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Electrochemical and Photocatalytic Decomposition of Perfluorooctanoic Acid with a Hybrid Reactor Using a Boron-doped Diamond Electrode and TiO_2 Photocatalyst

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The efficient decomposition of environmentally persistent perfluorooctanoic acid (PFOA) was achieved by a hybrid of electrolysis and photocatalysis. The rate constant of PFOA decomposition in the hybrid system was larger than the sum of the constants in electrolysis-only and photocatalysis-only systems. The hybrid system was able to accelerate the PFOA decomposition by complementally support of two kinds of reaction kinetics. These results could be useful for development of a new continuous system for practical treatment of waste water containing perfluorinated acids.

Perfluorinated acids have been widely used in industry (e.g., surfactants, surface treatment agents, and flame retardants). However, some of them, particularly PFOA ($C_7F_{15}COOH$), have been detected in the environment.[1,2] Analytical studies have revealed their toxicological properties and high stability.[3] Thus, techniques for decomposing them under mild conditions are desirable. Recently, we reported the development of electrochemical and photocatalytic water treatment using a boron-doped diamond (BDD) electrode and TiO_2 photocatalyst.[4] High-level waste water containing environmentally persistent compounds was converted to low-level waste water by the electrolysis on BDD electrode. The low-level waste water was then purified by photocatalysis on TiO_2. Therefore, these two methods for water treatment are complementary. We also reported the electrochemical decomposition of PFOA by use of a BDD electrode.[5] From these results, here we report the efficient electrochemical and photocatalytic decomposition of PFOA with a hybrid reactor using a BDD electrode and TiO_2 photocatalyst.

PFOA was obtained by Tokyo Kasei Kogyo Co., Ltd. TiO_2 nanoparticles (P25) were obtained from Evonik Industries. A schematic view of the hybrid system used for PFOA decomposition is shown in Figure 1. The photocatalysis unit consists of a glass vessel (inner diameter 133 mm × height 40 mm, nominal volume, 0.5 L), equipped with a quartz window, sampling ports, and a medium pressure ultraviolet (MPUV) lamp (U46C18, Heraeus). The electrolysis unit consists of a single compartment electrochemical flow cell using BDD and Pt electrodes. In the present research, two types of reactor, plate type and tube type, were used for electrolysis (Figure 2). The plate reactor has been used for previous research.[4] The tube reactor consists of commercially available BDD electrode (Element six) as the anode and a Pt foil as the cathode. Both electrodes had area of 27 cm^2, and the electrode gap was 1 cm. In a typical run, an aqueous suspension (0.5 L) containing PFOA (2.5 mM), $NaClO_4$ (0.1 M), and P25 TiO_2 nanoparticles (1.5 wt%) was filled into the photocatalysis unit and circulated through the electrolysis unit by a pump at a flow rate of 0.2 L min^{-1}. The UV intensity for the photocatalysis and the current density for the electrolysis were maintained at 600 mW cm^{-2} (at 254 nm) and 0.6 mA cm^{-2} (3.0 V), respectively. For comparison, decomposition behaviors by electrolysis-only and photocatalysis-only were evaluated. During the reaction, the aqueous phase was analyzed by HPLC to quantify the concentration of PFOA and to identify the decomposition products in the aqueous phase. Analytical procedures have been previously reported.[5] The experiments were carried out at room temperature and atmospheric pressure.

Figure 3 shows the electrolysis time dependence of the survival rate of PFOA for plate and tube reactors without a

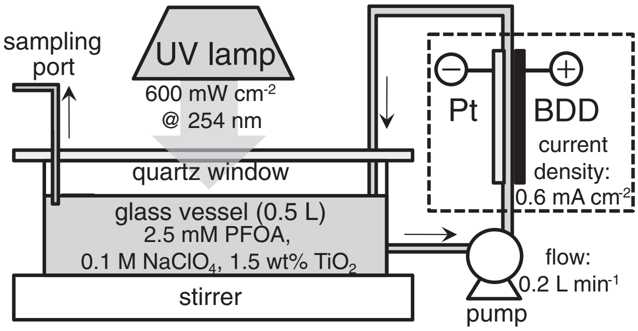

Figure 1. Schematic view of electrolysis–photocatalysis hybrid system.

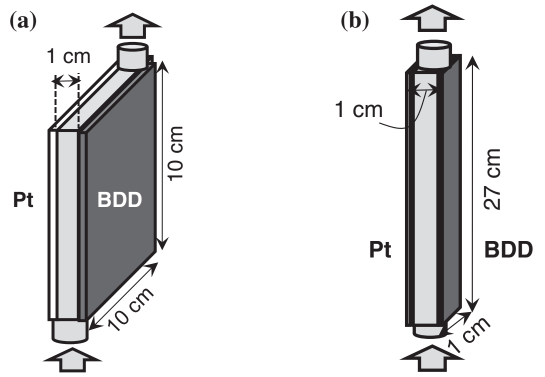

Figure 2. Schematic illustrations of electrolysis unit (inside the broken rectangle in Figure 1). (a) plate-type, (b) tube-type.

