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The effect of oxygen in the photocatalytic oxidation pathways of perfluorooctanoic acid

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ABSTRACT

The influence of oxygen in the photocatalytic oxidation of perfluorooctanoic acid (PFOA) promoted by a commercial nano-sized titanium dioxide was studied by testing the reaction in different conditions: static air, oxygen flux, nitrogen flux and pre-saturated nitrogen flux. The reaction was monitored by Total Organic Carbon (TOC) analysis and Ionic Chromatography (IC). Shorter chain perfluorocarboxylic acids (PFCAs; C_n, $n = 1–7$) intermediate degradation products were quantitatively determined by High-Performance Liquid Chromatography combined with Mass Spectrometry (HPLC–MS) analysis. The presence of shorter chain PFCAs in solution was also monitored by ^{19}F NMR. The experimental findings are in agreement with two major oxidative pathways: $C_n \rightarrow C_{n-1}$ photo-redox and β-scissions routes mediated by COF_2 elimination. Depending on the experimental conditions, the mutually operating mechanisms could be unbalanced up to the complete predominance of one pathway over the other. In particular, the existence of the β-scissions route with COF_2 elimination was corroborated by the isolation and characterization of carbonyl difluoride, a predicted fluorinated decomposition by-product.

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1. Introduction

PFOA and its salts are exogenous very stable perfluorinated surfactants, utilized till now for the preparation of the majority of fluoropolymers that are worldwide employed in thousands of everyday life essential applications, such as manufacturing, aerospace, automotive, electronics, semiconductors and textile [1]. PFOA UV stability and high surface-active effects are due to its completely perfluorinated structure [2–4]. However, perfluorocarboxylic acids (PFCAs) are nowadays source of great concern due to their proved persistence in the global abiotic and biotic environment, including food and humans [5–7]. These compounds, in fact, are among the most widely diffused fluorinated surfactants into waste streams [8–10].

The 2015 is the deadline for the complete phase out of perfluorooctanoic acid; this phase out plane was launched in the PFOA Stewardship Program by US-EPA and by eight major companies in 2006 [1]. As a direct consequence of this program, the fluoropolymer industry has been forced to develop new environmentally friendly surfactants suitable for emulsion polymerization. In addition, from that moment on, many important research studies on PFOA substitutes and related materials appeared in the specialized literature [11–17]. Furthermore, due to recent findings on the extreme difficulty to decompose PFOA by using standard methodologies, new and effective degradation techniques like electrochemical [18], modified Fenton reagent [19], sonochemical [20], plasma [21], microwave [22], photochemical [23,24] and photocatalytic methods [25–29] have been studied and published. In addition extensive technological reviews are also available in the literature [30–32].

In this study, we analyzed the influence of oxygen in PFOA photocatalytic oxidation induced by UV-activated TiO_2. Semiconductors, in particular TiO_2, are characterized by an electronic band structure in which electrons from the valence band (V_b) are promoted to the conductive band (C_b) with the simultaneous generation of positively charged holes (h^+) in the V_b by the absorption of a photon flux of energy equal or higher to the

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bandgap energy. The electron–hole pairs can recombine in a few nanoseconds, or they can be trapped in surface states where they can react with donor or acceptor species adsorbed on the photocatalyst surface [33]. Interface redox reactions involving both excited electrons and photogenerated holes must compete effectively with the recombination processes of the electron–hole pairs [34,35]. In the presence of water and oxygen, hydroxyl radicals $^{\bullet}OH$ and superoxide ions $O_2^{-\bullet}$ are generated [36]. These intermediates are strong oxidizing species able to mineralize organic compounds [37,38]. However, an extensive debate on the oxidative pathway of PFOA exists nowadays, because it has been demonstrated that $^{\bullet}OH$ radicals generated by Fenton reagent are not very effective in the PFOA mineralization [30,19] and that $Ti^{IV}OH^{\bullet +}$ can take an active part in the mineralization reaction [27,39,40].

Despite the numerous studies on PFOA oxidation, at the moment a complete rationalization of the decomposition pathways is not available. The interpretation of experimental findings, as well as *a priori* calculations reported in the literature, are often in apparent contradiction [19,26,30] and provide an incomplete interpretation of the PFOA oxidation mechanism [25] or, in some cases, the experimental findings are complementary [18,21]. The intent of this work is to give our contribution to the understanding of this intriguing reaction. In particular, we focused on the influence of oxygen in the photocatalytic oxidation of PFOA induced by UV-activated TiO_2 and we obtained that, differently from static conditions, a continuous oxygen feeding enhanced the decomposition of PFOA till its mineralization. On the contrary, PFOA photooxidation was hindered in a nitrogen-saturated reaction environment.

