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UNIVERSIDAD DE CANTABRIA

Trabajo Fin de Grado

Preliminary study of perfluorooctanoic acid decomposition by heterogeneous photocatalysis

(Estudio preliminar de la descomposición del ácido perfluorooctanoico mediante fotocatálisis heterogénea)

Para acceder al Título de

Graduada en Ingeniería Química

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1. INTRODUCTION

1. INTRODUCTION

1.1. Motivation

Over the latest years, industrial processes are intended to meet the growing consumers' needs. Environmentally sustainable and safer products must be offered in order to reduce the disposal of many compounds that, although already extended in the environment, have been included in the international regulations. Among various pollutants, there are those which can resist natural degradation processes building up in the environment and being toxic to human and wildlife. This is the case of the so-called Persistent Organic Pollutants (POPs) that collect diverse compounds (aldrin, chlordane, DDT among others) and also fluorinated hydrocarbons known as perfluoroalkyl substances (PFASs) being perfluorooctanoic acid (PFOA) one of them. The major concern of PFOA is due to its high production and emission rates into the environment in comparison with other PFASs (Estrellan, Salim y Hinode, 2010; Yates et al., 2014). Then, it is necessary to develop efficient treatment technologies for PFOA removal, particularly from water media (Wang et al., 2008; Carter and Ferrel, 2008; Wang and Zhang, 2012).

The present document gathers a little introduction to PFASs and PFOA dealing with their physical-chemical characteristics and properties, presence in the environment and more. A treatment operation based on photocatalytic technology is proposed introducing the results obtained in the experimental analysis. Finally, relevant conclusions about the effectiveness and possible future tasks are drafted.

1.2. Perfluoroalkyl substances(PFASs)

1.2.1. Characteristics and properties

PFASs are anthropogenic compounds that have been widely used in industrial and commercial applications exhibiting POPs behaviour once moved into the environment

(Wang et al., 2008; Phan Thi et al., 2014). I.e., these compounds persist in the environment, accumulate in foodchains and spread far away from their sources. Chemical inertness, stability in water, soil and hydrophobic and lipophobic properties explain that behaviour (Chen et al., 2015). PFASs' molecular chain has carbon-fluorine (C-F) bonds instead of carbon-hydrogen (C-H) bonds giving them physical and chemical stability (Hori et al., 2005; Cao et al., 2010;Phan Thi et al., 2013; Chen et al., 2015). Unlike the C-H bond, C-F bond is stronger because fluorine is more electronegative. The chain can be fully or partly fluorinated bonded with different functional groups. PFASs have been detected in aquatic media, drinking water, soils, outdoor and indoor air and consumer products. And for aquatic media, PFASs have been reported in tap water, groundwater, wastewater, surface water, seawater and coastalwater (Xiao et al., 2013; Zhang et al., 2014; Appleman et al., 2014). These compounds can be easily moved from domestic, commercial or industrial discharges into natural waters because of their high solubility, very low vapour pressure and moderate sorption to solids resisting natural degradation processes (Estrellan, Salim y Hinode, 2010; Xiao et al., 2013; Flores et al., 2013).

One well-known PFASs is perfluorooctanoic acid (PFOA) whose chemical formula is $CF_3(CF_2)_6COOH$. It is a fully fluorinated carbon chain with a carboxylic end-group as a hydrophilic functional unit (see Figure 1) (Lau et al., 2007; Panchangam et al., 2009)

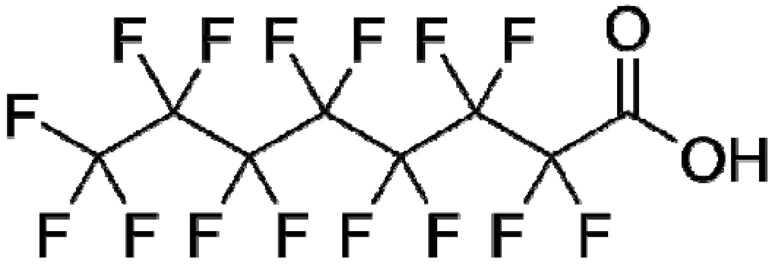

Figure 1. Molecular structure of PFOA

PFOA has a low pKa value between 2 and 3 and in aqueous media is expected to dissociate almost entirely to PFO^-, perflorooctanoate anion. The solubility of PFO^- in water is estimated to be 4.1 g/L at 22ºC and it increases sharply with temperature as the compound begins to form micelles. The solubility of PFOA in water,conversely, is expected to be less soluble than PFO^- (Prevedouros et al., 2006). Some PFOA properities are depicted in Table 1.

Table 1. PFOA characteristics (Prevedouros et al., 2006).

Melting point (ºC)	58-60
Boiling point (ºC)	189-192
Density (g/cm^3)	17
Solubility (g/L)	3.4
Vapor pressure (25ºC)	4.2 Pa

The presence of PFOA in the environment has its origen in the production and consumption of perfluorinated chemicals, fluorinated polymers and consumer items (Flores et al., 2013). Figure 2 displays several products that could contain PFOA (Estrellan, Salim y Hinode, 2010; Xiao et al., 2013; Urtiaga et al., 2014).

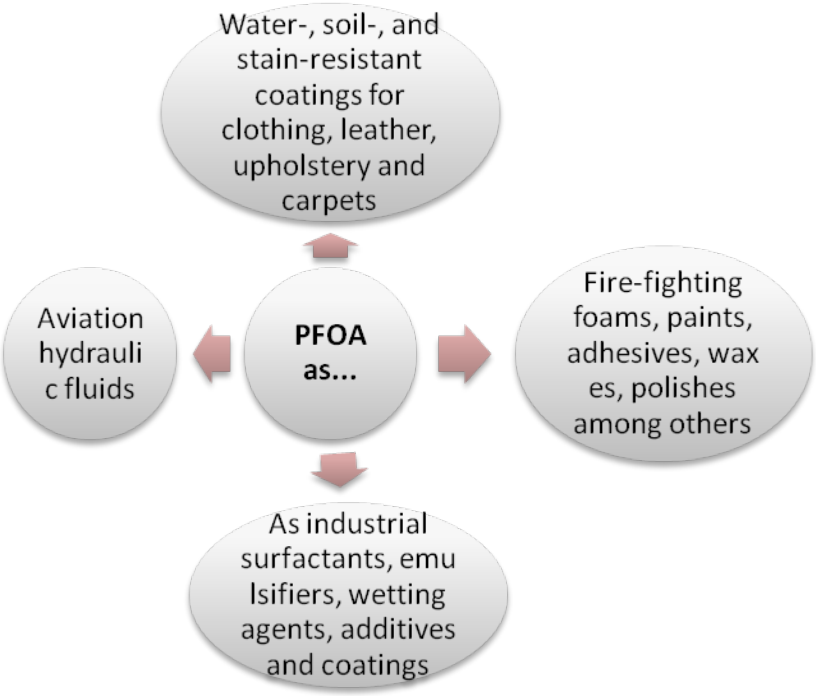

Figure 2. PFOA uses

1.2.2. Source and transport of PFASs

PFASs emissions into the environment can be from direct and indirect sources (Wang et al., 2008). Direct sources represent the manufacture and use of PFASs. The production of ammonium perfluorooctanoate (APFO) and its subsequent use in the produccion of perfluorinated chemical and fluorinated polymers,as aprocessing aid, are the major pathways of direct emissions, near 80 %. On the other hand, the indirect sources are referred to those in which the breakdown of precursor compunds such as fluorotelomer alcohols (FTOH) and perfluorooctane sulfonyl fluoride (POSF) are taking place. I.e., chemical reaction through biodegradation in soil, sludge and wastewater as well as through chemical reactions in the atmosphere may degrade to form PFASs. The indirect emissions account for near 10 % of PFOA emission (Post et al., 2007; Pistocchi and Loos, 2009). A more detailed scheme of the direct and indirect sources is offered in Figure 3.

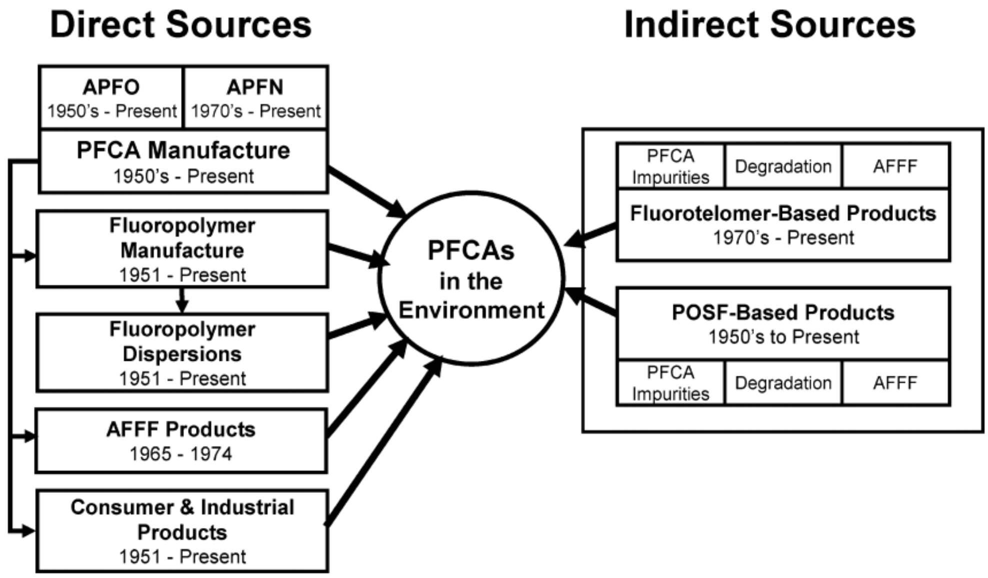

Figure 3. Sources of perfluorocarboxylates (PFCAS) $F(CF_2)_nCOO^-$: APFO= ammonium perfluorooctanoate; APFN=ammonium perfluorooctanoate; AFFF=aqueous fire-fighting foam; POSF=perfluooctylsulfonyl fluoride (taken from Prevedouros et al., 2006)

Regarding to the long-range transport of these compounds, two pathways can be promoted: atmospheric and aqueous transport. The atmospheric transport implies the transport of the volatile precursors that later suffer oxidation to PFOA and others PFASs and then are deposited onto the land or water. The aqueous transport involves the dissolution of PFASs, as PFOA in the anionic form, and transport by the currents on the ocean's surface, rivers and others. In this way, the presence of these components can be explained in areas as far away as the Arctic although with unknown contribution of each pathways at the present time (Prevedouros et al., 2006;Post et al., 2007;Wang et al., 2008; Pistocchi and Loos, 2009).

