



Solar Photocatalysis for Gas-Phase Air Cleaning: from lab to pilot plant studies

*Thesis submitted in partial fulfilment of the requirements for the
degree of Doctor of Philosophy in Environmental Engineering, at the
Faculty of Engineering, University of Porto*

Ricardo André Ribeiro Monteiro

Supervisor: Dr. Vítor Jorge Pais Vilar
Co-Supervisors: Dr. Adrián Manuel Tavares da Silva
Dr. Rui Alfredo Rocha Boaventura

Associate Laboratory LSRE-LCM
Department of Chemical Engineering
Faculty of Engineering
University of Porto
October, 2014

Acknowledgements

The four years of this doctoral program symbolize a long and tough path, especially in the beginning. It was only possible because of all the people and institutions supporting me in many ways to whom I would like to acknowledge.

First of all, I would like to deeply thank my supervisor Dr. Vítor Vilar, for the opportunity of developing my scientific work fulfilling all the required conditions in the research group (LSRE-FEUP). His scientific supervision and suggestions were essential to bring this dissertation towards fruition. To Dr. Rui Boaventura I thank him for his time in proofreading, for giving useful comments and suggestions to improve this manuscript. A very special thanks is addressed to Dr. Adrián Silva for being supportive at all levels. His ideas, advises and contributions were and will always be invaluable.

A mention must be made to the following institutions that supported this work: the Foundation for Science and Technology (FCT) for the doctoral grant: SFRH/BD/69323/2010 and project PTDC/EQU-EQU/100554/2008); the Associate Laboratory of Separation and Reaction Engineering (LSRE) and Catalysis and Materials (LCM). The projects PEst-C/eqB/LA0020/2013 and PEst-OE/QUI/UI0616/2014, financed by FCT and FEDER through COMPETE, and by QREN, ON2 (North Portugal Regional Operational Programme) and FEDER through projects NORTE-07-0162-FEDER-000050, NORTE-07-0162-FEDER-000015.

I consider myself very fortunate to have had the opportunity to collaborate with Prof. Adélio Mendes and Prof. Joaquim Faria and their research staff. Their contributions have broadened and enriched the contents of this dissertation.

I gratefully acknowledge Yas Yamin, Marlène Rouhet, Anne Roemer, Nicolas Keller and Valerie Keller from ICPEES– Institut de Chimie et Procédés pour l’Energie, l’Environnement et la Santé, CNRS and University of Strasbourg, France, for the human and scientific knowledge shared, as well as for providing experimental facilities. *Merci beaucoup!*

A word for those who became my friends: João Pereira, Ariana Pintor, Livia Xerez, Bianca Souza, Tânia Silva, André Fonseca, Caio Rodrigues-Silva, Catarina Ferreira, Filipe Lopes and Joana Pereira. Thank you for the odd lunches, for the invigorating morning coffees, for the ramblings about the real and the absurd. Thank you for everything.

To my family, I express my sincere gratitude for being there for me. Even not knowing the how or when they are my lifeline at all times.

Finally, to Catarina, my inexhaustible source of love, friendship, complicity and solidarity at all moments, even in those I did not deserve. This is for you! Thank you so much!

With love to my parents, brother and Catarina.

Abstract

Heterogeneous photocatalysis or photocatalytic oxidation (PCO) has been recognized over the recent decades as one of the most promising technologies for air treatment.

The present thesis aims to evaluate the efficiency of solar gas-phase PCO as well as to provide fundamental understanding of different titanium dioxide (TiO₂)-based photocatalysts toward the elimination of air pollutants such as volatile organic compounds (VOCs). The following objectives were addressed: (i) synthesis and characterization of TiO₂ nanotubes as well as nitrogen modified TiO₂ nanotubes and nanoparticles; (ii) preparation of TiO₂-based materials and their immobilization as thin films on different supports using the *dip-coating* technique; (iii) evaluation of photocatalytic activity of the prepared photocatalysts and its dependence on different operational conditions (flow rate – Q_{feed} ; pollutant concentration – $C_{\text{voc, feed}}$; relative humidity – RH , irradiance – I ; presence/absence adsorbed molecular oxygen) using a lab-scale single-pass continuous-flow annular photoreactor; (iv) description of PCO mechanisms; (v) evaluation of photocatalytic activity of selected materials in a pilot-scale photoreactor for continuous removal of VOCs.

Gas-phase PCO of perchloroethylene (PCE) (574 – 2442 ppm) was carried out in a lab-scale annular photoreactor ($r = 23.2$ mm) under catalytic (UV TiO₂) conditions. The photoreactor was assembled with a catalytic bed made of glass spheres packed with the benchmark TiO₂ P25 catalyst (Evonik®) filling the voids between the spheres. A UVC lamp ($\lambda = 253.7$ nm) was located inside an inner tube (quartz or glass) of the photoreactor. The PCO of PCE was evaluated upon three parameters and employing the photoreactor with the glass inner tube (mimicking UV fraction of solar radiation); briefly: (1) for a 4.25 fold increase in $C_{\text{PCE, feed}}$ (from 574 ppm to 2442 ppm), a reduction of ~76 % (from 63 % to 35 %) on the PCE conversion was observed; (2) increasing the Q_{feed} (from 59 cm³ min⁻¹ to 300 cm³ min⁻¹) led to lower PCE conversions (from 81 % to 33 %); (3) for a 3.33 fold reduction in RH (from 40 % to 12 %), the PCO efficiency merely decreased ~1.2 times. Although 97 % of initial PCE was converted into CO₂ and water through pure photolysis using the quartz inner tube, only 51 % of mineralization was attained through PCO when the glass inner tube was used. A mathematical model was developed taking into consideration the following main assumptions: (a) steady-state operation; (b) isothermal and isobaric conditions; (c) ideal gas behaviour; (d) axial symmetry; (e) constant porosity of the bed (uniform packing shape and distribution); (f) axially dispersed plug flow; (g) no heat transfer resistance and no thermal and UV radiation gradients; (h) no mass, velocity, and UV radiation gradients in the radial direction. Assuming that only PCE and H₂O are the major species as well as that intermediates and/or reaction products do not influence PCE degradation kinetics, it was

shown that PCE and H₂O molecules may have to be considered in association with different specific active sites of the TiO₂ surface since Langmuir-Hinshelwood bimolecular non-competitive two types of sites model described better the experimental data.

PCO of gas-phase PCE and *n*-decane was also assessed employing the lab-scale annular photoreactor under simulated solar radiation. Cellulose acetate monolithic structures coated with two different TiO₂ photocatalytic films (prepared from aqueous suspensions of P25 from Evonik® and PC500 from Cristal®) were employed as catalytic bed ($L_{\text{catalytic bed}} = 160$ mm). The reactor was equipped with a compound parabolic collector (CPC) allowing the whole reactor and bed illumination. PC500 film provided higher conversion and mineralization of PCE and *n*-decane than those obtained with P25 film, most likely due to the higher specific surface area of TiO₂ PC500. Conversions of both pollutants ($C_{\text{dec, feed}} = 71$ ppm and $C_{\text{PCE, feed}} = 1095$ ppm) were close to 100 % using PC500 film when $Q_{\text{feed}} = 150$ cm³ min⁻¹, $I = 38.4$ W_{UV} m⁻² and $RH = 20$ %. Competitive adsorption between the pollutants and water molecules on the PC500 film surface was found above 20 % of RH . Results showed that gas-phase molecular oxygen has a fundamental role in the PCO reaction, as the conversion of pollutants is drastically impaired in its absence, suggesting that photocatalytic mechanism consists of: (i) oxidation reactions promoted by reactive species formed from the adsorbed molecular oxygen (O₂^{•-}, HOO[•]); (ii) contribution of the oxygen from the lattice of TiO₂; (iii) hydroxyl radical (HO[•]) formation on the TiO₂ surface. PCO mechanism of chlorinated compounds such as PCE, may also include a series of reactions involving Cl[•] radicals.

