ti/SnO₂–Sb anode when the j values were increased from 5 to 40 mA cm^{-2} after 90 min of electrolysis. Fig. 2a and b shows a slightly changed in PFOA oxidation at higher j of 225.25 A m^{-2} because O_2 discharge reaction and diffusion control suppressed the PFOA degradation.

Moreover, higher j leads to higher energy consumption and shorter electrode life. Thus, it is very essential to select an appropriate j for PFOA removal in practical application. Fig. 2c has shown the difference of SEC at different j and various time intervals. An increase in j and t , the SEC values increased because the PFOA conversion into stable intermediates by-products increased that oppose the more oxidation behind a definite time of treatment, therefore the SEC value was increased. The SEC value for higher PFOA degradation and TOC reduction at $j=168.94 \text{ Am}^{-2}$ was found to be $660.23 \text{ kWh/kg TOC}^{-1}$. Fig. 2d shown straight lines of PFOA degradation with time at different j because the PFOA degradation kinetics were followed the pseudo-first order at different j values. Table 1 illustrates the different values of k and R^2 for TOC reduction at different j . The k and R^2 values were increased from 7×10^{-3} to 15×10^{-3} and 0.963-0.997, respectively at j from 56.31-225.25 Am^{-2} .

3.3 Effect of electrolyte concentration

An electroconductive medium of electrolysis was provided by using the supporting electrolytes to minimize the resistance of electrochemical reactor and the voltage drop [19,23]. A better pollutant removal was occurred with higher conductivity which leads to the quick electrons transport [1]. Fig. 3a and b shows the PFOA and TOC removal efficiencies, these values were increased with increasing the amount of NaCl electrolyte concentration. The concentration of NaCl was increased from 150 to 250 mgL^{-1} then the PFOA and TOC removal were also increased from 70 to 95% and 67 to 84%, respectively, however, at a certain level of NaCl concentration which is about 300 mgL^{-1} no further removal were formed. Fig. 3c shows the value of SEC increased with different electrolyte concentration. However, a certain change was formed with time for a particular time interval. This is the reason of maximum TOC reduction was attained between 30-150 min of electrolysis, therefore the PFOA degradation was significantly influenced by the dose of electrolyte. Higher the dose of NaCl facilitates electron transfer between the pollutant

and the electrode via offering the active species such as OH radicals and chlorine. Chloride ions (Cl^-) were produced in via the electrochlorination when NaCl used as an electrolyte.

The main chlorination reactions formed during EO via the anodic and cathodic reactions of Cl^- ions with electro-generated $\cdot\text{OH}$ radicals are discuss (Eq. 11-14) [24]. At anode, the Cl^- ions oxidized directly into soluble Cl_2 (Eq.10):

Even though the Cl_2 and H^+ concentrations are not sufficient, the Cl_2 potentially contributes in the formation of other active chloro species such as ClO^- (Eq.11), HOCl (Eq.12), ClO_2 (Eq.13) and $\text{Cl}^\bullet$ (Eq.14) by the disproportionate reactions which could effective enhanced the PFOA degradation.

Moreover, when electrolyte concentration increased, the conductivity of solution also enhanced because increasing the electron transfer rate which enhanced the PFOA degradation rate [22]. The straight lines of PFOA degradation with time at different m in Fig.3d depicted the degradation was followed the pseudo-first order kinetics. Table 1 shows the values of k and R^2 for TOC reduction at various m. The k and R^2 values were increased from 9×10^{-3} to 14×10^{-3} and 0.994-0.996, respectively at m from 150 to 300 mg L^{-1} and illustrated the about 67 to 89% TOC reduction.

Figure 3: Effect of NaCl dose (mg L^{-1}) for the PFOA mineralization (a) PFOA removal, (b) TOC removal efficiency, (c) kinetics studies, and (d) SEC (kWh/kg TOC) at $j=168.9 \text{ Am}^{-2}$, $\text{pH}=3.8$ and $C = 100 \text{ mg L}^{-1}$ at different time intervals.

3.4 Mineralization mechanism of PFOA

The EO mechanisms of organic pollutants removal concerned the OH[•] mediated oxidation or e⁻ transfer from target molecules to the anodic surface via the direct or mediated EO. Many previous reports have been confirmed that OH[•] mediated oxidation was not more effective for PFOA degradation, the EO studies of PFOA removal was mainly ascribed to the direct oxidation [1]. GC-MS analysis was employed to analyze the samples collected at different time intervals during the treatment at the optimal treatment conditions and identified the various intermediates by-products. There are different paths of PFOA degradation as describe in the plausible degradation mechanism represented in Fig. 4 based on the previously reported studies on PFOA degradation and intermediates identified [1,25]. Electrochemically generated main active species such as electrons (e⁻), OH[•], and O₂^{•-} radicals were formed during EO. At the beginning, C-F bond more preferable cleavage via the interaction of electrochemically generated e⁻ (Eqs.15-18).