1.2.3. Pollution of Spanish waters

PFOA has had an extensive historical production and easy transfer into the environment being detected across the whole globe. Flores et al. (2013) reviewed the literature on PFOA concentration for the 2004-2012 period in Spanish waters (see some values in Table 2) being 2004 the year when PFOA presence was described for first time in Spain. Concentrations of PFOA in Spanish coastal waters were measured up to 2.25 ng/L and in northeastern rivers, PFASs occurence lead to concentration as high as 43 ng/L. On the other hand, metropolitan areas of the country gathered maximum values of 57.43 ng/L for PFOA and in the effluents of wastewater treatment plants, whose determination of PFASs is restricted to the North East part, ranged from 0.16 to 61.9 ng/L.

Table 2. PFOA in Spanish water samples (2004-2012). Mean or concentration ranges expressed in ng/L (Flores et al., 2013)

	PFOA (ng/L)
Coastal waters	
Catalan harbors	0.38-2.25
Cantabric harbors	0.05-0.31
Wastewaters (effluents)	
WWTP (North-East Spain)	3.47-61.90

WWTP(North Spain)	0.16-3.53
Surface waters	
Llobregat river	43
Ebro river	1.90-2
Catalan rivers	0.79-9.63
Drinking water	
Catalonia	<0.85-57.43
Valencia area	<0.1-7.6

In comparison with the rest of the Earth, the greatest industrialized cities have much higher PFASs levels for coastal waters as, for example, Asian coasts with a value of 68.6 ng/L for PFOA in Western Korea. While in underdeveloped countries, PFOA concentration decreases drastically because of the low production rate of this compound as it happens in South East Brazil (between 1-2 ng/L for PFOA) and North Sea (around 0.07 ng/L)(Flores et al., 2013).

For Spanish rivers, PFASs concentration was reported to be in the range of other worldwide rivers. In European rivers, the Nordic surface waters have the lowest PFASs concentration (less than 0.36 ng/L in Sweden) in comparison with the rest of Europe as in Po, Rhone and Seine Rivers.(Flores et al., 2013).

Finally, in the treated drinking water from municipal waters, maximum values of 57.43 ng/L for PFOA and others relevant compounds such as perfluorobutane sulfonate (PFBS) (up to 69.43 ng/L) and perfluorononanoate (PFNA) (up to 58.21 ng/L) were measured. In this kind of waters, PFOA has the highest concentration indicating incomplete removal in sewage treatment plants, potabilization processes and industrial discharges whose PFOA levels can reach higher concentration in the effluents from wastewater facilities than those measured in the influents (Flores et al., 2013).

1.2.4. Human exposure, serum level and adverse effects by PFOA

PFOA can’t be metabolized by the body and, therefore, it has been found in almost all world’s population (see some values in Table 3), considering an average life of 2 years in human being (Wang et al., 2008; Flores et al., 2013).The human exposure results from direct exposure to PFOA itself and to precursor compounds such as FTOH and polyfluoroalkyl phosphoric acid diesters (diPAPs). Sources of exposure include drinking water, food, migration from food packaging into food, treated fabrics, house dust, use of protective sprays, ski waxes and inhalation of indoor and outdoor air(Appleman et al.,2014). I. e., there are mainly three ways of PFOA absorption: oral, through the skin and by inhalation of the dust. The food is considered the predominant exposure channel, a typical adult total exposure of about 2-3 ng/kg/day in Europe or North America is estimated. Once it gets into the body, PFOA spreads to the liver and serum and less to kidney and other organs (Post et al., 2007;Sansotera et al., 2014). However, it still unknown neither the extent of population which is affected nor the health endpoints although USEPA Science Advisory Board recommended PFOA to be considered a human carcinogen (Wang et al., 2008; Zhao et al., 2012).

Table 3. PFOA concentration in human serum (Post et al., 2012)

Country	PFOA mean concentration (ng/ml)
Industrialized countries	2-8
USA	4.13-7.9
Greece	2
Italy	3.32
Norwegian	2.7
Australia	6.4
Afghan	1.5

1.2.5. Legal framework

Because of the possible potential harm to human and the need to provide treatment options, PFASs are included in many international regulations. In U.S., the Environmental Protection Agency (EPA) established Provisionary Health Advisory (PHA) values for PFOA and perfluorooctane sulfonic acid (PFOS) of 0.4 µg/L and 0.2 µg/L in drinking water respectively. Also, those contaminants are added to the EPA's Contaminant Candidate List 3 of chemicals under consideration for future drinking water regulation and EPA's Unregulated Contaminant Monitoring Rule 3 (UCMR 3) with the aim to provide data for regulatory decision making by measuring the public water suppliers (Appleman et al., 2014; Sansotera et al., 2014).

On the other hand, in Europe, PFOA and PFOS are collected in the OSPAR List of Chemicals for Priority Action. The higher risk of PFOS included it in the Annex B of Stockholm Convention for the production and use control. Furthermore, PFOS is defined as a priority substance in European water policy according to Directive 2013/39EC and as a Substance of Very High Concern under the European regulation REACH (Flores et al., 2013; Urtiaga et al., 2014).

In Table 4, several frameworks are summarized for the target compounds with corresponding values.

Table 4. Summary of regulation/guideline values for PFASs (Zushi and NarteyHogarh, 2012)

Regulation/Guideline	Country/Institute	Contents
Production, use, import		
Stockholm convention on POPs	Ratifying countries	PFOS and PFOSF: Partially regulated
EU Directive2006/122/ECOF	EU member countries	PFOS and the derivatives: partially regulated
Water guideline value		
Drinking water guideline value	DWI (UK)	PFOS and PFOA: 0.3 µg/L in tier 1
Drinking water guideline value	DWC (Germany)	PFOS and PFOA: 0.3 µg/L
Drinking water guideline value	USEPA	PFOS and PFOA: 0.2 µg/L and 0.4 µg/L respectively
Others		

Voluntary phase out	3M Company	PFOS and its related chemicals: stop their production
EU Directive 2013/39/EC	EU member countries	PFOS and the derivatives: partially regulated

1.2.6. PFOA removal technologies

Over the years, many technologies have been developed without guarantee of total removal of the PFASs. Processes as anion exchange, granular activated carbon, nanofiltration and reverse osmosis were evaluated at bench scale(Appleman et al., 2014). However, these non-destructive methods are based on the transfer of the contaminant that later must be managed to minimize the impact of its disposal (Urtiaga et al., 2014). So, technologies that cleavage C-F bonds are more appealing. As an alternative, photochemical and sonochemical methods have been reported to be candidate treatment technologies.

Heterogeneous photocatalysis is based on direct or indirect absorption of energy (visible light or UV),equal to or more than its energy gap, by the solid. Then, negatively charged electron and positively charged hole pairs are generated that may migrate to the surface of the photocatalyst particle and react with adsorbed substances resulting in a oxidation and reduction reactions (see Figure 5 for more detail). Usually, holes react with water to produce hydroxyl radicals(·HO) which cause decomposition of almost all organic matter. Heterogeneous photocatalysis with TiO_2 is the most used for the treatment of the organic matter presented in water including halogenated organics (Panchangam et al., 2009; Gatto et al., 2015). TiO_2 is an available catalyst, non-toxic, chemical and biological stable, photo-stable and it has a low cost. During PFOA decomposition process, shorter-chain PFASs are formed following the next sequence: $C_6F_{13}COOH \rightarrow C_5F_{11}COOH \rightarrow C_4\ F_9COOH \rightarrow C_3F_7COOH \rightarrow C_2F_7COOH$ undergoing stepwise decomposition. Each PFASs removes CF_2 unit, generating CO_2 molecules and fluoride ions (Wang et al., 2008; Chen et al., 2015).