The best performing photocatalyst (TiO₂ PC500) was then incorporated into an exterior (water based) vinyl paint, supported on the cellulose acetate monolithic structure and tested under simulated solar radiation. 60 % of the PCE ($C_{\text{PCE, feed}} = 1100$ ppm) and 98 % of the *n*-decane ($C_{\text{dec, feed}} = 41$ ppm) feed concentrations were converted when using $Q_{\text{feed}} = 75$ cm³ min⁻¹, $RH = 40$ % and $I = 38.4$ W_{UV} m⁻². In addition, the results revealed an optimum surface density (~0.87 mg cm⁻²) to achieve the highest performance; also, increasing the exposed area to radiation by removing the outer wall of the monolithic structure, the PCO of PCE was enhanced by, approximately, 58 % (from 38 % to 60 %) under the same experimental conditions.

Considering that TiO₂ is a wide bandgap semiconductor, only active under UV radiation, TiO₂ modification with nitrogen was studied to enhance its performance for solar applications. TiO₂ nanotubes were synthesized by hydrothermal treatment of TiO₂ P25 and chemical modification was performed by grinding urea (nitrogen source) with the TiO₂ nanotubes, followed by thermal treatment. The same procedure was applied to bare TiO₂ P25 nanoparticles. The results revealed that nitrogen-modification of TiO₂ P25 decreased the photocatalytic activity

towards PCO of gas-phase PCE under simulated solar radiation: bare TiO₂ P25 presented the highest activity (67 % of PCE conversion) whereas only 35 % of conversion was attained over N_{0.50}P25-380 (material with a urea:TiO₂ weight ratio of 1:2 and calcined at 380 °C). However, when these particular materials were tested in aqueous-phase, N_{0.50}P25-380 showed the highest photocatalytic activity for PCO of diphenhydramine (emerging water pollutant of pharmaceutical origin) and inactivation of *Escherichia coli* bacteria under visible ($\lambda > 430$ nm) and UVA ($\lambda = 365$ nm) radiation, respectively.

The PCO over nitrogen-modified TiO₂ nanotubes was also investigated for the conversion of methylethylketone (MEK) and hydrogen sulfide (H₂S). MEK showed high resistance to photocatalytic degradation over these materials, but a high photocatalytic activity towards H₂S degradation under UVA ($\lambda = 365$ nm) radiation and moderate photocatalytic activity under solar light radiation were observed.

Finally, based on lab-scale experimental data, modelling simulations and predictions of PCO of pure-targeted VOCs, a pilot-scale annular photoreactor ($r = 32.8$ mm, $L_{\text{catalytic bed}} = 144$ cm) was designed and manufactured. The photoreactor features a CPC to capture both direct and diffuse solar radiation and/or UVA lamps, in order to work continuously day and night. The PCO of *n*-decane ($C_{\text{dec, feed}} = 10$ ppm, $Q_{\text{feed}} = 2$ L min⁻¹, $\tau = 44$ s) over cellulose acetate monolithic structures coated with different TiO₂-based photocatalytic films (P25, PC500 and photocatalytic paint) was studied under solar and artificial UVA radiation. Conversions up to 100 %, were attained using P25 or PC500 films under solar irradiances of 15 W_{UV} m⁻² (morning, increasing temperature) and 3 W_{UV} m⁻² (afternoon, decreasing temperature). The photocatalytic paint film promoted up to 45 % of *n*-decane conversion under 48 W_{UV} m⁻² in both periods of the day. The excess of photons reaching the photocatalytic bed seems to favour the direct reaction pathway of CO₂ production. The PCO of *n*-decane under artificial UVA radiation was 29 % higher using the PC500 film in comparison with the P25 film (resulting in 100 % of conversion), while over the photocatalytic paint film no more than 25 % of *n*-decane was converted. Results suggest that a 24 h continuous PCO process towards the removal of *n*-decane can be accomplished by combining both radiation sources (artificial UVA and solar).

Resumo

A fotocatalise heterogénea ou oxidação fotocatalítica (OFC) tem sido considerada nas últimas décadas uma das mais promissoras tecnologias para o tratamento do ar.

Esta dissertação pretende avaliar a eficiência da OFC em fase gás assim como proporcionar conhecimento fundamental sobre fotocatalisadores baseados em dióxido de titânio (TiO_2) na eliminação de poluentes do ar tais como compostos orgânicos voláteis (COVs). Foram estabelecidos os seguintes objectivos: i) síntese e caracterização de nanotubos de TiO_2 bem como de nanotubos e nanopartículas de TiO_2 modificados com azoto; ii) preparação de materiais à base de TiO_2 e a sua imobilização como películas finas em diferentes suportes utilizando a técnica de *dip-coating*; iii) avaliação da actividade fotocatalítica dos materiais preparados quando utilizadas diferentes condições de operação (caudal – $Q_{\text{alimentação}}$; concentração – $C_{\text{COV, alimentação}}$; humidade relativa – HR ; irradiância – I ; presença/ausência de oxigénio molecular adsorvido) à escala laboratorial utilizando um reator anular de fluxo contínuo e passo único; iv) descrição de mecanismos de OFC; v) avaliação da actividade fotocatalítica de materiais seleccionados utilizando um reactor à escala piloto destinado à remoção contínua de COVs.

A OFC em fase gasosa de percloroetileno (PCE) (574 – 2442 ppm) foi realizada num reactor anular ($r = 23.2 \text{ mm}$) à escala laboratorial (UV/ TiO_2). O fotoreator compreendia um leito catalítico constituído por esferas de vidro e empacotado com o catalisador de referência TiO_2 P25 (Evonik®), este catalisador preenchendo assim os espaços vazios entre as esferas. Uma lâmpada UVC ($\lambda = 253.7 \text{ nm}$) foi colocada dentro do tubo interno (quartzo ou vidro) do reator. A OFC de PCE foi avaliada em três parâmetros utilizando neste caso um tubo interno de vidro (mimetizando a fracção UV da radiação solar); resumidamente: (1) aumentando 4.25 vezes a $C_{\text{PCE, alimentação}}$ (de 574 ppm para 2442 ppm), observou-se uma redução de ~44 % (de 63 % para 35 %) na conversão de PCE; (2) o aumento do $Q_{\text{alimentação}}$ (de $59 \text{ cm}^3 \text{ min}^{-1}$ para $300 \text{ cm}^3 \text{ min}^{-1}$) levou à redução da conversão de PCE (de 81 % para 33 %); (3) para uma redução de 3.33 vezes na HR (de 40 % para 12 %), a eficiência da OFC apenas diminuiu ~1.2 vezes. Apesar de 97 % de PCE inicial ter sido convertido em CO_2 e água através da fotólise com um tubo interno de quartzo, apenas 51 % do PCE inicial foi mineralizado através de OFC usando o tubo interno de vidro. Foi desenvolvido um modelo matemático pressupondo o seguinte: (a) operação em estado estacionário; (b) condições isotérmicas e isobáricas; (c) comportamento de gás ideal; (d) simetria axial; (e) porosidade constante do leito (empacotamento e distribuição uniformes); (f) escoamento pistão com dispersão axial; (g) sem resistência na transferência de calor nem gradientes térmicos e de radiação UV; (h) sem gradientes de massa, velocidade e radiação UV em direcção radial. Presumindo que as espécies principais são apenas PCE e H_2O e que intermediários e/ou produtos

de reação não influenciam as cinéticas de degradação do PCE, demonstrou-se que as moléculas de PCE e H₂O devem ser consideradas em associação com diferentes sítios ativos específicos da superfície do TiO₂ uma vez que o modelo bimolecular não-competitivo de dois tipos de sítios Langmuir-Hinshelwood descreveu melhor os resultados.

A OFC de PCE e *n*-decano em fase gás foi também avaliada empregando um fotoreator anular à escala laboratorial sob radiação solar simulada. Utilizaram-se estruturas monolíticas de acetato de celulose revestidas com duas películas fotocatalíticas de TiO₂ (preparadas a partir de suspensões aquosas de P25 da Evonik® e PC500 da Cristal®) como leito catalítico ($L_{\text{leito catalítico}} = 160 \text{ mm}$). O reator foi equipado com um coletor parabólico composto (CPC) permitindo a iluminação de todo o reator e leito. A película de PC500 originou valores de conversão e mineralização de PCE e *n*-decano mais elevados do que a película de P25, muito provavelmente devido à maior área de superfície específica do TiO₂ PC500. Foram obtidas conversões próximas de 100 % para ambos os poluentes ($C_{\text{dec, alimentação}} = 71 \text{ ppm}$ e $C_{\text{PCE, alimentação}} = 1095 \text{ ppm}$) usando a película de PC500 para $Q_{\text{alimentação}} = 150 \text{ cm}^3 \text{ min}^{-1}$, $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ e $HR = 20 \text{ \%}$. A adsorção competitiva entre as moléculas de poluente e água na superfície da película de PC500 ocorreu para valores de HR superiores a 20 %. Os resultados demonstraram que o oxigénio molecular gasoso tem um papel preponderante na reação de OFC uma vez que a conversão dos poluentes é drasticamente prejudicada na sua ausência, sugerindo que o mecanismo fotocatalítico consiste em: (i) reações de oxidação iniciadas por espécies reativas, formadas a partir do oxigénio molecular adsorvido ($\text{O}_2^{\bullet-}$, $\text{HOO}^{\bullet}$); (ii) contribuição do oxigénio da estrutura do TiO₂; (iii) formação do radical hidroxilo ($\text{HO}^{\bullet}$) na superfície do TiO₂. O mecanismo da OFC de compostos clorados, tal como o PCE, pode incluir uma série de reações que envolvem radicais $\text{Cl}^{\bullet}$.

