

DECOMPOSITION OF PERFLUOROOCCTANOIC ACID WITH ELECTROCHEMICAL OXIDATION METHOD

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Introduction

Perfluorooctanoic acid (PFOA, C₇F₁₅COOH) belongs to a new class of persistent organic pollutants. Because of their hydrophobisity and oleophobisity, they have been widely used in non-stick polymers, oxidative protective coating on metals and fire retardants^[1]. The extensive use of PFOA and their stability have resulted in exposure of humans sera^[2], livers of birds^[3] and waters^[4]. In order to reduce and restrict impact of PFOA on ecosystem and human being, PFOA has been added to the Stockholm convention on persistent organic pollutants in the Fourth Conference of Parties held in Genevese in May 2009.

Various techniques have been performed to remove PFOA. Totally, they are classified into three categories: photocatalysis, ultrasonication and incineration. Here, a new technique is promoted to decompose PFOA, which is electrochemical oxidation with Ti/SnO₂-Sb-Bi electrode.

Materials and methods

Titanium sheet of 42mm×42mm was polished with dry grinding cloth of 180 mesh, water proof abrasive paper of 300 mesh and 800 mesh respectively to remove the oxide film on the titanium. After that it was washed in the MillQ water. And the sheet was kept in 40 % sodium hydroxide at 80 °C for two hours to removal grease. Then, it was etched in boiling 18 % hydrochloric acid at the temperature of 98 °C for 2h to produce gray surface with uniform roughness.

The painting solution for Ti/SnO₂-Sb-Bi electrode was prepared by Pechini method. Firstly, citric acid and ethylene glycol were kept and agitated at 60 °C, until dissolved. Then, adjust the temperature to 90 °C, in which SnCl₃ and SbCl₄ dissolved in the isopropanol were added while stirring with the molar ratio of Sb : citric acid : ethylene glycol = 1 : 3 : 10. Finally, BiCl₃ dissolved in the isopropanol was added in the previous solution with the molar ratio of Sn : Sb : Bi = 89 : 3 : 8. Such solution was maintained at 90 °C for two hours to get sol-gel.

10 μL sol-gel was dripped onto the both side of the Ti sheet with finnpipette. And then disperse the sol-gel by a brush as uniformly as possible. After that, they were dried at 120 °C for 10 min in the oven, and then sintered at 600 °C for 10 min in the muffle furnace. These procedures were repeated 16 times. The last baking was maintained at 600 °C for 60 min.

Electrochemical oxidation of PFOA was carried out in 200 mL container made of organic glass equipped with a

magnetic stirrer. The working anode was Ti/SnO₂-Sb-Bi with 42mm×42mm. Ti sheet with the same area was used as cathode. And the gap of the electrode was 10mm. For the electrolysis test, 200mL of PFOA solution (100 mg/L) was placed in the cell with 1.4 g/L NaClO₄ as the electrolyte. The current was controlled at 0.25 A at Chronopotentiometry technique with CHI636B electrochemical workstation. The stirring rate was 1500 r/min.

An ion-chromatograph system (Dionex ICS-1000, USA) consisting of an automatic sample injector (sample injection volume:25 μL), a degasser, a pump, a guard column (Dionex AG22, 4×50 mm, USA), a separation column (Dionex AS22, 4×250 mm, USA), a column oven (30 °C), and a conductivity detector with a suppressor device was used to measure the F⁻ ion concentrations. The mobile phase was composed of 4.5 mM Na₂CO₃/1.4mM NaHCO₃ and flow rate was set at 1 mL/min.

The concentrations of PFOA were determined using an LC-10ADvp HPLC with a CDD-6A conductivity detector from Shimadzu (Japan). The TC-C18 column (4.6 × 250mm) from Agilent Technologies (USA) was adopted and the mixture of methanol/0.02 M NaH₂PO₄ (65/35, v/v) was used as the mobile phase at 1.2 mL/min flow rate. The sample volume injected was 20 μL. In this study, the detection limits of PFOA were about 0.7 mg/L and a column oven was set at 40 °C.