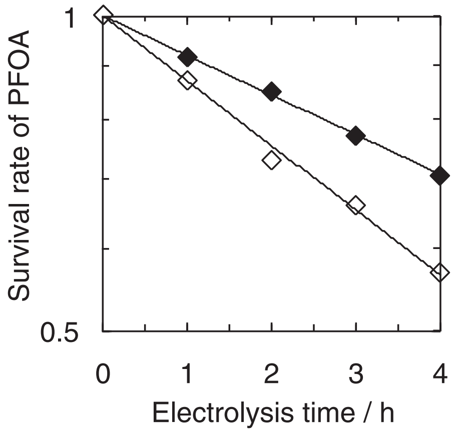

Figure 3. Comparison of efficiency for PFOA decomposition by plate (solid diamonds) and tube (open diamonds) reactor without suspension of TiO_2.

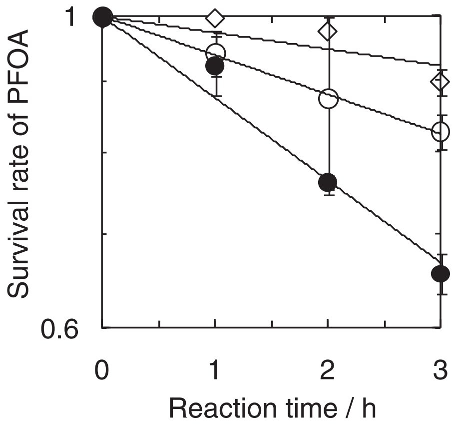

Figure 4. Comparison of efficiency for PFOA decomposition by electrolysis-only (open diamonds), photocatalysis-only (open circles), and hybrid system (solid circles).

suspension of TiO_2. Survival rate was calculated from the ratio of the PFOA concentration to the initial concentration of PFOA. In the plate reactor, the PFOA decomposition followed pseudo-first-order kinetics with an observed rate constant of 0.34 $mL\,h^{-1}\,cm^{-2}$, similar to a previous report.[5] On the other hand, the tube shows a rate constant of 3.7 $mL\,h^{-1}\,cm^{-2}$, approximately 11 times greater than the plate reactor. The HPLC chromatograms of both reaction solutions using plate and tube reactors showed a decrease of the PFOA peak and several additional peaks eluting before the PFOA peak (data not shown). These peaks could be assigned to short-chain perfluorocarboxylic acids bearing C_4–C_6 perfluoroalkyl groups, indicating that electrochemical decomposition of PFOA occurred.[5,6] This indicates that fluid dynamics in the reactor are critical for optimization of the electrolysis efficiency.[7] Therefore, in the present study, the tube reactor was used for the hybrid system.

Decomposition behaviors of PFOA by electrolysis-only, photocatalysis-only, and hybrid are shown in Figure 4. Under 0.6 $mA\,cm^{-2}$ of applied current without UV light irradiation (electrolysis-only system), direct electrochemical oxidation cleaves the C–C bond between the C_7F_{15} and COOH in PFOA and generates a C_7F_{15} radicals and CO_2. The C_7F_{15} radical in water undergoes thermal transformation and hydrolysis to produce another F^- and the perfluorocarboxylic acid with one less CF_2 unit, $C_6F_{13}COOH$. By repeating these processes, PFOA can finally be totally mineralized to CO_2 and F^-.[5] Effective decomposition of PFOA can also be seen under UV irradiation without applied current (photocatalysis-only system). PFOA molecules adsorb onto the TiO_2 surface according to an adsorption equilibrium. Adsorbed PFOA molecules can be easily cleaved at the C–C bond between the C_7F_{15} and COOH by holes and radicals generated by TiO_2.[8] C_7F_{15} radicals react with OH radicals on the TiO_2 surface efficiently. The survival rate of PFOA at hybrid system is lower than that at electrolysis-only and photocatalysis-only systems. The PFOA decomposition follows pseudo-first-order kinetics, with observed rate constants of 13.4, 32.1, and 67.3 $mL\,h^{-1}$ in electrolysis-only, photocatalysis-only, and hybrid systems, respectively. Interestingly, although with the same UV intensity and applied current, the rate constant in the hybrid system was larger than the sum of the constants in electrolysis-only and photocatalysis-only systems. HPLC chromatograms of electrolysis-only system indicate that the short-chain perfluorocarboxylic acids bearing C_4–C_6 perfluoroalkyl groups were produced gradually (Supporting Information Figure S1),[9] which degraded efficiently with the reaction evolution. In contrast, the short-chain perfluorocarboxylic acids were produced in the photocatalysis-only system at the early reaction state, which degraded gradually with the reaction evolution. Thus, the hybrid system was able to accelerate the PFOA decomposition by a synergy of two kinds of reaction kinetics as shown in Supporting Information Scheme S1.[9]

Although we used a simple batch system under atmospheric pressure and room temperature, without any addition of gases, it would be attractive to develop a similar new continuous system for the practical treatment of waste water containing perfluorinated acids.

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9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.