O fotocatalisador com melhor desempenho (TiO₂ PC500) foi incorporado numa tinta vinílica (base aquosa) para exterior, suportada em estruturas monolíticas de acetato de celulose e testado sob radiação solar simulada. 60 % de PCE ($C_{\text{PCE, alimentação}} = 1100 \text{ ppm}$) e 98 % de *n*-decano ($C_{\text{dec, alimentação}} = 41 \text{ ppm}$) foram convertidos fotocataliticamente usando as condições experimentais, $Q_{\text{alimentação}} = 75 \text{ cm}^3 \text{ min}^{-1}$, $HR = 40 \text{ \%}$ e $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$. Além disso, os resultados revelaram uma densidade de superfície ótima ($\sim 0.87 \text{ mg cm}^{-2}$) para se obter o melhor desempenho; ademais, aumentando a área exposta à radiação através da remoção da parede exterior do monólito, a OFC do PCE aumentou cerca de 58 % (de 38 % a 60 %) sob as mesmas condições experimentais.

Tendo em conta que o TiO₂ é um semiconductor de *bandgap* ampla, apenas ativo sob radiação UV, a modificação química e morfológica do TiO₂ foi estudada de forma a aumentar o

seu desempenho em aplicações solares. Nanotubos de TiO_2 foram sintetizados a partir do tratamento hidrotérmico de TiO_2 P25 e a modificação química foi conseguida através da moagem de ureia (fonte de azoto) com nanotubos de TiO_2 , seguida de tratamento térmico. O mesmo procedimento foi aplicado no TiO_2 P25 puro. Os resultados demonstraram que a modificação com azoto do TiO_2 P25 reduziu a OFC de PCE gasoso, sob radiação solar simulada: TiO_2 P25 puro apresentou a atividade mais alta (67 % de conversão de PCE) enquanto se obteve apenas 35 % de conversão com $\text{N}_{0.50}\text{P25-380}$ (material com um rácio ureia: TiO_2 de 1:2, calcinado a 380 °C). Contudo, quando estes materiais em particular foram testados em fase aquosa, $\text{N}_{0.50}\text{P25-380}$ exibiu uma atividade fotocatalítica superior ao TiO_2 P25 na OFC da difenidramina (poluente emergente em águas residuais da indústria farmacêutica) e na inativação da bactéria *Escherichia coli*, respectivamente sob radiação visível ($\lambda > 430$ nm) e UVA ($\lambda = 365$ nm).

A atividade fotocatalítica de nanotubos de TiO_2 modificados com azoto foi também investigada na conversão de metiletilcetona (MEC) e sulfeto de hidrogénio (H_2S). MEK mostrou elevada resistência à degradação fotocatalítica com estes materiais, contudo, observou-se elevada atividade fotocatalítica na degradação de H_2S sob radiação UVA ($\lambda = 365$ nm) e moderada atividade sob radiação solar.

Finalmente, com base nos dados experimentais obtidos à escala laboratorial, na simulação de modelos e previsões de OFC de COVs, foi concebido e construído um fotoreator anular à escala piloto ($r = 32.8$ mm, $L_{\text{leito catalítico}} = 144$ cm). O fotoreator dispõe de um CPC para capturar a radiação solar direta e difusa e/ou de lâmpadas UVA de forma a operar continuamente dia e noite. A OFC de *n*-decano ($C_{\text{dec, alimentação}} = 10$ ppm, $Q_{\text{alimentação}} = 2$ L min⁻¹, $\tau = 44$ s) em estruturas monolíticas de acetato de celulose revestidas com películas fotocatalíticas à base de TiO_2 (P25, PC500 e tinta fotocatalítica) foi estudada sob radiação solar ou UVA artificial. Foram obtidas conversões até 100 %, com películas de P25 e PC500 sob irradiâncias solares de 15 W_{UV} m⁻² (de manhã) e 3 W_{UV} m⁻² (à tarde). A película de tinta fotocatalítica converteu até 45 % de *n*-decano para irradiâncias na ordem de 48 W_{UV} m⁻² em ambos os períodos do dia. O excesso de fotões que incidem no leito fotocatalítico parece favorecer a via direta da mineralização. A OFC do *n*-decano sob radiação UVA artificial foi 29 % superior usando a película de PC500 em comparação com o de P25 (resultando em 100 % de conversão), enquanto com a película de tinta fotocatalítica não mais de 25 % de *n*-decano foi convertido. Os resultados sugerem que se pode conseguir um processo contínuo de 24 h de OFC de *n*-decano combinando ambas as fontes de radiação (UVA artificial e solar).

Table of Contents

	Page
1. Introduction	3
1.1. History of air pollution.....	5
1.2. Indoor air: exposure to Volatile Organic Compounds (VOCs).....	6
1.3. Elimination of Volatile Organic Compounds (VOCs).....	7
1.4. Advanced Oxidation Processes (AOPs).....	9
1.5. Heterogeneous photocatalysis.....	10
1.5.1. General reaction mechanism.....	10
1.5.2. Air treatment applications.....	11
1.6. Common semiconductors used as photocatalysts	15
1.6.1. The preferred semiconductor: titanium dioxide (TiO ₂)	17
1.6.2. Strategies to enhance the TiO ₂ photocatalytic properties	19
1.6.2.1. Increasing the life time of charge carriers	19
1.6.2.2. Red shifting of TiO ₂ absorption: towards solar applications	22
1.6.2.3. Increasing the oxidizing potential: quantum size effect (QSE)	25
1.7. Titania nanotubes (TNTs)	25
1.7.1. Synthesis of TNTs by hydrothermal method	27
1.7.2. Main parameters influencing TNT synthesis.....	29
1.7.3. Enhancing titania nanotube photocatalysts.....	30
1.7.4. Applications.....	31
1.8. Substrates for immobilization of photocatalyst powders	33
1.8.1. Routes for photocatalyst immobilization	35
1.9. Photocatalytic reactors	37
1.9.1. Flat plate reactors (FPRs)	37
1.9.2. Tubular reactors	38
1.9.3. Annular reactors.....	43
1.9.4. Radiation reflective collectors	44
1.10. Aim of the work and thesis outline	45
1.11. References.....	49
2. Gas-phase UV TiO ₂ photocatalysis of PCE using a lab-scale packed bed annular photoreactor.....	65
2.1. Introduction.....	67
2.2. Experimental	68
2.2.1. Materials and chemicals.....	68
2.2.2. Photocatalytic experimental apparatus	68
2.2.1.1. Feed generation.....	69
2.2.1.2. Lab-scale photoreactor	70
2.2.1.3. Photoreactor feed and exit streams analysis	72
2.2.3. UV photochemical and UV-TiO ₂ photocatalytic conversion of PCE.....	73
2.3. Theoretical	74
2.3.1. Photoreactor mathematical model.....	74
2.3.2. PCO rate expressions.....	76
2.4. Results and discussion	78