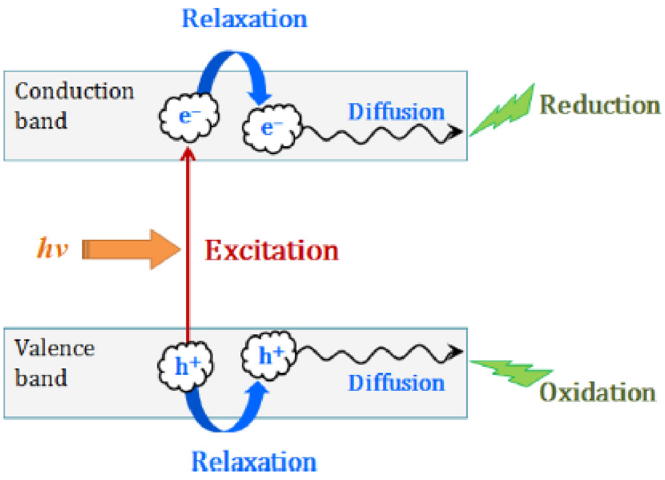

Figure 4.Schematic illustration of the formation of photoinduced charge carriers (e-/h$^+$) on absorption of UV light (taken from Lee and Park, 2013)

However, TiO_2 activity to remove PFOA is low because PFOA is almost inert to hydroxyl radicals without no hydrogen atoms available to be removed by hydroxyl radicals (Zhao et al., 2012; Li et al., 2012). Only under specific conditions, as highly acidic solutions, it is possible enhance the degradation by TiO_2. On the other hand, it has been reported that doped TiO_2 particles have better activity and stability for photocatalytic degradation of some persistent pollutants (Li et al., 2012; Chen et al., 2015). Graphene is one of the most promising materials because of it large specific area, flexible structure, good electrical and thermal conduction and high mobility of charge carriers. For this reason, in this project is evaluated the graphene oxide (GO)-TiO_2composite catalyst for PFOA removal from water (Leary and Westwood, 2011).

1.3. Objectives

This project is attempted to contribute to the study of photochemical decomposition technologies for PFASs removal in polluted waters. To this end, the following objectives are defined:

1. Review of the literature about PFASs photodecomposition by TiO_2

2. Start-up of an experimental test in order to assess the photocatalytic activity of new co -doped graphene oxide (GO) -TiO_2 composite catalyst

2. DEVELOPMENT

2. DEVELOPMENT

2.1. Bibliography search

A short literature review of photocatalytic decomposition of PFOA in aqueous media under UV irradiation is offered in Table 5. Scopus data base that BUC of University of Cantabria provides for students was used in the search. In the section of *"Document Search"* keywords were introduced: "photocatalytic decomposition", "PFOA", "TiO_2 catalyst" and similar. The results displayed some of the reports that are collected in Table 5. Afterwards, an overview of the reports and Table 5 was built. Table 5 gathers the pollutant concentration in water, catalyst used and its concentration, experimental conditions and the results obtained as % of PFOA decomposed and fluoride generated.

Table 5. Literature review of photocatalytic PFOA decomposition by TiO_2

Article	Initial PFOA concentration to treat (mg/L)	Type of catalyst and concentration (g/L)	Lamp	pH	Treated volume (L) and Temperature (ºC)	Results of degradation (%) and fluoride content (%)
Sansotera et al., 2014	(1) 1,700 (2) 3,000 (3) 5,000	TiO2 P25 (75% Anatase, 25% Rutile) 0.66 g/L and 1 g/L	Low pressure mercury UV lamp 500W Light wavelength: 310-400 nm Specific power: 75 and 95 W/m2	Not described	1L/30ºC	Dark test: PFOA+TiO2 without UV: No PFOA removal Photolysis: PFOA+UV without TiO2: No PFOA removal After 6h, using 0.66 g/L TiO2 and 75 W/m2: (1) 1,700 mg/L PFOA: 30% and 22% (2) 3,000 mg/L PFOA: 24% and 16% (3) 5,000 mg/L PFOA: 17% and 10% And using 1,700 mg/L PFOA and 75 W/m2 0.66 g/L: 30% and 22% 1 g/L: 28% and 21% After 4h, using 0.66 g/L TiO2 and 1,700 mg/L PFOA: 95 W/m2: 32% 75 W/m2: 21%

Gatto et al., 2015	1,700	TiO2 P25 (75% Anatase, 25% Rutile) 0.66 g/L	Iron halogenide UV lamp 500W Light wavelength: 315-400 nm Specific power: 95 W/m2	Not described	1L/30ºC	Dark test: PFOA+TiO2 without UV: No PFOA removal Photolysis: PFOA+UV without TiO2: No PFOA removal After 4 h, 32% and 29%
Panchangam et al., 2009a	50	TiO2 RdH Surface area: 10.3 m2/g Particle diameter: 100-200nm 0.66 g/L	Low pressure mercury UV lamp 16W Light wavelength: 254 nm	Neutral pH	3L/25ºC	Dark test: PFOA+TiO2 without UV: 3% Photolysis: PFOA+UV without TiO2: 7 % After 7h, 22%
Panchangam et al., 2009b	50	TiO2 Surface area: 10.3 m2/g Particle diameter: 100-200nm 0.66 g/L and 2 g/L	Low pressure mercury UV lamp 16W Light wavelength: 254 nm Specific power: 4.5 W/m2	Less than 3	2L/25ºC	Dark test: PFOA+TiO2+HCl04 without UV: less than 1% Photolysis: PFOA+UV without TiO2: 4 % After 7 h, using 50 mg/L PFOA and 0.15 HCl04: 2g/L TiO2: 50% and 49% 0.66 g/L TiO2: 100% and 3% After 48h, using 50 mg/L PFOA and 2g/L TiO2 0.15M: 73% and 7% 0.225 M: no PFOA detected and 54%
Chen et al., 2015	50	TiO2 P25 Degussa 99.5 purity 0.5 g/L	UV lamp 400W Light wavelength: 254 nm	pH 5	1L/25ºC	Dark test: PFOA+TiO2 without UV: 5.9% After 12 h, 14% and no F detected
Li et al., 2012	41	TiO2 P25 Degussa (80% Anatase, 20% Rutile) Surface area: 50 m2/g 0.5 g/L	Low pressure mercury UV lamp 23W Light wavelength: 254 nm	Between pH 3 and 4	0.4L/25ºC	Photolysis: PFOA+UV without TiO2: 9.8% After 4 h, 15.9% and no F detected
Estrellan et al., 2010	41	Comertially aeroxide TiO2 P25 0.5 g/L	Medium pressure mercury lamp 150W Light wavelength: 200-600 nm	pH 4.3	0.65L/-	Almost insignificant degradation

The revised reports revealed that model solutions were treated whose PFOA concentration is much higher than the values found in natural waters. Under optimal experimental conditions of 0.66 g/L TiO_2 catalyst dosage and under UV irradiation wavelength between 254-400 nm, the highest degradation rates were observed. However, the process is ineffective and shows slow kinetics. Therefore, changes in the operational conditions, catalyst among others, were required.

2.2. Experimental Procedure

2.2.1. Materials

For the experimental part of this study, the following reagents were used.

- **Perfluorooctanoic acid (PFOA):** organic compound to degrade

Obtained from	Sigma Aldrich, 96% purity
Reference number	171468,CAS 335-67-1
Molecular formula	$C_8F_{15}H_2O_1$
Density (at 20ºC)	1.7 g/cm^3
Solubility (at 20ºC)	3.4 g/cm^3
Molecular weight	414.1 g/mol
Hazard	Corrosive

- **Titanium dioxide (TiO_2) :** photocatalyst

Obtained from	Aeroxide, TiO2 DegussaP25
Reference number	13463-67-7
Surface area	50 m^2/g
Particle diameter	21 nm

- Reagents used to synthesize graphene oxide (GO)-TiO_2composite catalyst

Graphite powder	
Obtained from	Arcos (organics)
Reference number	385031000 CAS 7782-42-5
Molecular weight	12.01 g/mol

Sodium nitrate	
Obtained from	Panreac
Reference number	141702.1211
Molecular weight	84.99 g/mol

Sulfuric acid 95-98% (USP-NF,BP.Ph. Eur.)	
Obtained from	Panreac
Reference number	141058.1611
Molecular weight	98.08 g/mol

Hydrochloric acid 37% PA-ACS-ISO	
Obtained from	Panreac
Reference number	131020.1611
Molecular weight	36.46 g/mol

Potassium Permanganate PA-ACS	
Obtained from	Panreac
Reference number	131527.1211
Molecular weight	158.04 g/mol

Hydrogen peroxide solution 30% w/w (110 vol), extra pure	
Obtained from	Scharlau

Reference number	CAS 7722-84-1
Molecular weight	34.01 g/mol
Density	1.11 g/cm^3

2.2.2. Synthesis of graphene oxide (GO)-TiO_2 composite

The GO-TiO_2 composite was prepared using hydrothermal procedure described in the literature (Pei et al., 2013). GO-TiO_2 is derived from reduced GO. And GO is prepared from graphite in a mixture of sulfuric acid, sodium nitrate and potassium permanganate. Figure 6 shows the summarized scheme of the synthesis procedure of GO-TiO_2 composite catalyst (Pei et al., 2013)..