Concentrations (C₃F₇COOH, C₄F₉COOH, C₅F₁₁COOH and C₆F₁₃COOH) was analyzed using ultra-performance liquid chromatography coupled with a tripe-stage quadrupole mass spectrometer(UPLC–MS/MS, Quattro Premier XE, Waters Corp., USA) equipped with Acquity UPLC BEH C18 column (2.1×50 mm, 1.7 μm) with an electrospray negative ionization mode. The mobile phase A was 2 mM ammonium Acetate in 100% methanol. The mobile phase B was 2 mM ammonium acetate in 5% methanol and 95% H₂O. The flow rate was 0.3 mL/min. A column oven was set at 50 °C. The sample volume injected was 10 μL with a automatic sampler.

Results and Discussion

The degradation of PFOA was carried out at an initial concentration of 100 mg/L. [Figure 1a](#) shows the time dependence of electrolysis degradation of PFOA. 90.03% of PFOA was removal after 3 hour electrolysis ([Figure 1a](#)). Pseudo-first-order kinetics ([Figure 1b](#)) were given in Eq. 1

$$\frac{d[\text{PFOA}]}{dt} = -k[\text{PFOA}] \quad (1)$$

Where k is the first-order-order rate constants for PFOA decomposed by Ti/SnO₂-Sb-Bi electrode. A linear fit of kinetic plots gives $k = 0.013\text{min}^{-1}$, which is higher than the $k = 0.0029\text{ min}^{-1}$ ^[5] in the reduction system of UV/KI, indicating that electrochemical oxidation with Ti/SnO₂-Sb-Bi electrode is also a kind of effective method to degrade PFOA. And the yield of F⁻ reached 51.91% in [Figure 1a](#). The extent of defluorination (F index = - [F⁻]_{produced}/[PFOA]_{degraded} ^[5]) was plotted as function of electrolysis time in [Figure 2](#). For the PFOA, the F index was almost unchanged in the three hours, with approximately one defluorination per carbon (i.e., 8 for PFOA). The detectable intermediates in the wastewater were C₆F₁₃COOH, C₅F₁₁COOH, C₄F₉COOH and C₃F₇COOH in [Figure 3](#).

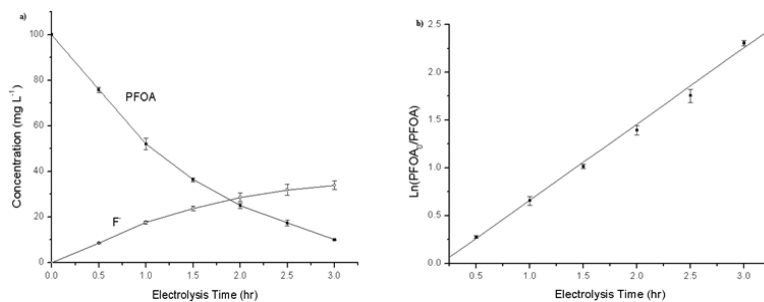


Figure 1 a) Change of PFOA concentration as a function of electrolysis time at current of 0.25 A (Ti/SnO₂-Sb-Bi of 42×42mm) at 32 °C. b) Pseudo-first-order plots of decomposition with time

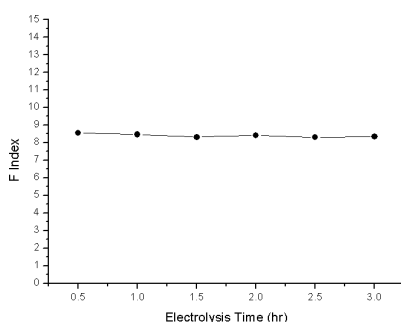


Figure 2 F index (defluorination extent) during the electrolysis of PFOA

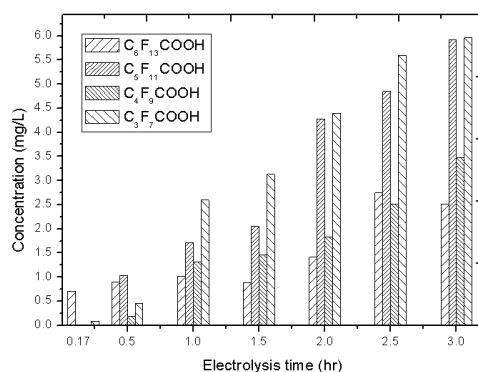


Figure 3 Time independence of intermediate products of PFOA decomposition with Ti/SnO₂-Sb-Bi electrode: detected concentration of PFCAs (C₆F₁₃COOH, C₅F₁₁COOH, C₄F₉COOH, C₃F₇COOH)

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