2.4.1.	UV photolysis of PCE	78
2.4.2.	UV-TiO ₂ photocatalytic conversion of PCE	79
2.4.2.1.	Influence of operation parameters.....	79
2.4.2.2.	Mathematical modelling.....	82
2.4.3.	Photooxidation reaction of PCE: product analysis and reaction mechanism	83
2.5.	Conclusions	89
2.6.	References	91
3.	Gas-phase solar photocatalysis of PCE and <i>n</i> -decane over different TiO ₂ photocatalysts using a lab-scale fixed bed annular photoreactor	93
3.1.	Introduction	95
3.2.	Experimental.....	96
3.2.1.	Materials and methods.....	96
3.2.2.	Experimental setup and photocatalytic experiments	98
3.3.	Results and discussion.....	100
3.3.1.	VOCs photolysis	100
3.3.2.	Catalytic film performances	100
3.3.2.1.	Influence of the feed flow rate and VOC	100
3.3.2.2.	Effect of the RH on PCO of <i>n</i> -decane and PCE over PC500 films.....	107
3.3.2.3.	Effect of oxygen on <i>n</i> -decane and PCE PCO over PC500 film	109
3.4.	Conclusions	111
3.5.	References	113
4.	Gas-phase solar photocatalytic oxidation of PCE over TiO ₂ based paint	119
4.1.	Introduction	121
4.2.	Experimental.....	123
4.2.1.	Materials and chemicals	123
4.2.2.	Photocatalytic films preparation and characterization	124
4.2.3.	Experimental setup and photocatalytic experiments	126
4.3.	Results and discussion.....	127
4.3.1.	Photocatalytic oxidation of PCE	127
4.3.1.1.	Influence of the number of photocatalytic paint coating layers and substrate configuration	127
4.3.1.2.	Operating parameters affecting PCE photodegradation.....	129
4.3.2.	PCE PCO reaction intermediated and pathway.....	134
4.4.	Conclusions	139
4.5.	References	141
5.	Gas-phase solar photocatalytic oxidation of <i>n</i> -decane over TiO ₂ based paint	151
5.1.	Introduction	147
5.2.	Experimental.....	149
5.2.1.	Materials and chemicals	149
5.2.2.	Photocatalytic films preparation and characterization	149
5.2.3.	Experimental setup and photocatalytic experiments	150
5.3.	Results and discussion.....	151
5.3.1.	Photocatalytic oxidation of <i>n</i> -decane	151

5.3.1.1.	Surface characterization of photo-TiO ₂ powder and PC samples.....	151
5.3.1.2.	Operating parameters effect on <i>n</i> -decane photoconversion.....	153
5.3.1.3.	Simulation and predictive studies of <i>n</i> -decane kinetics through PCO.....	158
5.3.2.	Reaction mechanism for the PCO of <i>n</i> -decane	161
5.4.	Conclusions.....	164
5.5.	References.....	167
6.	N-modified TiO ₂ photocatalytic activity towards organics degradation	173
6.1.	Introduction.....	175
6.2.	Experimental	177
6.2.1.	Chemicals and materials	177
6.2.2.	Catalyst preparation and characterization	178
6.2.3.	Photocatalytic experiments	179
6.2.3.1.	Gas-phase photocatalytic experiments	179
6.2.3.2.	Diphenhydramine photocatalytic degradation	180
6.2.3.3.	Bacterial inactivation tests.....	182
6.3.	Results and discussion	183
6.3.1.	Characterization	183
6.3.2.	Gas-phase PCO of PCE under simulated solar light.....	187
6.3.3.	Diphenhydramine photocatalytic degradation under visible light	188
6.3.4.	Escherichia coli inactivation.....	189
6.4.	Conclusions.....	191
6.5.	References.....	193
7.	Visible-light-driven photocatalytic properties of N-modified titania nanotubes toward air purification.....	197
7.1.	Introduction.....	199
7.2.	Experimental	200
7.2.1.	Hydrothermal synthesis of titanate nanotubes (TiNT).....	200
7.2.2.	Nitrogen-modified TiO ₂ nanotubes (NTiNT)	200
7.2.3.	Characterization of N-modified TiO ₂ nanotubes	200
7.2.4.	Gas-phase photocatalytic experiments.....	201
7.3.	Results and discussion	203
7.3.1.	Material characterization	203
7.3.2.	Photocatalytic tests	206
7.4.	Conclusions.....	209
7.5.	References.....	211
8.	Evaluation of a solar/UV annular pilot scale reactor for 24 h continuous PCO of <i>n</i> -decane	217
8.1.	Introduction.....	219
8.2.	Experimental	221
8.2.1.	Photocatalytic films preparation	221
8.2.2.	Solar/UV pilot-scale experimental unit	222
8.2.2.1.	Feed generation.....	222
8.2.2.2.	Pilot-scale photoreactor	223
8.2.2.3.	Compound parabolic collector (CPC) and radiation sources.....	223

8.2.2.4. Photoreactor feed and exit streams analysis.....	224
8.2.3. Photocatalytic experiments.....	224
8.3. Results and discussion.....	225
8.3.1. Solar/artificial UVA photolysis of <i>n</i> -decane	225
8.3.2. Solar/artificial UVA PCO of <i>n</i> -decane.....	226
8.4. Conclusions	232
8.5. References	235
9. Final remarks and suggestions for future work	237
9.1. Final Remarks.....	239
9.1.1. Photolysis	239
9.1.2. Photocatalysis using a lab-scale photoreactor	240
9.1.2.1. TiO ₂ photocatalytic properties enhancement	244
9.1.3. Photocatalysis using a pilot-scale photoreactor.....	245
9.2. Suggestions for future work	246
A. Master gas chromatography (MGC).....	251
A.1. MGC calibration curves.....	251
A.2. MGC data treatment.....	253
A.3. References.....	257

Table of Figures

	Page
Figure 1.1. Steps of a photocatalytic reaction in a solid semiconductor particle: (1) light photons of energy $h\nu$ matching or exceeding the semiconductor band-gap energy; (2) excited electron, e_{cb}^- , migrates from valence band to conduction band leaving a hole, h_{vb}^+ , in the valence band; (3) h_{vb}^+ migrates to surface and initiates oxidation reactions; (4) e_{cb}^- migrates to surface and initiates reduction reactions; (5) charge carrier recombination liberating heat.	11
Figure 1.2. Band positions (top of valence band and bottom of conduction band) for several common semiconductors together with the band-gap energy [95].	16
Figure 1.3. TiO_2 crystallographic phases of anatase (a), rutile (b) and brookite (c) (adapted from Carp <i>et al.</i> [112]).	17
Figure 1.4. Photoexcitation and charge transfer in a metal-modified TiO_2 photocatalyst (adapted from Serpone <i>et al.</i> [143]).	20
Figure 1.5. Photoexcitation and charge transfer between two light active semiconductors: (a) injection of an e^- in the TiO_2 conduction band and injection of a h^+ in the valence band of the other semiconductor; (b) injection of an e^- in the conduction band of the other semiconductor and injection of a h^+ in the TiO_2 valence band (adapted from Serpone <i>et al.</i> [152]).	21
Figure 1.6. Different morphologies of TiO_2 nanostructures.	22
Figure 1.7. Mechanisms proposals for the changes that may occur to the bandgap electronic structure of N-doped TiO_2 : (a) undoped TiO_2 ; (b) bandgap narrowing as a result of VB broadening; (c) introduction of localized states above VB or below CB; (d) electronic transitions from localized states near VB to the corresponding excited states for Ti^{3+} (Jahn-Teller split $^2T_2 \rightarrow ^2E$) and F^+ (equivalent to a single electron associated with the O vacancy) centres; (e) sensitization by compounds containing nitrogen species (adapted from Serpone [163]).	23
Figure 1.8. Photoexcitation and charge transfer of TiO_2 using dye molecule sensitizer (adapted from [197]).	24
Figure 1.9. Schematic representation of TNTs synthesis by hydrothermal method.	28
Figure 1.10. Cellulose acetate polymer: (a) commercially available monolith-like structure – TIMAX CA50-9/S, Wacotech GmbH & Co. K.G.; (b) transmittance in the UV-Vis range.	35
Figure 1.11. Schematic representation of a FPR (adapted from Águia <i>et al.</i> [367])	38
Figure 1.12. Schematic representation of a multi-parallel FPR (adapted from Leung <i>et al.</i> [314]).	38
Figure 1.13. Schematic representation of a FBR (adapted from Dibble and Raupp [300]).	39
Figure 1.14. Schematic representation of a PBR with glass spheres coated with the photocatalyst (adapted from Tsoukleris <i>et al.</i> [372]).	40