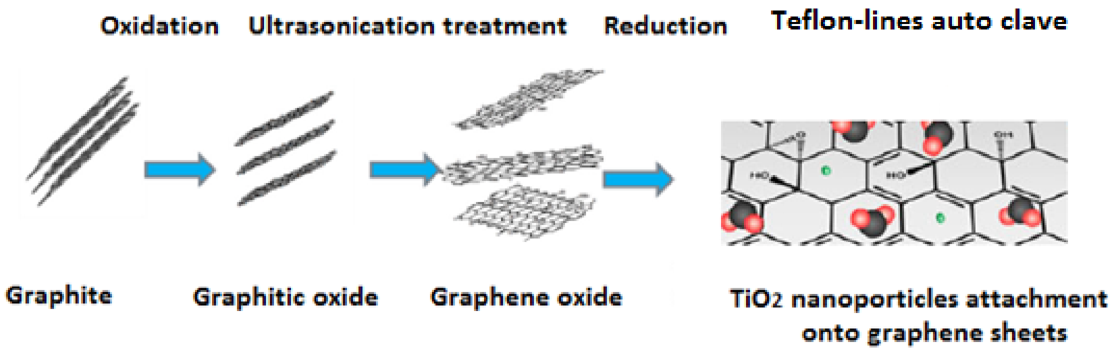

Figure 5. Synthetic procedure of GO-TiO_2 composite catalyst (Pei et al., 2013)

In an ice bath at 0ºC under stirring, graphite (3 g) and sodium nitrate (1.5 g) were added to concentrated sulfuric acid (70 ml). Later on, potassium permanganate (9 g) was slowly introduced holding the temperature at 20ºC. Successively, the reaction was heated up to 35ºC for about 30 minutes and then, 50 ml of ultrapure water was poured increasing the temperature up to 98ºC and stirring further on for 15 minutes. After addition of 170 ml of ultrapure water and 40 ml of H_2O_2 (30%), the solution colour turned from brown to bright yellow. Then, the mixture was washed with HCl (10%) and centrifuged three times with ultrapure water for 5 minutes and 11,000 rpm. The overall solid was collected and suspended in ultrapure water up to 70 ml and then subjected under ultrasonication for 30 minutes. The obtained solution was washed with ultrapure water and centrifuged for 15 minutes and 11,000 rpm. Finally, the solid was dried in an oven at 80ºC all night (Pei et al., 2013).

The next day, the solid was collected and cut into pieces from which 0.038 g of the sample was weighted and added to 200 ml of ultrapure water. The solution, afterwards, was subjected to ultrasonication for about 30 minutes. Later on, 0.762g of TiO_2 was mixed with GO and placed in a Teflon-lined auto-clave at 120ºC for 3 hours. The GO-TiO_2 composite was centrifugated, rinsed with ultrapure water and dried at 80ºC for 12 hours.

2.2.3. Photocatalytic set up

The experimental setup used in photocatalytic experiments is schematized in Figure 7 and Figure 8.

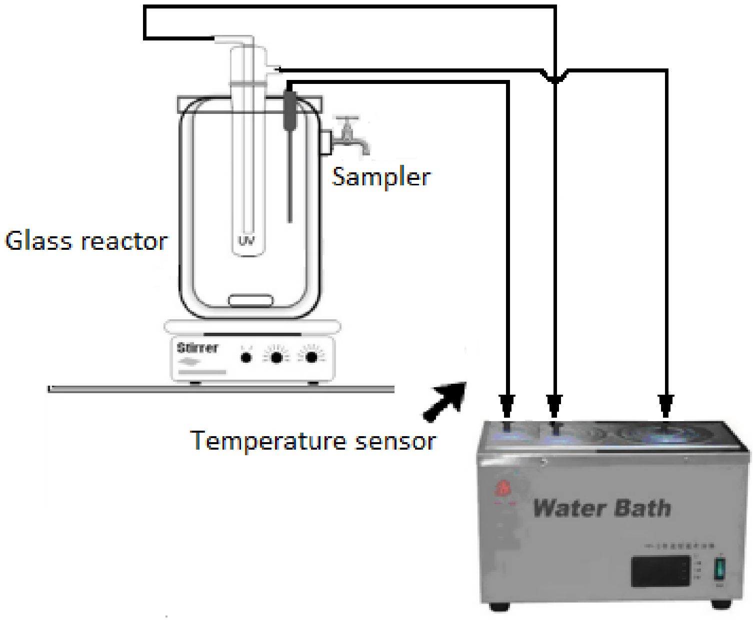

Figure 6.Photochemical experiments setup

Figure 7.Photograph of real experimental set up

The experiments were carried in a Heraeus Laboratory UV Reactor of 1 L equipped with a 150 W medium-pressure Hg lamp (Heraeus Noblelight TQ 150 z1) with an emission spectrum of 200-600nm located in the center of the reactor. An external covering of cardboard and aluminium foil were supplied to avoid inconveniences owing to the emitted light. Also, water/ethylene-glycol cooling jacket (PolyScience Digital Temperature Controller) was used to keep the experimental temperature at 20ºC. For continuous mixing of the solution, the reactor was placed on the top of an Agimatic-S magnetic stirring plate (JP Selecta, Spain) during the irradiation.

Initially, the set up was switched on (lamp and cooling system) and after 30 minutes of stabilization, 800 ml of PFOA solution (100 mg/L) was poured into the glass reactor. In UV/catalyst experiments, the PFOA solution was previously mixed with 0.5 g/L catalyst powder in a beaker to obtain a uniform suspension and, afterwards, the experiment was started. Aliquots of sample were taken at selected intervals of time and necessary filtrated with 0.45 µm filters to remove photocatalyst for subsequent analysis of PFOA concentration and decomposition.

2.2.4. Analytical Methods: total organic carbon (TOC) analysis, ion chromatography(IC) and high performance liquid chromatography (HPLC)

TOC equipment analyses the carbon content of the solution, i.e., compound mineralization. The value was calculated as the difference between the total carbon and inorganic carbon measured by TOC-V CPH (Shimadzu). The data were obtained using a calibration curve that establishes relationship between the area under the peak of the CO_2 signal of the sample and its concentration.

On the other hand, the fluoride concentration generated during PFOA degradation was monitored by IC based on a separation column equipped with ion exchange resins and a conductivity detector with suppressor device. IC analysis was performed with ICS-1100 chromatograph using separation column AS9-HC supplied by Dionex.

Finally, HPLC-DAD system (Waters 2695) eqipped with a X Bridge C18 column (5 µm, 250 nm x 4.6 mm, Waters) was used to monitorize PFOA concentration over the experimental time. In a column, samples were injected with methanol/$NaH_2PO_4$65:35 as mobile phase by means of autosampler and two pumps. The retention time of different compounds was measured and identified by UV-Visible spectrophotometric detector.

2.3. Results and discussion

Three types of practical tests were carried out under the same operational conditions displayed in Table 6.

Table 6. Experimental conditions of practical tests

Operational Condition	Value
PFOA concentration	100 mg/L
Treated volume	800 ml

pH	Initial pH 3.34
Temperature	20 ºC

These tests are:

- Control 1: PFOA adsorption
- Control 2: Direct photolysis of PFOA
- Experiment: PFOA photocatalytic decomposition

2.3.1. Control 1: PFOA adsorption

PFOA adsorption onto the reactor and both TiO_2 and GO-TiO_2composite catalyst were reviewed. The experimental procedure consists of PFOA solution residence in the reactor under dark conditions with and without catalyst presence respectively. Aliquots at selected intervals of time were taken and then analysed by HPLC, IC and TOC. Figure 9 discloses the results of those tests.

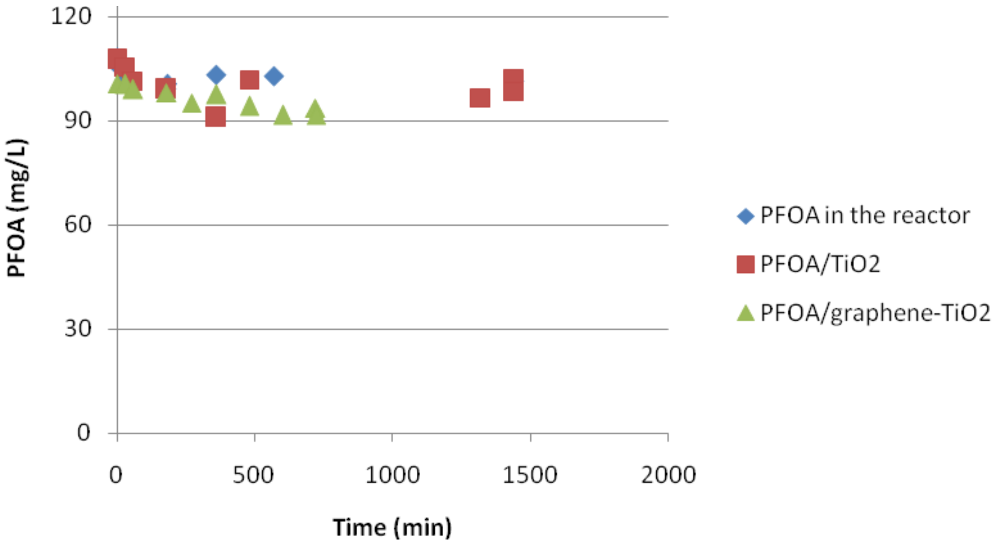

Figure 8. Control 1: trends of PFOA concentration in the solution

The amount of PFOA adsorbed onto the reactor, TiO_2 and GO-TiO_2 composite catalyst was found to be 4.3 %, 8.3 % h and 9% after 12 h respectively. Therefore, a little amount of PFOA (<5%) was absorbed just by the materials of the experimental systems, and the adsorption was increased to a maximum of 9% when the catalyst material was presented. PFOA adsorption onto the catalyst is due to the join of negatively charged PFOA (ionized) and positively charged catalyst in acidic media although that small amount adsorbed probably suggests that compound stereo-chemical configuration is unsuitable for the coupling with the catalysts. On the other hand, fluoride content was not detected in the solution, possible owing to the fact that no PFOA decomposition was occurring. Finally, no TOC values could be displayed as analysed samples were not correctly measured.