The use of excess oxygen directed the PFOA decomposition through a reaction pathway involving the formation of oxygen-centered perfluorinated radicals as major intermediates. As already hypothesized, the perfluorinated oxyradicals preferentially followed a β-scission route by releasing carbonyl difluoride, COF_2, as a specific by-product, which can be hardly isolated due to its rapid hydrolysis in aqueous media [41]. Carbonyl difluoride is an important intermediate for the industrial synthesis of key fluorinated monomers and it is essential in the preparation of fluoroplastics and perfluororubbers [42–44]. In this work, we firstly report that the intermediate COF_2 can be isolated in pure form and in good selectivity by performing the photocatalytic oxidation of PFOA in a suitable perfluorinated aprotic solvent, instead of water. Moreover, in these conditions the catalyst deactivation due to fluoride ions is mostly inhibited [27]. As often happens, a more complete understanding of a reaction mechanism gives more options in the utility of the reaction under study [45,46]. In particular, in the photocatalytic oxidation of PFOA a new chemical route has been identified for the synthesis of carbonyl difluoride, COF_2.

2. Materials and methods

2.1. Materials

Perfluorooctanoic acid (purity 96% – from Sigma–Aldrich®) was used as received. PFOA is soluble in water (9.5 g/L) and its critical micelle concentration (CMC) is 7.80×10^{-3} mol/L at 25 °C [47]. Titanium dioxide P-25 (75% Anatase, 25% Rutile) was supplied by Evonik® and it was tested as a titanium-based photocatalyst. The coexistence of anatase and rutile in commercial P-25 causes the catalyst photoactivity to be enhanced if compared to pure anatase [48]. The presence of small rutile crystallites, in fact, creates a structure characterized by a more stable charge separation, slowing recombination reactions on anatase; moreover, the smaller band gap of rutile extends the useful range of photoactivity into the visible region [48]. Water was purified by using an Elga Option 3 deionizer and it was used to prepare PFOA solutions for the different kinetic tests. Milli-Q water was employed for ion chromatography. HPLC–MS analyses were carried out by using as an eluting phase a mixture of methanol (CHROMASOLV®, for HPLC, ≥99.9% – from Sigma–Aldrich®) and 2 mM aqueous ammonium acetate solution. The evaluation of COF_2 formation during PFOA abatement was specifically monitored by degrading a solution of PFOA in Galden® HT-170 (from Solvay Specialty Polymers), a PFPE-based solvent with boiling point of 170 °C and formula as follows: $CF_3O(CF_2CF(CF_3)O)_p(CF_2O)_nCF_3$ (AMW = 760).

2.2. Photocatalysis

The photocatalytic apparatus was a 1 L glass stirred reactor equipped with an iron halogenide UV lamp (500 W, Jelosil® HG500) emitting light at wavelengths of 315–400 nm and able to irradiate the reactor with a specific power of 75 W/m^2. The UV lamp was placed beside the reactor, which was cooled with water at a temperature of 30.0 ± 0.5 °C [27]. Titanium dioxide was introduced in the reactor at the beginning of each test (0.66 g/L) [27]. The variation of the surfactant concentration in solution was monitored by Total Organic Carbon (TOC) analysis and Ionic Chromatography [27]. The PFOA initial concentration ($[PFOA]_0$ = 4 mM) was maintained lower than its CMC (7.8 mM [47]) in order to avoid the formation of emulsions that would reduce the TiO_2-promoted photodegradation rates [27,28]. Moreover, the PFOA initial concentration was high enough to allow the detection of the degradation intermediates, even at very low concentrations. Each kinetic test was repeated three times in order to evaluate the error extent and realized by collecting samples (10 mL) of the reaction mixture at predetermined reaction times. Samples were centrifuged and filtered through a 0.45 μm polycarbonate membrane in order to separate the TiO_2 powder from the solution.

Photocatalytic process could be commonly described in terms of a modified Langmuir–Hinshelwood (L-H) model, which has been successfully used for heterogeneous photocatalytic degradation by determining the relationship between the apparent first-order rate constant and the initial content of the organic substrate [49,50]:

$$r = -\frac{dC}{dt} = \frac{k_r K_S C}{1 + K_S C_0} = k_{app} C \quad (1)$$

In Eq. (1), r is the reaction rate, C is the pollutant concentration in solution, C_0 is the initial organic content, k_r is the reaction rate constant, K_S is the adsorption rate constant, t is the time and k_{app} the apparent first-order rate constant. In the original L-H model the rate constant k_r and the adsorption constant K_S are independent of light intensity and K_S should not vary with the light intensity because it represents the adsorptive affinity of a substrate on the catalyst surface. Differently, in the modified L-H model the light intensity can affect both kinetic constants (k_r, K_S), as reported in the literature [49,50].

The effects on PFOA photocatalytic oxidation due to both oxygen excess and deficiency in the reaction environment were evaluated by running and comparing the results of specific kinetic tests; in particular, PFOA degradation trends were monitored in atmospheric conditions (*Air test*), in the presence of a constant O_2 flux (*O_2 test* – $F_{O_2} = 7$ NL/h) and in the presence of a constant N_2 flux ($F_{N_2} = 7$ NL/h). The latter case comprehended two different oxygen starvation tests: PFOA degradation under N_2 flux with an air-saturated initial solution (*N_2 test*) and with a N_2-presaturated reaction environment (*N_{2sat} test* – PFOA solution fluxed with N_2 for 12 h until saturation, then $F_{N_2} = 7$ NL/h during the kinetic test). Dark and photolysis tests were also conducted (Table S.I.9 and Table S.I.10, respectively).

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