Figure 1.15. Schematic diagram of a PDC reactor packed with photocatalytic pellets (adapted from Kim <i>et al.</i> [377]).	41
Figure 1.16. Schematic representation of a tubular reactor filled with a monolithic solid structure.	42
Figure 1.17. Schematic representation of an OFR filled with photocatalyst-coated fibres.	42
Figure 1.18. Schematic representation of a CWR.	43
Figure 1.19. Schematic representation of an annular reactor: a) side and b) cross section point of view.	44
Figure 1.20. Schematic representation of a multi-annular reactor (adapted from Imoberdorf <i>et al.</i> [398]).	44
Figure 1.21. Schematic representation of three non-concentrating reflective collectors' geometries.	45
Figure 2.1. Schematic representation of the lab-scale experimental unit used for the study of decontamination of air contaminated with PCE: a) lab-scale facility used for the generation of air streams containing PCE and water vapour; b) single-pass continuous-flow annular UV-photoreactor; c) master gas chromatographic analysis system used for the analysis of the photoreactor feed and exit streams.	69
Figure 2.2. LabView routine designed to control/monitor the mass flow controllers and thermocouples throughout the experimental time.	70
Figure 2.3. Detailed schematic representation of single-pass continuous flow packed bed annular photoreactor employed in the study of decontamination of air contaminated with PCE: a) side view; b) frontal view.	71
Figure 2.4. a) Transmissivity of glass (----) and quartz (—) inner tubes compared to the solar spectrum (—, [30]). b) PCE photolysis using different photoreactor inner tubes: glass (—○—) and quartz (--△--); $C_{\text{PCE, feed}} = 1221 \text{ ppm}$, $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$, $RH = 40 \%$, and $T = 298 \text{ K}$; operation conditions reported in Table 2.2 * measured at 298 K and 1 bar.	79
Figure 2.5. Effect on PCE conversion fraction through PCO ($C_{\text{PCE, exit}} / C_{\text{PCE, feed}}$, at steady-state conditions) for air feed streams contaminated with different concentrations of PCE [$C_{\text{PCE, feed}}$]: experimental points (△) and M-1 (—), M-2 (·····), M-3 (----), M-4 (---), M-5 (—), M-6 (—·—); $Q_{\text{feed}}^a = 150 \text{ cm}^3 \text{ min}^{-1}$, $RH^a = 40 \%$, $T = 298 \text{ K}$, and $I = 0.8 \text{ W m}^{-2}$; operation conditions reported in Table 2.2 (runs 1-6) [^{a} measured at 298 K and 1 bar].	80
Figure 2.6. Effect on PCE conversion fraction through PCO ($C_{\text{PCE, Exit}} / C_{\text{PCE, Feed}}$, at steady-state conditions) for air contaminated with PCE applying different feed flow rates [Q_{feed}]: experimental points (○) and M-1 (—), M-2 (·····), M-3 (----), M-4 (---), M-5 (—), M-6 (—·—); $C_{\text{PCE, feed}} = 1221 \text{ ppm}$, $RH^a = 40 \%$, $T = 298 \text{ K}$, and $I = 0.8 \text{ W m}^{-2}$; operation conditions reported in Table 2.2 (runs 1, 7-10) [^{a} measured at 298 K and 1 bar].	81
Figure 2.7. Effect on PCE conversion fraction through PCO ($C_{\text{PCE, exit}} / C_{\text{PCE, feed}}$, at steady-state conditions) for air contaminated with PCE applying different humidity contents [RH]: experimental points (□) and M-1 (—), M-2 (·····), M-3 (----), M-4 (---), M-5 (—), M-6 (—·—); $C_{\text{PCE, feed}} = 1221 \text{ ppm}$, $Q_{\text{feed}}^a = 150 \text{ cm}^3 \text{ min}^{-1}$, $T = 298 \text{ K}$, and $I = 0.8 \text{ W m}^{-2}$; operation conditions reported in Table 2.2 (runs 1, 11-13) [^{a} measured at 298 K and 1 bar].	82

Figure 3.1. Schematic representation of the lab-scale experimental set-up and the continuous-flow photoreactor: a) generation of air streams containing *n*-decane and water vapour; b) sunlight simulator containing the photoreactor: b₁) side view and b₂) frontal view; c) master gas chromatograph analytic system used for the analysis of the photoreactor feed and exit gas streams..... 99

Figure 3.2. Effect of feed flow rate [Q_{feed}^*] on the conversion of *n*-decane (a) and PCE (c) and on the photocatalytic reaction rate, r_{VOC} ((b) and (d), respectively). Experimental points for incident irradiances of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,■), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,■), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (□, □), measured within the spectral range of 280 – 400 nm, at steady-state conditions; $C_{\text{dec, feed}} = 71 \text{ ppm}$, $C_{\text{PCE, feed}} = 1095 \text{ ppm}$, $RH^* = 40 \%$ and 21 % oxygen. Blue columns represent TiO_2 PC500 (■,■,■) and orange columns P25 (■,■,■). * measured at 298 K and 1 bar..... 102

Figure 3.3. Effect of VOC feed concentration ($C_{\text{dec, feed}}$, and $C_{\text{PCE, feed}}$) on the conversion of *n*-decane (a) and PCE (c) and on the photocatalytic reaction rate, r_{VOC} ((b) and (d), respectively). Experimental points for incident irradiances of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,■), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,■), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (□, □) measured within the spectral range of 280 - 400 nm, at steady-state conditions; $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$, $RH^* = 40 \%$ and 21 % oxygen. Blue columns represent the activity of PC500 (■,■,■) and orange columns P25 (■,■,■) films. * measured at 298 K and 1 bar..... 104

Figure 3.4. Mineralization yields of PCE and *n*-decane over PC500 and P25 films. Experimental points for incident irradiances of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,■), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,■), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (□, □) measured within the spectral range of 280 - 400 nm, at steady-state conditions; $C_{\text{PCE, feed}}^* = 1095 \text{ ppm}$, $C_{\text{dec, feed}}^* = 71 \text{ ppm}$, $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$, $RH^* = 40 \%$ and 21 % oxygen; Blue columns represent the activity of PC500 (■,■,■) and orange columns P25 (■,■,■) films. * measured at 298 K and 1 bar..... 105

Figure 3.5. Effect of water content [RH^*] on the conversion over PC500 film, at steady-state conditions, of: (a) *n*-decane for $C_{\text{dec, feed}} = 71 \text{ ppm}$ (■), $C_{\text{dec, feed}} = 142 \text{ ppm}$ (■) and $C_{\text{dec, feed}} = 284 \text{ ppm}$ (■); (b) PCE ($C_{\text{PCE, feed}} = 1095 \text{ ppm}$) for $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$ (■) and $Q_{\text{feed}}^* = 300 \text{ cm}^3 \text{ min}^{-1}$ (■); $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$, measured within the spectral range of 280 - 400 nm. * measured at 298 K and 1 bar. 108

Figure 3.6. Effect of water content [RH^*] on: (a) *n*-decane conversion at steady-state conditions for $C_{\text{dec, feed}} = 71 \text{ ppm}$ and $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$; (b) PCE conversion at steady-state conditions for $C_{\text{PCE, feed}} = 1095 \text{ ppm}$ and $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$. Blue columns (■,■,■) and orange columns (■,■,■) represent, respectively, the presence and absence of oxygen; Incident irradiances of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,■), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,■), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (□, □) were measured within the spectral range of 280 – 400 nm. * measured at 298 K and 1 bar. 110

Figure 4.1. Annular photoreactor schematic representation: a) side view; b) frontal view of the two configurations used (PC1 and PC2)..... 124

Figure 4.2. Influence on photocatalytic conversion, at steady-state conditions, of the (a) number of layers under xPC1 configuration and (b) structure configuration; I of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■) and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (□), measured within 280 - 400 nm; $C_{\text{PCE, feed}} = 1100 \text{ ppm}$, $Q_{\text{feed}}^* = 75 \text{ cm}^3 \text{ min}^{-1}$, and $RH^* = 40 \%$; experimental conditions reported in Table 4.3. * measured at 298 K and 1 bar. 128

Figure 4.3. Effect of feed flow rate [Q_{feed}^*] on PCE conversion (a) and on the reaction rate, r_{PCE} (b) at steady-state conditions: experimental points for I of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,■), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,■), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (□, □), measured within 280 - 400 nm; $C_{\text{PCE, feed}} = 1100 \text{ ppm}$, $RH^* = 40 \%$; experimental conditions reported in Table 4.3. Blue

columns represent 5PC2 first use (■,■,■) and orange columns represent 50 h under simulated solar radiation and continuous feeding (■,■,■). * measured at 298 K and 1 bar. 130