2.3.2. Control 2: Direct photolysis of PFOA

Survey of PFOA decomposition and mineralization by 150 W medium-pressure Hg lamp with an emission spectrum of 200-600nm has been examined. To this end, PFOA solution was introduced into the glass reactor and then it was irradiated by UV lamp without catalyst presence. The laboratory experiment was conducted twice and the results are displayed in Figure 10 (PFOA and fluoride) and Figure 11 (TOC).

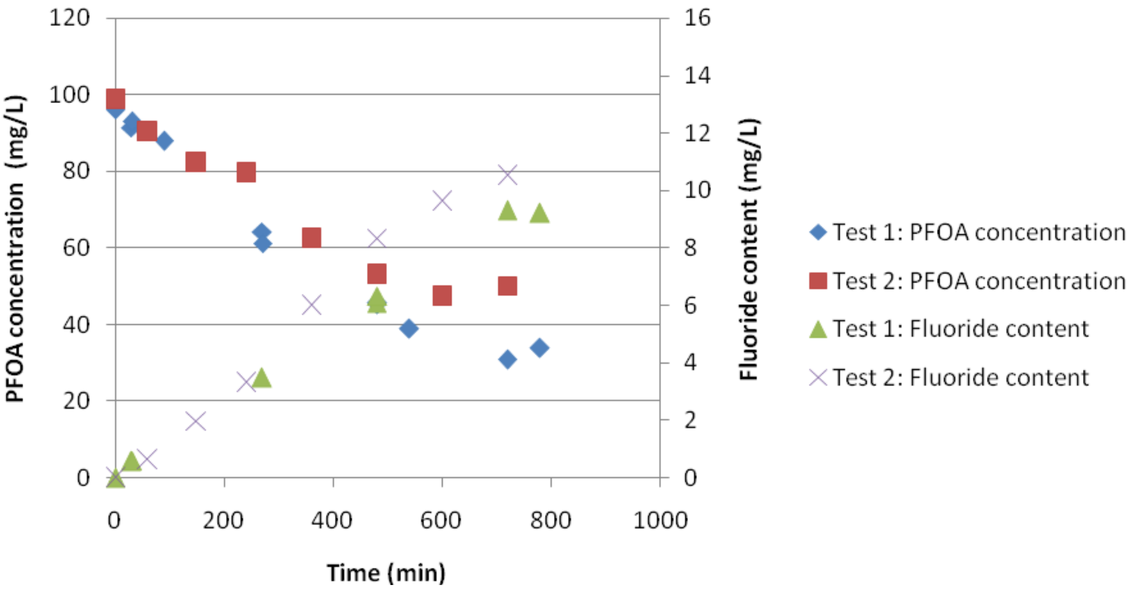

Figure 9.Control 2, direct photolysis: trends of fluoride ions release and PFOA concentration in the solution

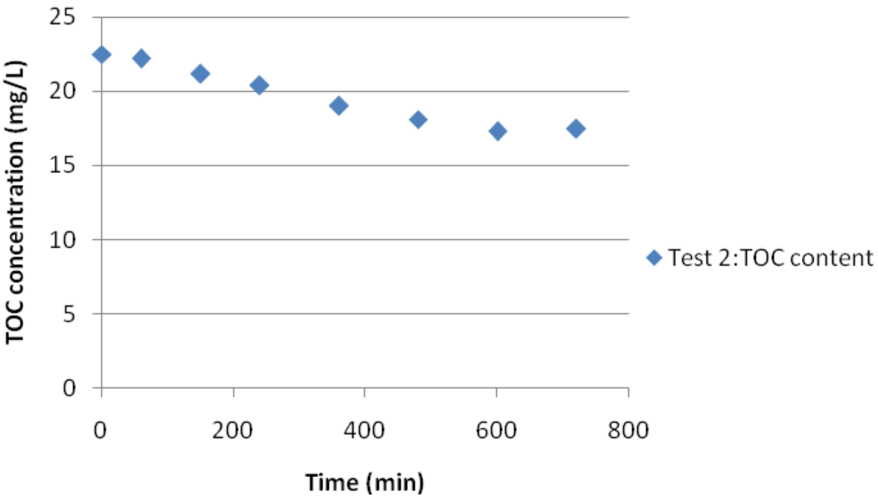

Figure 10. Control 2, direct photolysis: trends of total organic carbon content in the solution

Direct photolysis showed a high decrease in PFOA concentration (up to 57 % after 12 h) while, at the same time, fluoride concentration was increasing in the solution (up to 6.8 % after 12 h). It has to be taken into consideration that fluoride content in the solution was lower than the theoretical fluoride concentration that would be obtained after complete PFOA mineralization as 15 moles of fluoride ions must be released per each PFOA mole that is completely mineralised (that is 100 mg/L of PFOA in 0.8 L must generate 17 mg/L of fluoride if 20% of PFOA is mineralized as described in Figure 11)

(Sansotera et al., 2014). The adsorption of fluoride ions onto the reactor, formation of fluoride by-products or incomplete PFOA mineralization are probable reason of fluoride ions loss in aqueous phase. Additionally, high PFOA decomposition could be related to the absorption of UV light, bearing in mind that in the experimental process a UV lamp that emits in the wavelength of 200-600 nm is used and PFOA has a strong light absorption from deep UV region to 220 nm. Also, minor adsorption of PFOA on the reactor is presented as it was concluded in Control 1.

On the other hand, PFOA mineralization represented by TOC values follow the same trend as PFOA decomposition (see again Figure 10, PFOA concentration in the solution) but at a much slower rate. TOC exhibit a decrease of 20 % that is an indicative of the formation of intermediate oxidation products, i.e. smaller perfluorocarboxylic compounds.

Finally, in both repeated test the trends of PFOA concentration and fluoride content seems to overlap although with slight difference in the trends of the curves after 500 minutes.

2.3.3. Experiment: Photocatalytic decomposition of PFOA

PFOA decomposition by TiO_2 and GO-TiO_2 composite catalyst under UV irradiation was studied. In order to carry out the experiments, PFOA solution and the catalyst were mixed and introduced into the glass reactor that was irradiated. Samples at different intervals of time were taken, analysed and depicted in Figure 9 and Figure 10. Both experiments were repeated twice.

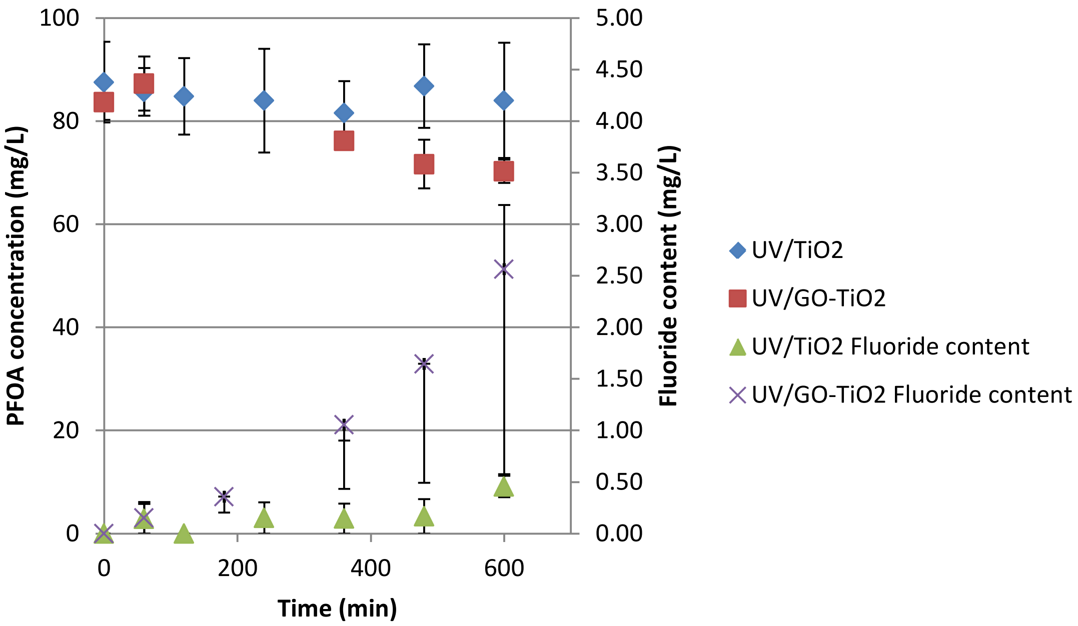

Figure 11. Trends of fluoride ions release and PFOA concentration in the solution in photocatalytic experiments

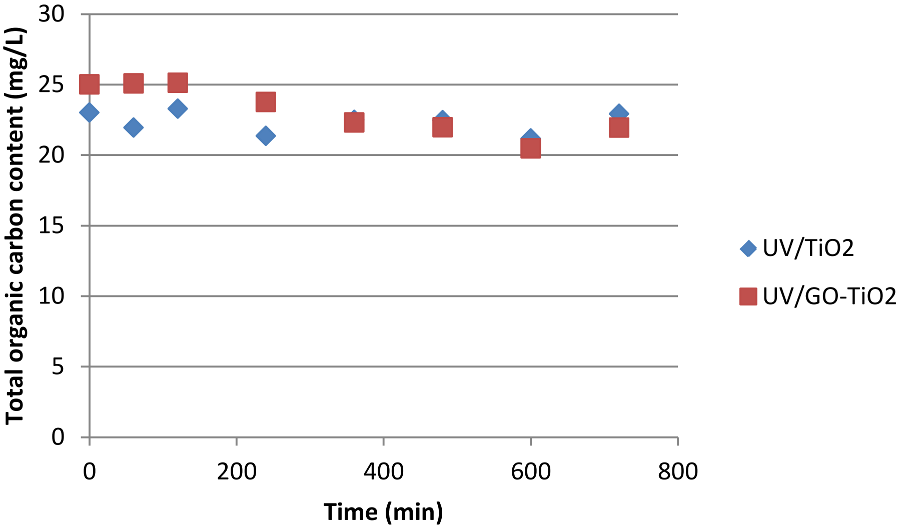

Figure 12. Trends of total organic carbon content in the solutionin photocatalytic experiments

In UV/TiO_2 and UV/GO-TiO_2 systems, 4 % and 16 % of PFOA was decomposed respectively after 10 hours. On the other hand, fluoride ions were released in small amounts, although noticeably larger when using GO-TiO_2 catalyst. For carbon content, almost no shift was observed: less than 0.5% in UV/TiO_2 and 12 % in UV/graphene-TiO_2.

