Photocatalytic Decomposition of Environmentally Persistent Perfluorooctanoic Acid

Jing Chen, Pengyi Zhang,* and Li Zhang
Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, P. R. China

(Received November 24, 2005; CL-051454; E-mail: zpy@mail.tsinghua.edu.cn)

Perfluorooctanoic acid was photocatalytically decomposed by using TiO_2/Ni–Cu, and a small bias potential (−0.1 V) applied on TiO_2/Ni–Cu electrode greatly enhanced its decomposition.

Perfluorocarboxylic acids (PFCAs) are a class of special chemicals used as emulsifying agents in polymer synthesis and as surface treatment agents in photolithography, paper coatings, and waxes and polishes.[1] Recently, perfluorinated acids especially perfluorooctanoic acid (PFOA, $C_7F_{15}COOH$) and perfluorooctanesulfonic acid (PFOS) have been widely identified in the environment such as human and marine biota plasma, blood and liver tissue,[2] surface water, fresh water, air and dust, sediments, and domestic sludge,[3] and even in remote areas such as the Arctic.[4] These compounds are very stable due to C–F bond, and do not decompose naturally. Thus, they persist and bioaccumulate in the environment. The temperature required for thermal decomposition is as high as 1200 °C. Thus, it is necessary to develop effective methods to decompose PFCAs to harmless species under mild conditions.

Recently, Hori et al.[5] reported the photochemical decomposition of PFCAs by use of persulfate ($S_2O_8^{2-}$) as oxidant or by a homogeneous photocatalyst i.e. tungstic heteropolyacid ($H_3PW_{12}O_{40}$) under UV–visible light irradiation (220–460 nm). They argued that PFCAs were oxidized by the photoexcited species ($SO_4^{\cdot -}$ or $[PW_{12}O_{40}]^{3-*}$), i.e. one electron was transferred from PFCAs to the photoexcited species. Moriwaki et al.[6] also reported the sonochemical decomposition of PFOS and PFOA under air or argon atmosphere. And they concluded that PFOS and PFOA were mostly pyrolyzed at the interfacial region between the bulk solution and the cavitation bubbles where the temperature was as high as several thousands due to sonication.

Except the C atom of carboxyl in PFOA, other C atoms are connected to F atoms. Because of high electronegativity of F atom, the C atom is highly positive, and thus PFOA is very difficult to be oxidized. It has been demonstrated that PFCAs including PFOA can not be decomposed by reaction with hydroxyl radicals (OH•), which is a strong oxidant only secondary to F atom.[5,6] Though it was difficult to be oxidized, PFOA may be decomposed through reduction. In general, electron–hole pair is generated when the semiconductor photocatalyst is illuminated with UV light, and the photogenerated electron is highly reductive. It was well reported that CCl_4[7] or perhalogenated bezenes[8] were reductively decomposed and dehalogenated in the photocatalytic process. Here, we firstly reported that PFOA was photoreductively decomposed and defluorinated by use of an immobilized TiO_2/Ni–Cu photocatalyst.

The TiO_2/Ni–Cu photocatalyst was prepared as follows. Firstly, nickle was electrodeposited on the copper sheet. And then a thin TiO_2 film was coated on the above sheet by sol–gel method. Finally, it was heated at 450 °C for 1 h. The photocatalytic decomposition reaction was conducted in a glass tubular photoreactor. A low-pressure mercury lamp (23 W) with main wavelength at 254 nm was used as UV source. The lamp was placed in the center of the photoreactor with quartz tube protection (external diameter 25 mm). The gap between the inner wall of the photoreactor and the external wall of quartz tube was 15 mm. An aqueous solution (250 mL) of PFOA (25 mg/L; 0.05 mM) was filled into the reactor. The TiO_2/Ni–Cu photocatalyst sheet (75 × 10 mm) was attached on the inner wall of the photoreactor. A saturated calomel electrode (SCE) and a platinum sheet (25 × 20 mm) were used as reference and counter electrodes, respectively. And an electrochemistry workstation (CHI660B) was used to control the potential at the surface of the photocatalyst electrode. Before turning on the lamp, nitrogen gas was bubbled into the reactor to remove the oxygen in water. The concentrations of PFOA and photocatalytic products were determined by LC-MS (ZQ 4000, Waters, U.S.A.). Fluoride ion (F^-) was determined by ion chromatography (761 compact IC, Metrohm).

Figure 1 shows the photocatalytic decomposition of PFOA in the presence of TiO_2/Ni–Cu. The direct photolysis of PFOA under 254 nm UV light was very slow and negligible. However, PFOA decomposed significantly in the presence of TiO_2/Ni–Cu, it almost disappeared after 6 h. And at the same time fluoride ion in aqueous solution was detectable, after reaction of 6 h, the defluorination was up to 40% (Figure 2), i.e. averagely 6 of 15 fluorine atoms in PFOA molecule were transformed into inorganic fluoride ion. However, when we used P25 TiO_2 powder or sol–gel prepared TiO_2 film as photocatalyst, no significant decomposition of PFOA was observed.