Figure 4.4. Effect of different concentrations of PCE [$C_{\text{PCE, feed}}$] on PCE conversion and on the reaction rate, r_{PCE} , at steady-state conditions: experimental points for incident irradiances of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■), measured within 280 - 400 nm; $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$ and $RH^* = 40 \%$; experimental conditions reported in Table 4.3. * measured at 298 K and 1 bar. 131

Figure 4.5. Effect of water content [RH^*] on PCE conversion at steady-state conditions in the presence of oxygen (blue columns coloured column) and in the absence of oxygen (orange columns): experimental points for incident irradiances of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,■), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,■), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,■), measured within 280 - 400 nm; $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$ and $C_{\text{PCE, feed}} = 1100 \text{ ppm}$; experimental conditions reported in Table 3. * measured at 298 K and 1 bar. 133

Figure 5.1. Schematic representation of the continuous-flow photoreactor: a) from a side point of view and b) from a frontal point of view.....150

Figure 5.2. SEM micrograph (a) and EDX spectrum (b) of photo-TiO₂ PC500 powder.....151

Figure 5.3. SEM micrographs (a-d) and EDX spectra (e, f) of PC before (left-side images) and after 50 h+ of use (right-side images) in PCO of *n*-decane.....152

Figure 5.4. Photographs (a-b) and SEM micrographs (c-d) of PC used in PCO of *n*-decane....153

Figure 5.5. Influence of feed flow rate (Q_{feed}) on *n*-decane conversion fraction ($C_{\text{dec, exit}} / C_{\text{dec, feed}}$, at steady-state conditions): experimental points for incident irradiance measured within 280 – 400 nm (sunlight UV fraction) of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (◆), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (△), and RE-1 (---), RE-2 (— · —), and RE-3 (—); $C_{\text{dec, feed}} = 73 \text{ ppm}$, $RH^* = 40 \%$, and $T = 298 \text{ K}$; operation conditions reported in Table 5.2; * measured at 298 K and 1 bar. 154

Figure 5.6. Influence of feed flow rate (Q_{feed}) on *n*-decane photocatalytic reaction rate (r_{dec}), at steady-state conditions: experimental points for incident irradiance measured within 280 – 400 nm (sunlight UV fraction) of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■); $C_{\text{dec, feed}} = 73 \text{ ppm}$, $RH^* = 40 \%$, and $T = 298 \text{ K}$; operation conditions reported in Table 5.2; * measured at 298 K and 1 bar.....155

Figure 5.7. Influence of the feed concentration ($C_{\text{dec, feed}}$) on *n*-decane conversion fraction ($C_{\text{dec, exit}} / C_{\text{dec, feed}}$, at steady-state conditions): experimental points for incident irradiance measured within 280 – 400 nm (sunlight UV fraction) of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (◆), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (△), and RE-1 (---), RE-2 (— · —), and RE-3 (—); $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$, $RH^* = 40 \%$, and $T = 298 \text{ K}$; operation conditions reported in Table 5.2; * measured at 298 K and 1 bar. 156

Figure 5.8. Influence of feed concentration ($C_{\text{dec, feed}}$) on the photocatalytic reaction rate (r_{dec}), at steady-state conditions: experimental points for incident irradiance measured within 280 – 400 nm (sunlight UV fraction) of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■); $C_{\text{dec, feed}} = 73 \text{ ppm}$, $RH^* = 40 \%$, and $T = 298 \text{ K}$; operation conditions reported in Table 5.2; * measured at 298 K and 1 bar.....157

Figure 5.9. Influence of the feed relative humidity (RH) on *n*-decane conversion fraction ($C_{\text{dec, exit}} / C_{\text{dec, feed}}$, at steady-state conditions): experimental points for incident irradiance measured within 280 – 400 nm (sunlight UV fraction) of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (◆), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$

(■), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (Δ), and RE-1 (---), RE-2 (— · —), and RE-3 (—); $Q_{\text{feed}}^* = 150 \text{ cm}^3 \cdot \text{min}^{-1}$, $C_{\text{dec, feed}} = 73 \text{ ppm}$, and $T = 298 \text{ K}$; operation conditions reported in Table 5.2; * measured at 298 K and 1 bar..... 158

Figure 5.10. *n*-Decane photoconversion fraction profiles ($C_{\text{dec, exit}}/C_{\text{dec, feed}}$, at steady-state conditions) for photoreactors with different lengths [L_R]: 0.16 (—), 0.24 (---), 0.32 (— · —), and 0.48 m (· · ·); (a) $C_{\text{dec, feed}} = 73 \text{ ppm}$, $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$, and $I = 18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (measured within 280 – 400 nm: sunlight UV fraction); (b) $C_{\text{dec, feed}} = 73 \text{ ppm}$, $Q_{\text{feed}}^* = 300 \text{ cm}^3 \text{ min}^{-1}$, and $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (measured within 280 – 400 nm: sunlight UV fraction); $RH^* = 30 \%$, and $T = 298 \text{ K}$; operation conditions reported in Table 5.2 (runs 3 and 7, respectively) (* measured at 298 K and 1 bar); experimental data (points); mathematical modelling with RE-3 (lines)..... 161

Figure 6.1. Schematic representation of the experimental unit used in DP photocatalytic degradation experiments (adapted from Gomes da Silva [80])...... 180

Figure 6.2. Schematic representation of the experimental unit used for the *E. coli* inactivation experiments..... 182

Figure 6.3. XRD patterns of the samples synthesized with different (a) urea contents and (b) calcination temperatures. XRD pattern of TiO_2 P25 is also shown as reference. A: anatase; R: rutile. 183

Figure 6.4. N_2 adsorption-desorption isotherms and pore size distribution (inset) of: a) $\text{N}_{0.75}\text{P25-380}$, b) $\text{N}_{0.50}\text{P25-380}$ and c) $\text{N}_{0.25}\text{P25-380}$ 185

Figure 6.5. UV-Vis absorption spectra of: a) $\text{N}_{0.25}\text{P25-380}$, $\text{N}_{0.50}\text{P25-380}$, $\text{N}_{0.75}\text{P25-380}$ and bare P25 and b) $\text{N}_{0.50}\text{P25-340}$, $\text{N}_{0.50}\text{P25-380}$, $\text{N}_{0.50}\text{P25-420}$ and bare TiO_2 P25..... 185

Figure 6.6. (a-b) SEM micrographs at different magnifications, and (c) EDS spectrum of $\text{N}_{0.50}\text{P25-380}$ 186

Figure 6.7. X-ray photoelectron spectra of $\text{N}_{0.50}\text{P25-380}$ and bare TiO_2 P25 samples: (a) N1s, (b) Ti2p and (c) O1s core levels..... 186

Figure 6.8. Gas-phase PCO of PCE ($C_{\text{PCE, feed}} = 1100 \text{ ppm}$; $Q_{\text{feed}}^* = 300 \text{ cm}^3 \text{ min}^{-1}$; $RH^* = 40 \%$) at steady-state conditions, under simulated solar radiation ($I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$, measured within the spectral range of 280 – 400 nm) for materials prepared with different urea content and bare P25 * measured at 298 K and 1 bar. 187

Figure 6.9. Photocatalytic degradation of DP (10 mg L^{-1}) under visible light illumination for (a)-(b) materials prepared with different urea contents and (c) different temperatures (340, 380 and 420 °C). Catalyst load = 1.0 g L^{-1} . Curves represent the fitting of the pseudo-first order equation to the experimental data. 188

Figure 6.10. *E. coli* growth under UVA for photocatalyst loads of (a) 0.500 mg mL^{-1} and (b) 0.125 mg mL^{-1} . Results are mean values ($n = 3$) and the error bars represent the standard deviation. 190

Figure 7.1. Lab-scale facility employed in MEK or H_2S degradation experiments comprising a photocatalytic annular concentric reactor 202