The results indicated that UV/TiO_2 system was ineffective in PFOA decomposition and that molecules of PFOA were mostly adsorbed onto the catalyst (remember that more than 8 % of PFOA was adsorbed onto TiO_2 in Control 1 run). However, the small amount of fluoride in the solution would indicate a very slight percentage of decomposition. The low rate of decomposition could be due to the phenomena of scattering, decreasing light penetration and, therefore, reducing the direct photolysis phenomena. In UV/GO-TiO_2 the same phenomenon may be found although better activity of the catalyst was denoted. TiO_2 doping possible resulted in the lowering of the band gap and electron trapping mechanisms reducing electron-hole recombination. However, it is not enough to enhance the decomposition processes in comparison with direct photolysis.

3. CONCLUSIONS

3. CONCLUSIONS

Perfluorooctanoic acid (PFOA) is an anthropogenic compound that belongs to the family of perfluoroalkyl substances (PFASs). Among literature reports, destructive and non-destructive methods were offered to remove PFASs. Destructive technologies such as photocatalysis with TiO_2 have reported low yield decomposition giving rise to proposals for changing the operational conditions. For this reason, GO-TiO_2 composite catalyst was evaluated in PFOA decomposition under UV irradiation.

This works presented an experimental study on photocatalytic decomposition of PFOA in aqueous solution by commercial TiO_2 and co-doped GO-TiO_2 composite synthesized in the laboratory using hydrothermal method. Also, adsorption and direct photolysis of PFOA were analysed.

The results showed that less than 9 % of PFOA could be adsorbed on both reactor and catalyst. Otherwise, in photocatalytic systems using TiO_2 and GO-TiO_2 composite catalyst, low efficiencies were noted: 4% and 16 % of PFOA was decomposed respectively with slight PFOA mineralization. The phenomena of scattering may be affect the catalyst performance and, therefore, PFOA decomposition. Lastly, direct photolysis reached the highest yield in PFOA decomposition and mineralization, near 60% and 20% respectively. UV lamp used in the experimental test probably provides enough energy in the far UV range that break C-F bond and mineralize PFOA.

Further investigation about use of GO-TiO_2 composite catalyst would be interesting to carry out. Also, catalytic dosage and other operational conditions could be assessed.

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4. REFERENCES

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5. ANNEXES

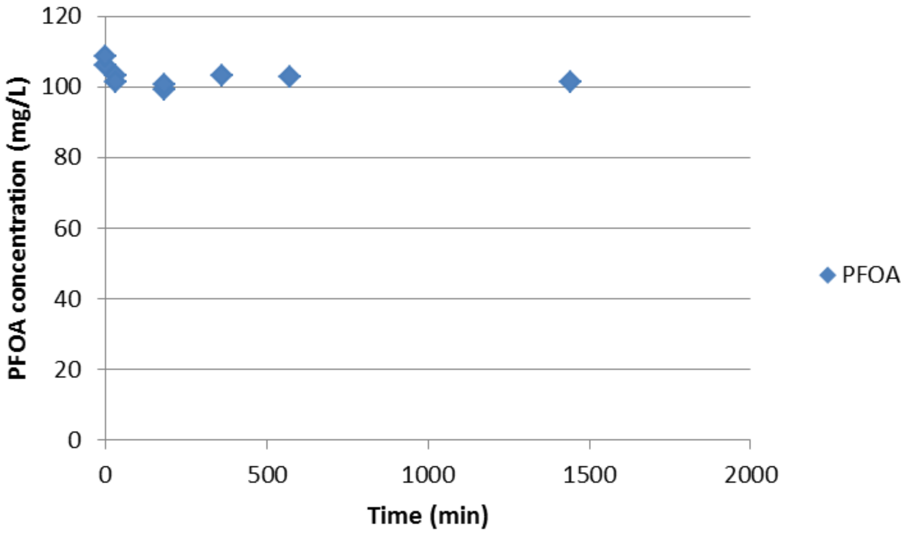
5. ANNEXES

5.1. Annex A. Laboratory experimental data of PFOA adsorption and decomposition

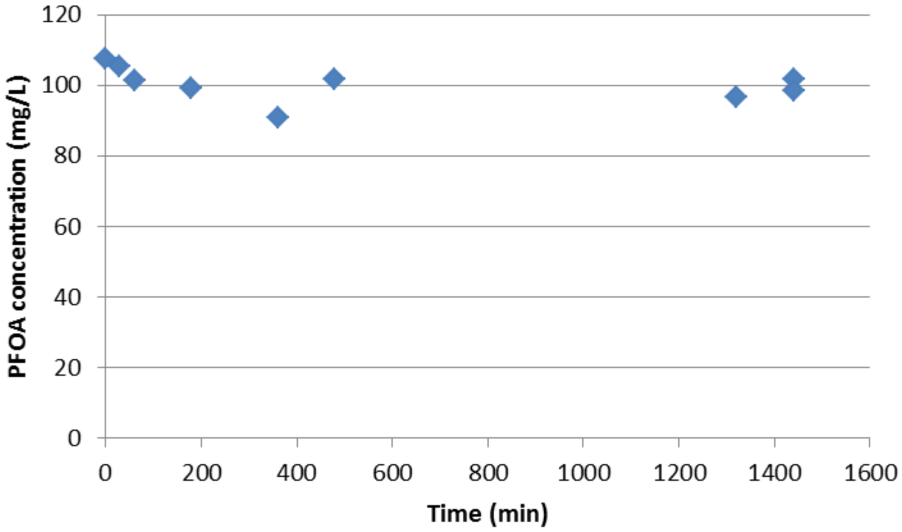
5.1.1. Control 1: PFOA adsorption by the reactor and both TiO_2 and GO-.TiO_2 composite catalyst

Time (min)	pH	PFOA (mg/L)	F (mg/L)
0.00	3.39	105.94	0.00
1.00	3.51	108.54	0.00
30.00	3.60	103.04	n.m.(1)
31.00	3.51	101.41	n.m.(1)
180.00	3.48	99.12	0.00
181.00	3.42	100.46	n.m.(1)
360.00	3.45	103.22	n.m.(1)
570.00	3.47	102.82	n.m.(1)
1440.00	3.47	101.39	0.00

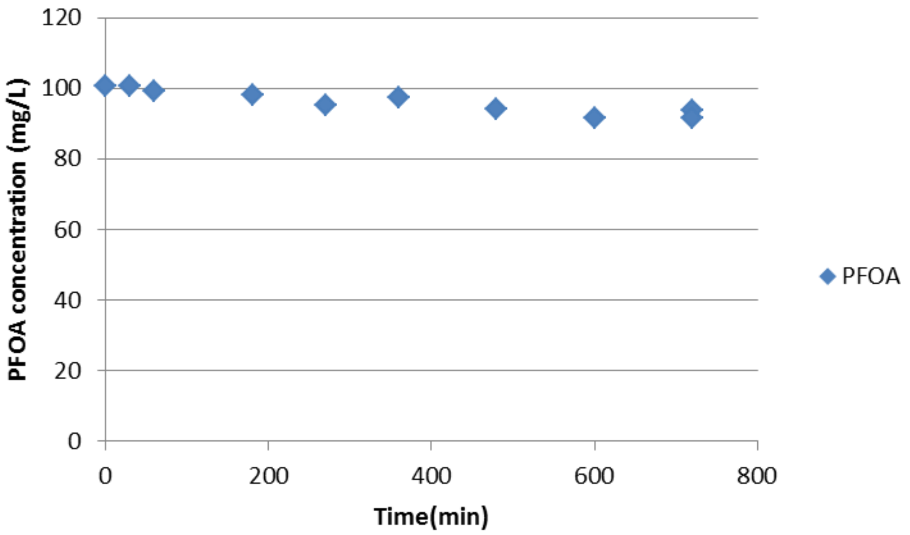
n.m.(1): not measured sample



Time (min)	pH	PFOA (mg/L)	F (mg/L)
0.00	3.79	107.50	0.00
30.00	3.58	105.52	0.00
60.00	3.58	101.49	0.00
180.00	3.50	99.13	0.00
360.00	3.39	90.83	0.00
480.00	3.26	101.86	0.00
1320.00	3.43	96.58	0.00
1440.00	3.45	101.73	0.00
1441.00	3.48	98.53	0.00