Furthermore, if the TiO_2/Ni–Cu photocatalyst electrode was applied with −0.1 V bias potential vs SCE, and 0.1 mol/L Na_2SO_4 was used as supporting electrolyte, the decomposition of PFOA was greatly enhanced as compared to open circuit condition. As shown in Figure 1, 92.5% PFOA was decomposed within 2 h, and it completely decomposed after 4 h. Defluorination ratio was also greatly enhanced, after 6 h reaction up to 85.6%.

The decomposition products of PFOA were also detected

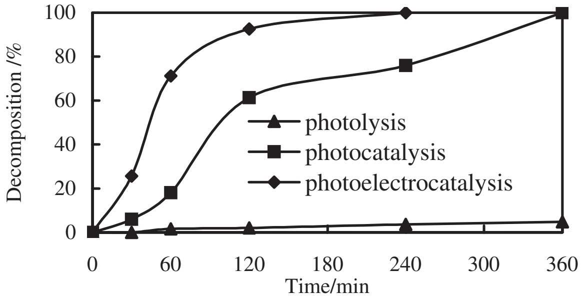

Figure 1. Decomposition of PFOA with reaction time.

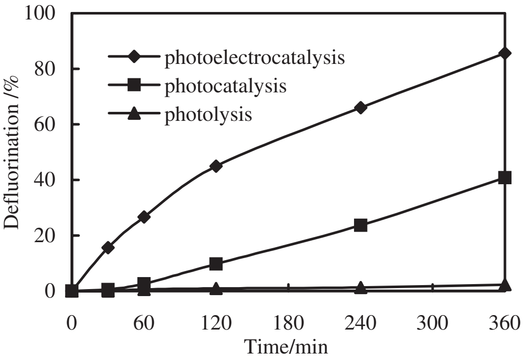

Figure 2. Defluorination of PFOA with reaction time.

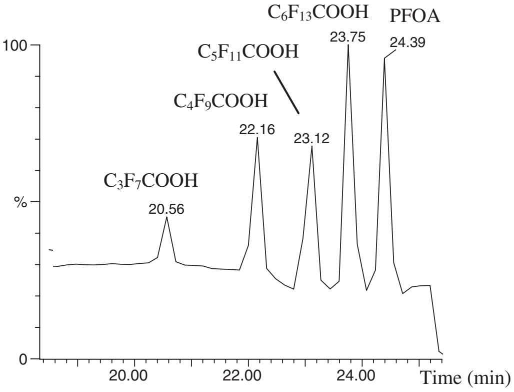

Figure 3. TIC spectra of PFOA and its decomposition products.

and identified by LC-MS according to their mass spectra and retention time (Figure 3). The main products were shorter perfluorinated carboxylic acids containing 4–7 carbon atoms, including perfluorobutyric acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), and perfluoroheptanoic acid (PFHpA). Small amount of trifluoroacetic acid (TFA) and pentafluoropropionic acid (PFPA) were also detected. The decomposition products are the same as those reported by Hori et al.[5] and Moriwaki et al.[6] The change of concentrations of PFBA, PFPeA, PFHxA, and PFHpA with reaction time in the photoelectrocatalysis was shown in Figure 4.

For the mechanism of PFOA photochemical decomposition, Hori et al.[5] proposed that oxidant ($S_2O_8^{2-}$) or homogeneous photocatalyst ($H_3PW_{12}O_{40}$) was firstly photoexcited, and then PFOA was oxidized by the photoexcited species ($SO_4^{\cdot -}$ or $[PW_{12}O_{40}]^{3-*}$), i.e. PFOA donated one electron. In our experiment, PFOA decomposition was carried out under nitrogen atmosphere, and no extra oxidant was added. For the TiO_2/Ni–Cu photocatalyst, the open circuit potential in the dark was −0.08 V vs SCE. When it was irradiated with 254 nm UV light, an instant photogenerated potential of over than 100 mV was observed. The potential of TiO_2/Ni–Cu photocatalyst positively increased to 0.02 V vs SCE. This suggests that photogenerated electrons and holes were quickly separated, and photogenerated electrons transferred to the surface of photocatalyst film and accumulated, whereas holes transferred to metal substrate (Ni deposited Cu). Because the surface of the photocatalyst was in contact with PFOA aqueous solution, the photogenerated electrons would initiate the PFOA decomposition and the negative bias potential (−0.1 V) effectively enhanced the decomposition. Hence, from our observations, C–F bond cleavage was initially induced by reduction mechanism. This mechanism was not strange, because it is difficult for PFOA to donate an electron. Fluoride atom in PFOA tends to accept an electron, which leads to break of C–F bond.

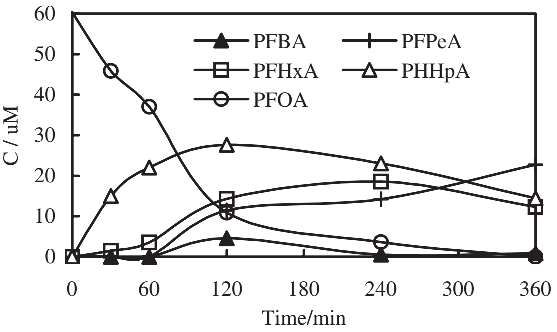

Figure 4. Changes in the concentrations of PFOA and intermediates.

This work was supported by NSFC (No. 20577026) and NCET (No. NCET-04-0090).

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Published on the web (Advance View) January 21, 2006; DOI 10.1246/cl.2006.230