Figure 7.2. BET surface area (S_{BET}) calculated by Brunauer-Emmet-Teller (BJH) formula (a), N_2 adsorption-desorption isotherms (b), and median pore diameter ($d_{p, \text{BJH}}$) calculated

by Barret-Joyner-Halenda (BJH) formula (c) of N ₁ TiNT to N ₄ TiNT samples calcined at 380 and 400 °C.....	203
Figure 7.3. UV-Vis absorption spectra of N ₄ TiNT and N ₁ TiNT calcined at 380 °C and 400 °C, TiNT and bare TiO ₂ P25 without thermal treatment.....	204
Figure 7.4. TG curves of TiNT, urea, and N ₄ TiNT samples without thermal treatment.	205
Figure 7.5. N1s X-ray photoelectron spectral details (a) and N/Ti and O/Ti area ratios during argon ion bombardment (b) of N ₂ TiNT-380, N ₃ TiNT-380, N ₁ TiNT-400, N ₂ TiNT-400, and N ₃ TiNT-400 samples.....	206
Figure 7.6. TEM images of N ₄ TiNT-380 (left side) and N ₄ TiNT-400 (right side).....	206
Figure 7.7. Gas-phase photooxidation under UVA or solar radiation of: a) MEK with N ₁ TiNT-380 photocatalyst ($\rho_A = 1.67 \text{ mg cm}^{-2}$, $C_{\text{MEK, feed}} = 500 \text{ ppm}$, $RH^* = 50 \%$, $Q_{\text{feed}}^* = 300 \text{ cm}^3 \text{ min}^{-1}$); b) H ₂ S with N ₁ TiNT-400 ($\rho_A = 0.21 \text{ mg} \cdot \text{cm}^{-2}$, $C_{\text{H}_2\text{S, feed}} = 15 \text{ ppm}$, $RH^* = 0\%$, $Q_{\text{feed}}^* = 500 \text{ cm}^3 \text{ min}^{-1}$. [* - measured at 298 K and 1 atm].	207
Figure 7.8. Schematic representation of reaction pathways for the photocatalytic degradation under UVA or solar radiation of MEK [58, 59] (a) and H ₂ S [63-66] (b).....	208
Figure 8.1. Schematic representation of the pilot unit: a) feed generator of air streams containing <i>n</i> -decane and water vapour; b) pilot scale continuous-flow annular photoreactor placed at the top of a CPC (at local latitude of 41° facing south); c) monitoring system used for the analysis of the photoreactor feed and exit streams.	222
Figure 8.2. Time evolution of <i>n</i> -decane PCO over P25 (a), PC500 (b) and PCP (c) films under solar radiation (irradiance measured within 280 - 400 nm). Solar radiation collected with a CPC and UV irradiance measured on the outer tube of the photoreactor. UV irradiance measured within 280 - 400 nm. Operating conditions: $C_{\text{dec, feed}} = 10 \text{ ppm}$; $Q_{\text{feed}}^* = 2 \text{ L min}^{-1}$ ($\tau = 44 \text{ s}$) as reported in Table 8.2.	228
Figure 8.3. <i>n</i> -Decane conversion (◆, morning, increasing irradiance; ◇, afternoon, decreasing irradiance) and mineralization (▲, morning, increasing irradiance; △, afternoon, decreasing irradiance) over P25 (a) PC500 (b) and PCP (c) films under solar radiation during the fourth day of experiment. UV irradiance measured within 280 - 400 nm. Operating conditions: $C_{\text{dec, feed}} = 10 \text{ ppm}$; $Q_{\text{feed}}^* = 2 \text{ L min}^{-1}$ ($\tau = 44 \text{ s}$) as reported in Table 8.2.	229
Figure 8.4. <i>n</i> -Decane PCO reaction rate (◆, ▲, ● morning, increasing irradiance; ◇, △, ○ afternoon, decreasing irradiance) over P25 (◆, ◇) PC500 (▲, △) and PCP (●, ○) films under solar radiation during the fourth day of experiment. UV irradiance measured within 280 - 400 nm. Operating conditions: $C_{\text{dec, feed}} = 10 \text{ ppm}$; $Q_{\text{feed}}^* = 2 \text{ L min}^{-1}$ ($\tau = 44 \text{ s}$) as reported in Table 8.2.	230
Figure 8.5. Time evolution of <i>n</i> -decane PCO over P25 (a), PC500 (b) and PCP (c) films under artificial UVA radiation. UV irradiance measured within 280 - 400 nm and facing the inner quartz tube of the photoreactor. Operating conditions: $C_{\text{dec, feed}} = 10 \text{ ppm}$; $Q_{\text{feed}}^* = 2 \text{ L min}^{-1}$ ($\tau = 44 \text{ s}$) as reported in Table 8.2.	231
Figure A.1. GC calibration curves for PCE and <i>n</i> -decane	252

Figure A.2. Effect on component (i)-relative vapour pressure ($\varphi_i = p_i/p_i^{\text{sat}}$) applying different air flow rates (Q_i): experimental data obtained for H ₂ O (points) determined at 281.15 K [^a measured at 293.15 K and 1 atm]; lines for eq. A.7.....	254
---	-----

Table of Tables

	Page
Table 1.1. Typical AOPs systems.....	9
Table 1.2. Current applications of PCO processes.	12
Table 1.3. Photocatalytic applications of TNTs and their derived materials.....	32
Table 1.4. Substrates and configurations used as photocatalyst supports.	34
Table 2.1. Photoreactor tubes dimensions employed in the gas-phase photooxidation of PCE under non-catalytic (UV) and catalytic (UV-TiO ₂) conditions; catalytic bed characteristics used in the PCE photocatalytic reaction.	71
Table 2.2 Experimental conditions employed in gas-phase PCO of PCE carried out in continuous-flow annular photoreactor under non-catalytic (UV) and catalytic (UV-TiO ₂) conditions.	74
Table 2.3. Kinetic and adsorption equilibrium parameters resulting from the application of rate expressions M-1 to M-6 in the complete mathematical model, including the statistical parameter squared correlation coefficient (R^2) and sum of squared residuals between experimental and calculated rates (S^2_R).	83
Table 2.4. Product analysis by GC/MSD for PCE photochemical reaction (reactor with a quartz inner tube); experimental conditions described in Table 2.2 (UV photolysis, run 1).....	85
Table 2.5. Product analysis by GC/MSD for PCE photocatalytic reaction (reactor with a glass inner tube); experimental conditions described in Table 2.2 (UV-TiO ₂ photocatalysis, run 1).	86
Table 3.1. Catalysts, catalytic bed properties and dimensions of the photoreactor employed in the PCO of <i>n</i> -decane and PCE under simulated solar radiation.	97
Table 4.1. TiO ₂ PC500 and paint properties and photoreactor dimensions employed in the gas-phase PCO of PCE under simulated solar radiation.	123
Table 4.2. Catalytic bed characteristics and configurations employed in the gas-phase PCO of PCE under simulated solar radiation.	125
Table 4.3. Experimental conditions employed in the study of PCE photodegradation.	127
Table 4.4. Reaction intermediates identified and quantified in the gas-phase photodegradation of PCE (experimental conditions reported in Table 4.3: run 4).....	135
Table 5.1. Catalytic bed characteristics employed in the gas-phase PCO of <i>n</i> -decane under simulated solar radiation.....	149
Table 5.2. Experimental conditions employed in the study of <i>n</i> -decane conversion.	150
Table 5.3. Mathematical model, boundary conditions, kinetic reaction rate expressions used for estimation of the kinetic and adsorption equilibrium parameters of the PCO of <i>n</i> -decane; Estimated kinetic and adsorption equilibrium parameters resulting of the mathematical model.	159

Table 5.4. Reaction by-products identified and quantified in the gas-phase photoconversion of <i>n</i> -decane (experimental conditions reported in Table 5.2: run 1).....	162
Table 6.1. Mass of photocatalyst (<i>m</i>) affixed onto the substrates surface and corresponding surface density (ρ_A); experimental conditions employed in the gas-phase PCO of PCE under simulated solar radiation.	179
Table 6.2. Pseudo first-order kinetic constant (<i>k</i>), respective coefficient of variation (CV) and regression coefficient (r^2) of DP degradation under visible light illumination.	181
Table 6.3. Optical, structural and textural properties of N _x P25-y and bare TiO ₂ P25.	184
Table 8.1. Photoreactor dimensions and photocatalytic thin-films characteristics employed in the gas-phase PCO of VOCs under solar and UV radiation.	221
Table 8.2. Experimental conditions employed in gas-phase PCO of <i>n</i> -decane carried under solar or artificial UVA radiation.	225
Table A.1. VOC(i) data obtained for the calibration of the MGC method: PCE and <i>n</i> -decane	252
Table A.2. Analytic parameters of PCE and <i>n</i> -decane calibration curves	253
Table A.3. Component(i)-specific Antoine coefficients: PCE, <i>n</i> -decane and water [2]	255