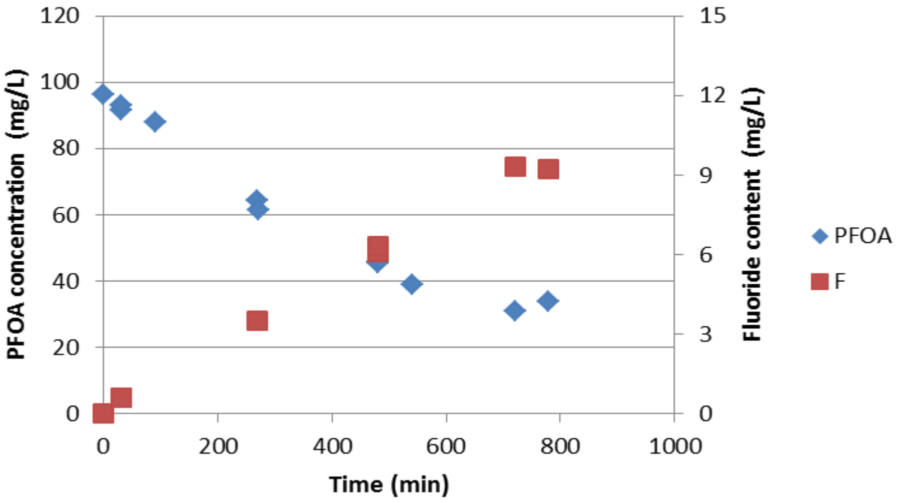
Time (min)	pH	PFOA (mg/L)	F (mg/L)
0.00	3.55	100.77	0.00
30.00	3.54	100.54	0.00
60.00	3.54	99.12	0.00
180.00	3.45	98.04	0.00
270.00	3.49	95.21	0.00
360.00	3.5	97.48	0.00
480.00	3.51	94.13	0.00
600.00	3.47	91.72	0.00
720.00	3.49	93.69	0.00
721.00	3.48	91.72	0.00



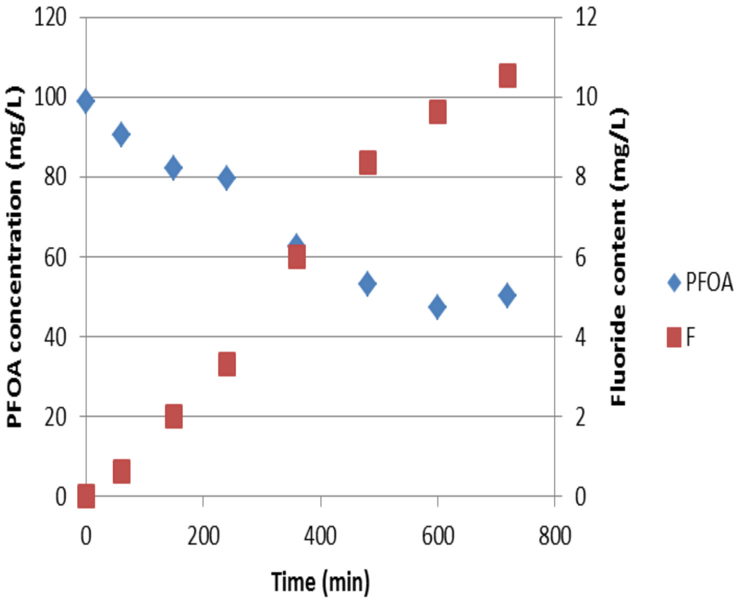
5.1.2. Control 2: Direct photolysis of PFOA (test 1 and test2)

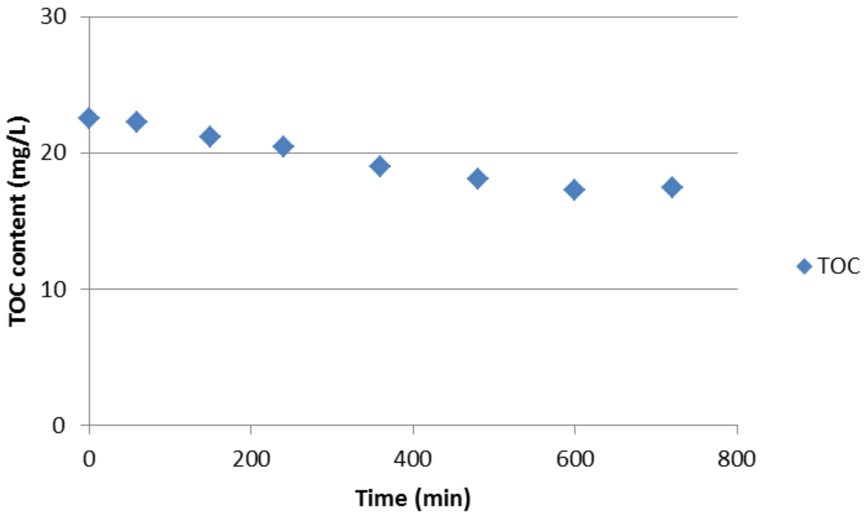
Time (min)	pH	PFOA (mg/L)	F (mg/L)
0.00	3.56	96.14	0
30.00	3.50	91.37	0.58
31.00	3.52	92.87	0.6
90.00	n.m.(1)	87.94	n.m.(1)
270.00	3.42	64.29	3.48
271.00	n.m.(1)	61.24	n.m.(1)
480.00	3.28	45.30	6.08
481.00	3.2	45.68	6.33
540.00	n.m.(1)	38.97	n.m.(1)
720.00	3.14	30.85	9.30
780.00	3.13	33.86	9.22

n.m.(1): not measured sample



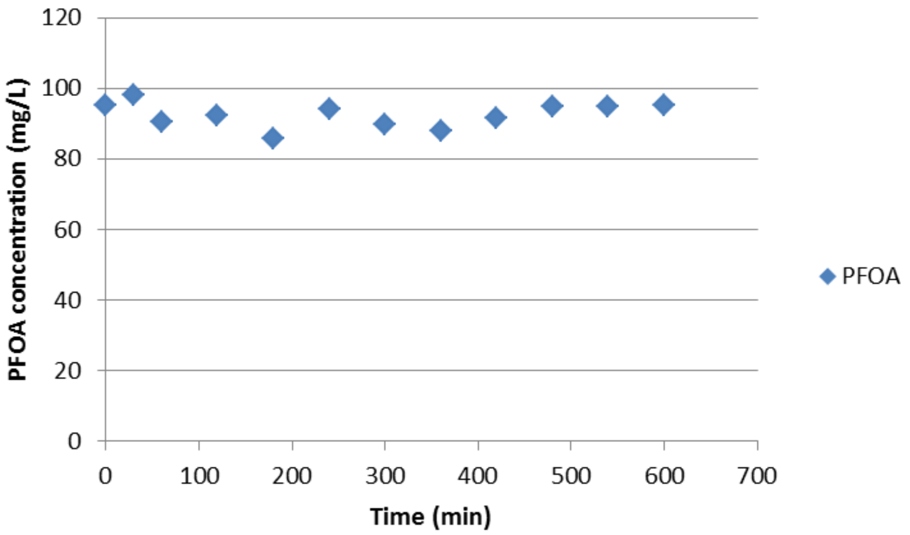
Time (min)	pH	PFOA (mg/L)	F (mg/L)	TOC (mg/L)
0.00	3.14	98.73	0.00	22.51
60.00	3.21	90.32	0.63	22.21
150.00	3.17	82.15	1.99	21.16
240.00	3.17	79.43	3.32	20.41
360.00	3.05	62.47	5.98	19.01
480.00	3.10	53.02	8.34	18.12
600.00	3.03	47.26	9.62	17.30
720.00	3.04	50,14	10.53	17.45





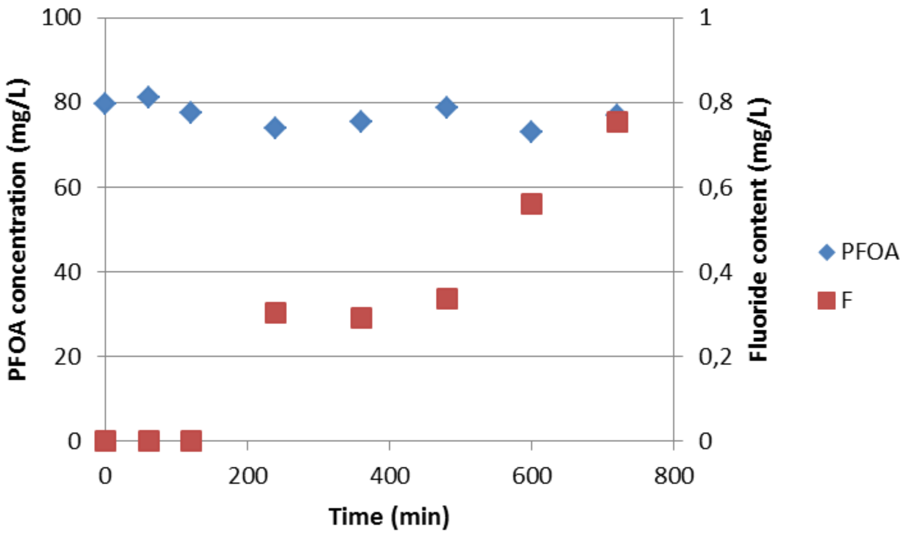
5.2.3. Experiments: photocatalytic decomposition of PFOA by TiO_2 and GO-TiO_2 composite catalysts