In addition, the inductive effect (IE) of the carboxyl group of PFOA supports the more easily C-F bond breaking via the attack of electrochemically generated e⁻ (Shown in Fig. 4).

Figure 4: EO mechanism of PFOA degradation on Ti/SnO₂-Sb₂O₅/PbO₂ anode.

C_6F_{13} radical, carbene ($:CH_2$) and $COOH$ radical were generated by the EO reactions of $C_7F_{13}H_2COOH$, then both C_6F_{13} and $COOH$ radicals could interact to form $C_6F_{13}COOH$ (PFHpA) (Eq. 19 and 20):

Figure 5: Plausible degradation mechanism of PFOA at the optimal treatment condition of electrochemical oxidation with $Ti/SnO_2-Sb_2O_5/PbO_2$ anodes.

Table 2: Different m/z values and their corresponding intermediate by-products.

m/z	412	368	364	318
Fragment ions	$C_7F_{15}CO_2^-$	$C_7F_{15}^-$	$C_6F_{13}CO_2^-$	$C_6F_{13}^-$
m/z	312	264	218	212
Fragment ions	$C_5F_{11}CO_2^-$	$C_4F_9CO_2^-$	$C_4F_9^-$	$C_3F_7CO_2^-$
m/z	168	164	118	114
Fragment ions	$C_3F_7^-$	$C_2F_5CO_2^-$	$C_2F_5^-$	$CF_3CO_2^-$

As a result, PFHpA was decaying into $C_6F_{13}CO_2^-$ (PFHxA) and $C_5F_{11}CO_2^-$ (PFPeA), which were further continually degraded into $C_3F_7CO_2^-$ (PFBA), $C_2F_5CO_2^-$ (PFPA) and $CF_3CO_2^-$ (TPA) in the similar way and was lastly, mineralized to CO_2 and F^- ions in a stepwise

approach [26,27]. The detail of GC-MS analysis at different time intervals was used to know the decomposition products and CF₂ flake-off process summarized in Table 2. The ions peaks C₇F₁₅CO₂ (m/z = 413), C₇F₁₇CO₂ (m/z = 385), C₇F₁₅ ((m/z = 369) (Eq.19), and C₆F₁₃CO₂ (m/z = 363) (Eq.20), which can give significant information for the CF₂ mechanism [25]. Based on the literature and experimental results [19,25], a plausible degradation mechanism including radical reaction, decarboxylation, decomposition and hydrolysis was described for the PFOA removal at the Ti/SnO₂-Sb₂O₅/PbO₂ anodes (Fig. 5). The Carboxyl group (–COOH) of PFOA transfer an e[–] to the anode and exist in form of PFOA radicals (C₇F₁₅CO₂•) (Eq. 15) via the path II [18]. The perfluoroalkyl radicals were formed via the decarboxylation reactions of very highly unstable C₇F₁₅CO₂• radicals (Eq.14).

Then C₇F₁₅• react with H₂O, O₂, or OH• to form C₇F₁₅OH and C₆F₁₃COF (Eq. 21–27) by the elimination of H⁺ and F–[19]. Moreover, C₇F₁₅• radicals may react with O₂ (Eq. 26) and another perfluoroheptylperoxy radical (R_fCO₂•) to form perfluoroalkoxy radical (C₇F₁₃O•) via the Eq. 27

Subsequently, the $C_7F_{13}O\cdot$ may follow the two degradation pathways: (i) hydrolysis with H_2O to form alcohol $C_7F_{15}OH$ (Eqs. 23 and 24) and (ii) decomposition to perfluorohexyl radical ($C_6F_{13}\cdot$) and carbonyl fluoride (COF_2) via the Eq. 28. Finally, COF_2 will again hydrolysis with complete decay (Eq. 29).

Conclusion

Present study proposed the electro oxidative degradation of PFOA with $Ti/SnO_2-Sb_2O_5/PbO_2$ electrode. More than 90% PFOA and 82% TOC removal efficiency were formed at j of $168.94 Am^{-2}$, pH of 3.58 and NaCl concentration of $250 mg L^{-1}$ after 120 min of electrolysis with keeping the electrode gap of 1 cm fixed. The reaction kinetic of TOC reduction was followed the pseudo-first-order kinetics. The value of k for PFOA was increased with increasing the j and electrolyte concentration, whereas the removal efficiencies were decreased with increasing the solution pH. Active species such as chloro species ($Cl\cdot$, $ClO\cdot$, $ClO_2\cdot$, $HClO$), $OH\cdot$, and $O_2\cdot^-$ were produced during electrolysis and play a significant role in the mineralization of PFOA. The short-chain (C_2-C_7) perfluorocarbons (PFCs) intermediate were detected and a plausible degradation mechanism of PFOA degradation was described during electrolysis based on the intermediate by-products formed during electrolysis.

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