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Surface fluorination on TiO_2 catalyst induced by photodegradation of perfluorooctanoic acid

Sara Gatto[a,c], Maurizio Sansotera[b,c,*], Federico Persico[b,c], Massimo Gola[b,c], Carlo Pirola[a,c], Walter Panzeri[d], Walter Navarrini[b,c], Claudia L. Bianchi[a,c]

[a] Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy
[b] Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano, Via Mancinelli 7, 20131 Milano, Italy
[c] Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Via G. Giusti 9, 50121 Firenze, Italy
[d] C.N.R.—Consiglio Nazionale delle Ricerche, Istituto di Chimica del Riconoscimento Molecolare, "U.O.S. Milano Politecnico", Via Mancinelli 7, 20131 Milano, Italy

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ABSTRACT

The photoabatement of perfluorooctanoic acid in aqueous solution has been performed with a commercial nano-sized TiO_2-based photocatalyst content of 0.66 g/L under an UV irradiation of 95 W/m^2. PFOA degradation intermediates were investigated by HPLC–MS and ^{19}F-NMR analysis. Evidences of a degradation mechanism based on two competitive pathways are discussed: photo-redox and β-scission pathways. Shorter perfluorinated carboxylic acids, $C_nF_{2n+1}COOH$ ($n = 1–6$), as expected degradation intermediates, were identified and their concentration trends over time were determined. The apparent pseudo-first order kinetic constant expressed as rate of PFOA disappearance was also measured: k_{app} 0.1296 h^{-1}. The influence of fluoride ions on TiO_2 surface was analyzed by XPS technique, revealing a surface modification that affects the performances of the catalyst.

1. Introduction

Perfluorooctanoic acid (PFOA), $C_8HF_{15}O_2$ (AMW = 414.07 g/mol), a representative of perfluorinated chemicals (PFCs), is largely used as surfactant in the fluoropolymers synthesis with the aim to obtain chemical compounds with specific properties for a wide range of industrial applications, such as manufacturing, aerospace, automotive, electronics, semiconductors and textile [1,2]. Moreover, PFOA is applied for the production of breathable membranes for clothing, e.g. Gore-Tex® [3]. Its strong stability and high surface-active effects are due to the presence of C—F bonds (about 130 kcal/mol) in its molecular structure [4,5].

However, many studies indicate that PFOA is environmentally persistent and bioaccumulative [6,7]. For these reasons, in the last years many research groups have devoted efforts to develop methods able to eliminate PFOA from the environment [8,9]. Actually, the US-EPA (Environmental Protection Agency) and EEA (European Environmental Agency) launched an industrial program aimed to reduce global emissions and product content of PFOA and related chemicals. In agreement with these directives, the eight major producers of fluoropolymers and fluorotelomers have been coerced into reducing global facility emissions and product content of PFOA and its related chemicals by 95% in 2010 as well as to completely eliminate emissions and product content of PFOA by 2015 [10,11].

Many procedures have been developed over the years for the removal of surfactants from water [12]. Traditional techniques include air stripping, biological processes, incineration and chemical treatments, but each method presents some negative aspect limiting its industrial feasibility [13,14]. For example, biological processes cannot reach a complete degradation of the pollutant and incineration can produce fully persistent and toxic by-products [12].

Therefore, besides classical wastewater treatment techniques, in the last decades advanced oxidation processes (AOPs) have increasingly become a valuable alternative [15–17]. In such processes, very reactive hydroxyl radicals are generated and, thanks to their high redox potential ($E_0 = 2.73$ V), they are responsible for the oxidation of organic pollutants [18–20]. AOPs methods can be distinguished on the basis of the oxidizing agent source involved in photolysis, photocatalysis, ultrasound, microwave or

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* Corresponding author at: Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Via Mancinelli 7, 20131 Milano, Italy. Tel.: +39 02 2399 3035; fax: +39 02 2399 3180.
E-mail address: maurizio.sansotera@polimi.it (M. Sansotera).

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ozone treatments and Fenton processes. Among these, we adopted photocatalysis based on a semiconductor in combination with UV light and oxygen. Many studies have been carried out using titanium dioxide for the degradation of organic pollutants in both water and air phase [21,22]. TiO_2 is characterized by chemical and biological inertness, high photocatalytic activity, photodurability, mechanical robustness and relative cheapness. Therefore, these features offer great potential, especially for industrial scale water treatment.

The present paper is focused on PFOA photodegradation promoted by commercial TiO_2 powder (P25 by Evonik®). The mineralization was monitored by total organic carbon (TOC) analysis and ionic chromatography (IC) and the intermediate degradation products were determined by high-performance liquid chromatography combined with mass spectrometry (HPLC–MS) analysis. The presence of the fluorinated surfactant in solution was also monitored by ^{19}F-NMR. HPLC–MS and ^{19}F-NMR analyses were performed on samples of PFOA solution collected from the photoreactor after different reaction times. The degradation and changes in the fluorinated solution during the process were assessed by these techniques highly endowed to reveal the structure changes of molecules that could take place in the reaction environment. Finally, XPS analysis allowed the evaluation of chemical modifications occurring on the surface of the photocatalyst powder.