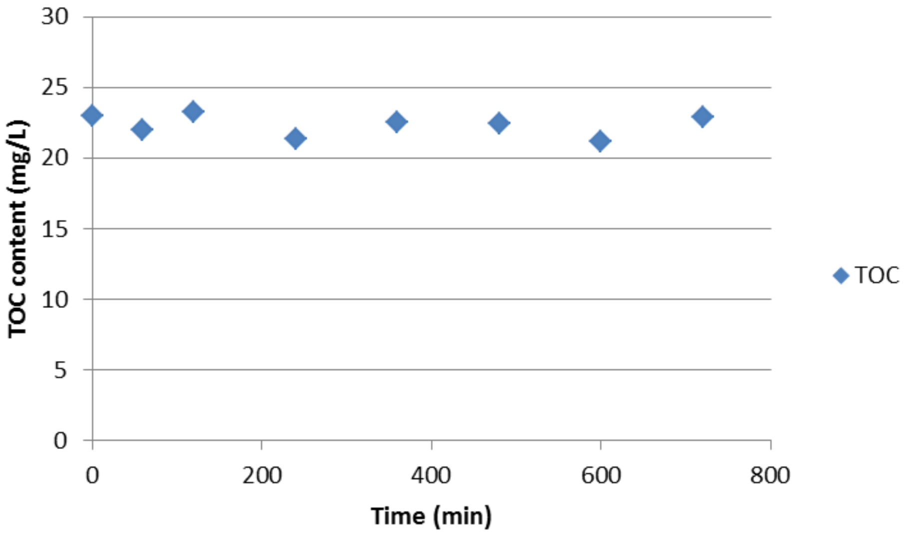
Time (min)	pH	PFOA (mg/L)	F (mg/L)
0.00	3.55	95.36	0.00
30.00	3.55	98.23	0.00
60.00	3.61	90.32	0.29
120.00	3.61	92.23	0.00
180.00	3.65	85.89	0.29
240.00	3.56	94.04	0.00
300.00	3.54	89.59	0.31
360.00	3.62	87.77	0.00
420.00	3.60	91.37	0.30
480.00	3.62	94.90	0.00
540.00	3.59	94.95	0.00
600.00	3.57	95.17	0.35



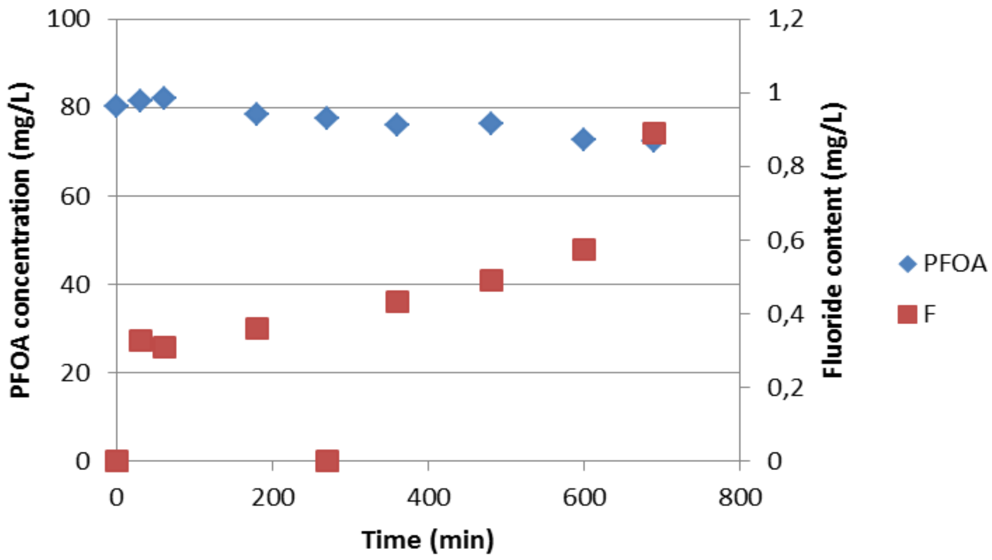
Time (min)	pH	PFOA (mg/L)	F (mg/L)	TOC (mg/L)	O_2dissolved (mg/L)
0.00	3.74	79.75	0.00	23.02	n.m.(1):
60.00	3.71	81.06	0.00	21.95	n.m.(1):
120.00	3.71	77.40	0.00	23.29	9.62
240.00	3.74	73.90	0.30	21.35	n.m.(1):
360.00	3.70	75.37	0.29	22.50	9.99
480.00	3.71	78.67	0.34	22.46	9.09
600.00	3.72	72.83	0.56	21.18	n.m.(1):
720.00	3.68	76.80	0.75	22.93	n.m.(1):

n.m.(1): not measured sample



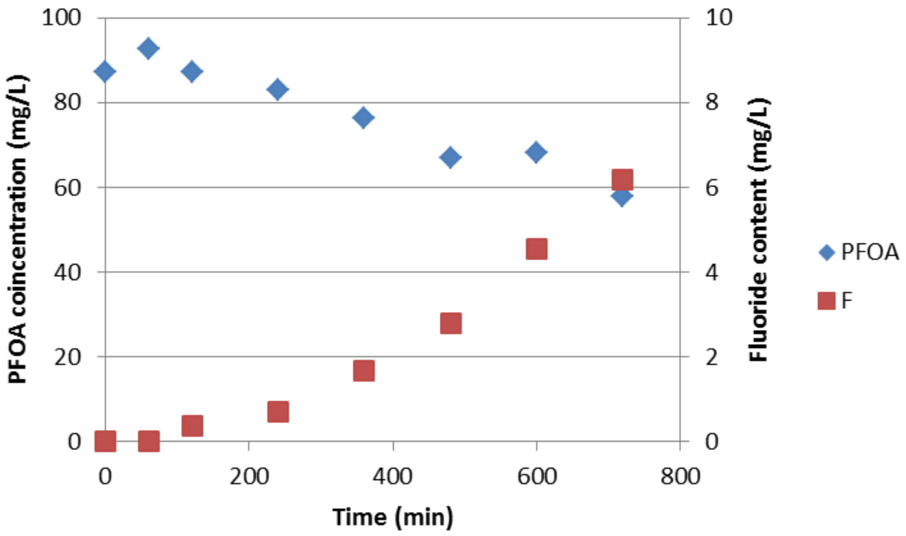


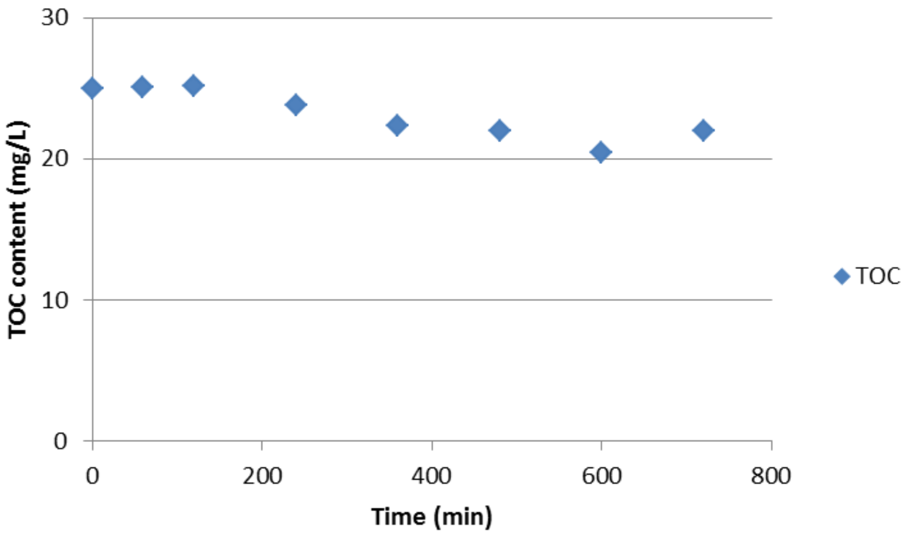
Time (min)	pH	PFOA (mg/L)	F (mg/L)
0.00	3.23	80.20	0.00
30.00	3.18	81.54	0.33
60.00	3.23	82.05	0.31
180.00	3.31	78.44	0.36
270.00	3.23	77.49	0.00
360.00	3.26	75.98	0.43
480.00	3.22	76.38	0.49
600.00	3.16	72.51	0.58
690.00	3.16	72.35	0.89



Time (min)	pH	PFOA (mg/L)	F (mg/L)	TOC (mg/L)	O_2 dissolved (mg/L)
0.00	3.73	87.11	0.00	25.01	n.m.(1)
60.00	3.72	92.51	0.00	25.07	7.80
120.00	3.71	87.04	0.35	25.12	n.m.(1)
240.00	3.67	83.06	0.70	23.77	n.m.(1)
360.00	3.58	76.32	1.68	22.31	n.m.(1)
480.00	3.54	66.95	2.80	21.97	n.m.(1)
600.00	3.43	68.01	4.55	20.46	7.77
720.00	3.37	57.88	6.19	21.94	8.29

n.m.(1): not measured sample




30
20
10
0
TOC content (mg/L)
0
200
400
600
800
Time (min)
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