



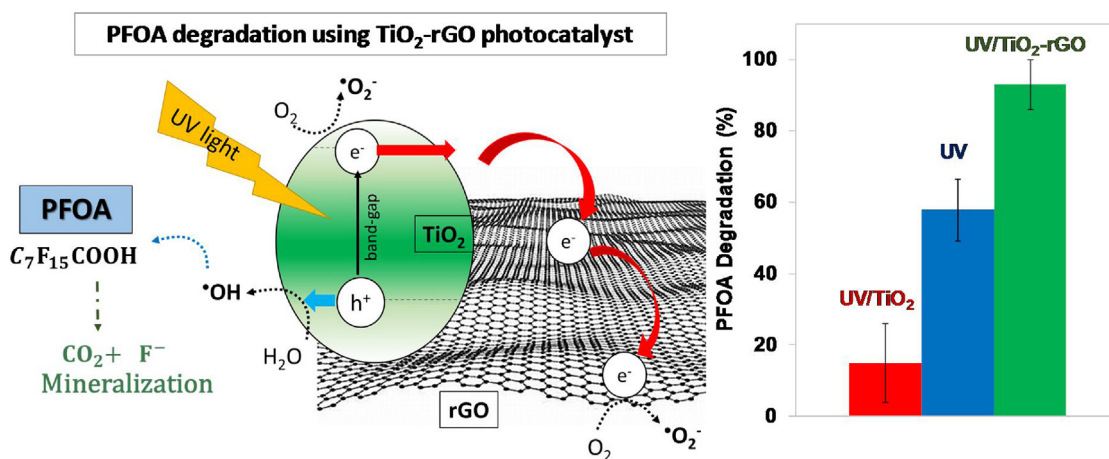
Photocatalytic degradation and mineralization of perfluorooctanoic acid (PFOA) using a composite TiO_2 –rGO catalyst

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GRAPHICAL ABSTRACT



HIGHLIGHTS

- Photocatalytic decomposition of PFOA using a TiO_2 -rGO catalyst was studied.
- TiO_2 -rGO catalyst (0.1 g L^{-1}) allowed $93 \pm 7\%$ PFOA removal under UV-vis irradiation.
- Formation of intermediate PFCAs and F^- elucidated the PFOA degradation mechanism.
- Faster degradation kinetics were observed for shorter carbon-chain PFCAs.

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ABSTRACT

The inherent resistance of perfluoroalkyl substances (PFASs) to biological degradation makes necessary to develop advanced technologies for the abatement of this group of hazardous substances. The present work investigated the photocatalytic decomposition of perfluorooctanoic acid (PFOA) using a composite catalyst based on TiO_2 and reduced graphene oxide (95% TiO_2 /5% rGO) that was synthesized using a facile hydrothermal method. The efficient photoactivity of the TiO_2 -rGO (0.1 g L^{-1}) composite was confirmed for PFOA (0.24 mmol L^{-1}) degradation that reached $93 \pm 7\%$ after 12 h of UV-vis irradiation using a medium pressure mercury lamp, a great improvement compared to the TiO_2 photocatalysis ($24 \pm 11\%$ PFOA removal) and direct photolysis ($58 \pm 9\%$). These findings indicate that rGO provided the suited properties of TiO_2 -rGO, possibly as a result of acting as electron acceptor and avoiding the high recombination electron/hole pairs.

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Titanium dioxide
Graphene oxide
Photocatalysis

The release of fluoride and the formation of shorter-chain perfluorocarboxylic acids, that were progressively eliminated in a good match with the analysed reduction of total organic carbon, is consistent with a step-by-step PFOA decomposition via photogenerated hydroxyl radicals. Finally, the apparent first order rate constants of the TiO₂-rGO UV-vis PFOA decompositions, and the intermediate perfluorocarboxylic acids were found to increase as the length of the carbon chain was shorter.

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1. Introduction

The presence of poly- and perfluoroalkyl substances (PFASs) in industrial emissions, drinking water sources and groundwaters is of increasing concern due to their extreme persistence and potential toxicity [1–3]. As a result, the Stockholm Convention on Persistent Organic Pollutants restricted the use and production of perfluorooctanesulfonate (PFOS) and its salts, and at present perfluorooctanoic acid (PFOA) and PFOA related compounds are under review for listing under the Convention [4]. The United States Environmental Protection Agency established health advisory levels for PFOA and PFOS in drinking water at 0.07 µg L⁻¹, both individually and combined [5].

Due to the inherent resistance of PFOA, PFOS and related compounds to biological degradation [6–8], there is an intense research on chemical oxidation/reduction technologies to degrade PFASs in water, including direct photolysis, photochemical oxidation, photochemical reduction, photocatalytic oxidation, electrochemical oxidation, persulfate oxidation and sonochemical pyrolysis [9–18]. Among these technologies, direct photolysis is an alternative that operates at ambient temperature and pressure and it does not require additional chemicals. However, the studies published so far have shown that PFOA was only efficiently decomposed using a light source emitting at wavelengths from deep UV-region to 220 nm [19,20] or under elevated irradiation intensity [21]. Therefore, direct photolysis application is constrained by the high energy demand needed to obtain the intensity of the active irradiating light and the long treatment times.