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 [6]. Titanium dioxide P25 (75% Anatase, 25% Rutile [23]) was supplied by Evonik® and it was tested as titanium-based photocatalyst. Water was purified using an Elga Option 3 deionizer and was used to prepare all solutions. Milli-Q water was employed for ion chromatography. HPLC–MS analyses were carried out using as eluting phase a mixture of methanol (CHROMASOLV®, for HPLC, ≥99.9%—from Sigma Aldrich®) and 2 mM aqueous ammonium acetate solution.

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 95 W/m^2. The UV lamp was placed beside the reactor, which was cooled with water at a temperature of 30 ± 0.5 °C [24]. Titanium dioxide was introduced in the reactor at the beginning of each test (0.66 g/L). As previously reported, the variation of the surfactant concentration in solution was monitored by total organic carbon (TOC) analysis and ionic chromatography [24]. The PFOA initial concentration ($[PFOA]_0 = 4$ mM) was maintained lower than its CMC (7.8 mM) in order to avoid the formation of emulsions during the kinetic tests. Thus, the PFOA initial concentration was high enough to allow the detection also of the degradation intermediates at low concentrations. Samples (10 mL) of the reaction mixture were collected at different reaction times: typically at 0 min (before the start of the reaction), 30 min, 1 h, 2 h, 3 h, 4 h, 6 h and 9 h. Each kinetic test was repeated three times in order to evaluate the error extent. Each sample was centrifuged and filtered through a 0.45 μm polycarbonate membrane in order to separate the TiO_2 powder from the solution. The residual photocatalytic performances of exhaust TiO_2 after 9 h of PFOA photodegradation were also evaluated by reusing it in an additional test performed on a standard 4 mM PFOA solution.

Photocatalysis follows the Langmuir–Hinshelwood model [25]. When the PFOA adsorption onto the photocatalyst surface is negligible, the reaction mechanism can be approximated to a pseudo-first order kinetic (1):

$$r = -\frac{dC}{dt} = k_{app}C \qquad (1)$$

In Eq. (1), r is the reaction rate, C is the surfactant concentration in solution, t is the time and k_{app} is the apparent first order rate constant. The reactions were conducted without a constant feed of oxygen as reported by Li et al. [9], but using just the naturally dissolved O_2 (DO), in order to simulate conditions of non-enriched water, as industrially feasible.

2.3. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy analysis was performed to study the photocatalyst surface before and after the photodegradation reaction, in order to monitor composition variations that might have occurred. X-ray photoelectron spectroscopy spectra were obtained by using an M-probe apparatus (Surface Science Instruments). The source was monochromatic Al K_α radiation (1486.6 eV). A spot size of 200 μm × 750 μm and pass energy of 25 eV were used. 1 s level hydrocarbon-contaminant carbon was taken as the internal reference at 284.6 eV. Fittings were performed using pure Gaussian peaks, Shirley's baseline, and without any constraints. XPS analyses were conducted on samples obtained centrifuging and filtering through a 0.45 μm polycarbonate membrane the surfactant solution at different reaction times (2 h, 4 h, 9 h); the TiO_2 samples were then dried in inert atmosphere for 24 h and analyzed. Subsequently, in order to remove possible fluorinated organic compounds deposited on the catalyst surface, the samples were suspended in the fluorinated solvent $CF_3OCFClCF_2Cl$, dried in inert atmosphere and analyzed again.

For each sample, survey analyses in the whole range of X-ray spectra and high resolution analyses in the typical zone of C-1s, Ti-2p, O-1s and F-1s were performed.

2.4. High-performance liquid chromatography combined with mass spectrometry

Analytes separation was performed by using an Agilent 1100 Series HPLC Value System, consisting of a quaternary pump, vacuum degasser and autosampler. The instrument was equipped with a Lichrocart® 55-4 Purospher® STAR RP-18 endcapped column (55 × 4.0 mm i.d., 3 μm) supplied by Merck KGaA. For quantitative determination, the chromatographic system was interfaced to a Bruker Esquire 3000 Plus quadrupole ion trap mass spectrometer (Bruker Daltonics) operating in negative electrospray mode. Instrumental parameters were optimized to transmit the $[M—H]^-$ ion for all expected degradation intermediates. Primary ions monitored for PFOA, perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), perfluorobutanoic acid (PFBA), perfluoropropionic acid (PFPrA) and trifluoroacetic acid (TFA) determinations were 413, 363, 313, 263, 213, 163 and 113 m/z, respectively. Samples of the reaction mixture collected at different reaction times were diluted in deionized water (1:10) and injected in the HPLC–MS with 2 mM ammonium acetate/methanol as the mobile phase starting at 10% methanol. At a flow rate of 200 μL/min the gradient increased to 90% methanol at 5 min; before reverting to original conditions at 20 min, the gradient decreased to 80% methanol at 15 min. Column temperature was maintained at 40 °C.