A literature survey about the photocatalytic PFOA degradation in aqueous media is summarized in Table S1 (Supplementary Material). Despite the suitable properties of TiO₂ catalyst, such as non-toxicity, photostability and low cost [22–24], the majority of the previous studies revealed the low PFOA degradation rate achieved by TiO₂ photocatalysis, which was comprised in the range 7–44% in most of the studies [12,21,25–33]. The limited performance of TiO₂ is attributed to its relatively large band-gap, high recombination rate of electron-hole pairs and limited use of visible light spectrum. Nevertheless, the comparison of previous research is hindered by the diversity of the applied experimental conditions, e.g.: light intensity (0.45–9.5 mW cm⁻²), wavelength spectrum emitted by the light source (200–600 nm), reactor volume (0.12–3 L) and treatment time. The reaction medium has been also widely varied, in terms of PFOA concentration, background electrolytes and O₂ or N₂ supply [34]. Yet, the catalyst dosage was quite homogeneous in all the reviewed research, and was varied in the range of 0.25–2 g L⁻¹. The highest reported PFOA removal rates, 98%, could be associated to the use of high intensity irradiation, a factor that would accelerate the degradation rates [21,34].

Recently, different strategies have been proposed to overcome TiO₂ limitations, such as the synthesis of titanate nanotubes (TNTs) out of a commercial TiO₂ catalyst, that doubled the PFOA degradation rate [21]. Other approaches consisted of modifying the process conditions. Within this group, TiO₂-mediated photocatalysis combined with perchloric acid [26] or ultrasonication [35], achieved 2-fold and almost 5-fold improvements in the PFOA degradation

rate, respectively. The addition of oxalic acid also accelerated PFOA decomposition using TiO₂, under nitrogen atmosphere [27]. However, these methods would involve adding different substances to the polluted water. A more promising strategy is focused on the synthesis of new composite catalysts that combine the photoactivity of TiO₂ with transition metals, e.g.: Fe, Nb, Cu, Pb [12,30,36] or with noble metal nanoparticles Ag, Pt or Pd [31]. Transition and noble metals have demonstrated to act as electron traps preventing the high electron-hole recombination, to successfully improve the photocatalytic features of TiO₂-doped composites [37]. Also Song et al. [32] showed that the use of composites of TiO₂ with multiple wall carbon nanotubes (TiO₂-MWCNT) enhanced the photocatalytic PFOA decomposition.

Among the new strategies to enhance the efficiency of photocatalysts, the combination of TiO₂ with graphene materials has been reported to increase the lifetime of electron-hole pairs, by reducing charge recombination, due to the excellent electron trapping and electrical conductivity properties of graphene. It is also thought that graphene provides a superior photoresponse by extending the excitation wavelength compared to bare TiO₂ [37–40]. The effective photocatalytic activity of the composite catalysts based on TiO₂ and graphene or graphene oxide has been demonstrated for the degradation of dyes as model of organic pollutants [39,41–44], and in a few seminal studies dealing with more complex organic contaminants, such as, dodecylbenzenesulfonate [45], diphenhydramine [46] or phenols [40]. A notable gap is that TiO₂-graphene composite photocatalysts have not been tested yet for the degradation of neither PFOA nor other PFASs.

This study aims to explore the photocatalytic degradation of PFOA by means of a composite catalyst of TiO₂ and reduced graphene oxide (TiO₂-rGO). Photocatalysis experiments under UV-vis irradiation examined the effect of TiO₂-rGO catalyst concentration on PFOA removal and defluorination, and evaluated the generation of shorter-chain perfluorinated intermediate products, as well as the total organic carbon reduction. Results were compared with bare TiO₂ and direct photolysis conditions to gain insight into factors influencing the significant photocatalytic enhancement that was provided by the TiO₂-rGO material. Finally, this work assessed the effect of the alkyl chain length on the kinetics of the photocatalytic degradation of perfluorocarboxylic acids by means of TiO₂-rGO composite catalyst.

2. Materials and methods

2.1. Chemical reagents

All chemicals were reagent grade or higher and were used as received without further purification. PFOA (C₇F₁₅COOH, 96% purity), perfluoroheptanoic acid (PFHpA, C₆F₁₃COOH, 99% purity), perfluorohexanoic acid (PFHxA, C₅F₁₁COOH, 96% purity), perfluoropentanoic acid (PFPeA, C₄F₉COOH, 97% purity) were purchased from Sigma Aldrich Chemicals. TiO₂ (P25, 20% rutile and 80% anatase, 50 m² g⁻¹, 21 nm) was obtained from Evonik Degussa. Graphite powder was supplied by Acros Organics. Sulfuric Acid 95–98% (H₂SO₄), chloride acid 37% (HCl), potassium permanganate

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