Table of Schemes

	Page
Scheme 2.1 Main pathways for the gas-phase photooxidation of PCE under UV radiation; adapted from Petit <i>et al.</i> (2007) [2].	84
Scheme 2.2. Reaction mechanism proposed for the gas-phase photooxidation of PCE under UV radiation; pathways: (A ₁) to (E ₄); intermediates in brackets: 1 to 9.	88
Scheme 4.1. HO [•] radical addition to PCE followed by Cl [•] radical generation.	136
Scheme 4.2. Cl [•] radical addition to PCE followed by O ₂ [•] radical addition forming chloroalkanes and phosgene.	137
Scheme 4.3. Chlorination of PCE by addition of Cl [•] radicals producing chloroalkanes.	137
Scheme 4.4. Esterification of ethyl, trichloroacetate and methyl, trichloroacetate.	138
Scheme 5.1. Schematic representation of the reaction pathways proposed for the gas-phase conversion of <i>n</i> -decane under simulated solar radiation (R: alkyl roots or hydrogen).	163

Notation

Latin letters

A_f	flow area [m ²]
C	cellulose acetate monolithic structure
C_{dec}	gas phase concentration of decane [ppm]
$C_{dec, exit}$	gas phase concentration of decane on the exit stream [ppm]
$C_{dec, feed}$	gas phase concentration of decane on the feed stream [ppm]
$C_{C-dec, exit}$	carbon atoms concentration of decane on the exit stream [ppm]
$C_{C-dec, feed}$	carbon atoms concentration of decane on the feed stream [ppm]
$C_{C-PCE, feed}$	carbon atoms concentration of PCE on the feed stream [ppm]
C_i	gas phase concentration of compound i [ppm]
$C_{i, C-PCE}$	carbon atoms concentration of compound i formed by PCE degradation [ppm]
C_{PCE}	gas phase concentration of PCE [ppm]
C_{H_2O}	gas phase concentration of H ₂ O [ppm]
$C_{PCE, exit}$	gas phase concentration of PCE on the exit stream [ppm]
$C_{PCE, feed}$	gas phase concentration of PCE on the feed stream [ppm]
d_{ch}^2	cellulose acetate monolith channel section [mm]
dec	n -decane
$d_{f,cc}$	film thickness of the capillary column [μm]
$d_{i,cc}$	diameter of the capillary column [mm]
$d_{in,e}$	external diameter of the glass and quartz inner tubes [mm]
$d_{in,i}$	internal diameter of the glass and quartz inner tubes [mm]
$d_{ot,e}$	external diameter of the Pirex-glass outer tube [mm]
$d_{ot,i}$	internal diameter of the Pirex-glass outer tube [mm]
d_{GS}	averaged diameter of the glass spheres [mm]
D_{ax}	axial dispersion coefficient [m ² s ⁻¹]
D_{ij}	binary diffusion coefficient [m ² s ⁻¹]
D_m	molecular diffusivity of the mixture [m ² s ⁻¹]
$D_{m,i}$	molecular diffusivity for compound i in the mixture [m ² s ⁻¹]
$e_{w,ch}$	cellulose acetate monolith wall thickness [mm]
FID	Flame ionization detector
GC-MS	Gas chromatography-mass spectroscopy
GC/MSD	Gas chromatography/mass selective detector
h	Planck constant [J s]
I	incident irradiance [W m ⁻²]

k	reaction rate constant [$\mu\text{mol m}^{-2} \text{s}^{-1} (\text{W}^{-1} \text{m}^2)^n$]
$K_{\text{H}_2\text{O}}$	H_2O adsorption equilibrium constant in a single site [μM^{-1}]
$K_{\text{H}_2\text{O},1}$	H_2O adsorption equilibrium constant on two types of sites (site 1) [M^{-1}]
$K_{\text{H}_2\text{O},2}$	H_2O adsorption equilibrium constant on two types of sites (site 2) [M^{-1}]
K_{dec}	n -decane adsorption equilibrium constant in a single site [M^{-1}]
$K_{\text{dec},1}$	n -decane adsorption equilibrium constant on two types of sites (site 1) [M^{-1}]
$K_{\text{dec},2}$	n -decane adsorption equilibrium constant on two types of sites (site 2) [M^{-1}]
K_{PCE}	PCE adsorption equilibrium constant in a single site [M^{-1}]
$K_{\text{PCE},1}$	PCE adsorption equilibrium constant on two types of sites (site 1) [M^{-1}]
$K_{\text{PCE},2}$	PCE adsorption equilibrium constant on two types of sites (site 2) [M^{-1}]
L_{C}	length of cellulose acetate monolithic structure channel [mm]
L_{cc}	length of the capillary column [m]
L_{in}	length of the glass and quartz inner tubes [mm]
L_{ot}	length of the Pirex-glass outer tube [mm]
L_{R}	length of the photocatalytic bed [mm]
m	mass [g]
$M(\text{C})$	molecular weight of a carbon atom [g mol^{-1}]
MGC	Master Gas Chromatographer/Chromatography
M_i	molecular weight of compound i [g mol^{-1}]
M_j	molecular weight of compound j [g mol^{-1}]
n	incident irradiance exponential order constant
$n(\text{C})$	number of carbon atoms of each component i
N	number of components in the gas stream mixture
p	total pressure of the contaminated air stream [atm]
P or PCP	photocatalytic paint immobilized
P25	TiO_2 from Evonik [®]
PC500	TiO_2 from Cristal [®]
PCE	perchloroethylene
Q_{feed}	total feed flow rate [$\text{cm}^3 \text{min}^{-1}$]
RH	relative humidity of the feed stream (water vapour content) [%]
r	photocatalytic reaction rate [mol min^{-1}]
R^2	squared correlation coefficient [-]
S_{R}^2	sum of squared residuals between experimental and calculated rates [$\mu\text{mol}^2 \text{m}^{-4} \text{s}^{-2}$]
S_{BET}	BET specific surface area [$\text{m}^2 \text{g}^{-1}$]
t	time [s]
T	temperature [K]

$u_{0,\text{feed}}$	inlet superficial velocity [$\text{m}\cdot\text{s}^{-1}$]
$\bar{u}_{0,\text{ch}}$	Superficial velocity (in the cross-section of each channel) [$\text{m}\cdot\text{s}^{-1}$]
UV	ultraviolet
Vis	visible
V_{GS}	volume of glass spheres [mm^3]
VOC(s)	Volatile Organic Compound(s)
V_{R}	volume of photocatalytic bed [mm^3]
z	partition of the photocatalytic bed length (L_{R}) [m]

Greek letters

α	exponential parameter for PCE [-]
α_1	kinetic coefficient [$\mu\text{mol m s}^{-1} \mu\text{M}^{-1}$]
α_2	kinetic coefficient [$\text{W}^{-1} \text{m}^2$]
β	exponential parameter for H_2O [-]
ε	photocatalytic bed porosity
$(\Sigma_v)_i$	sum of the diffusion volume for component i
$(\Sigma_v)_j$	sum of the diffusion volume for component j
η_{min}	mineralization efficiency [%]
λ	UV/visible wavelength [nm]
ν_i	stoichiometric coefficient of compound i in the overall reaction
ρ	density [g cm^{-3}]
ρ_{A}	surface density [g cm^{-2}]
ν	frequency energy [s^{-1}]
ϕ	wavelength averaged quantum efficiency [-]

Part I

Chapter 1. Introduction

1. Introduction

This first chapter presents an overview of the problematic of airborne volatile organic compounds (VOCs) present in both indoor and outdoor atmospheres as well as of current and potential removal methods. Photocatalysis as an advanced oxidation process for removing VOCs is herein described. Crystalline structural and morphological properties of TiO₂ semiconductor-based catalyst and their effect on photocatalytic activity are discussed. Methods to enhance TiO₂ properties are also explained. An overview regarding photoreactors is presented in this chapter. The objective and the thesis outline are provided at the end of the chapter.

1.1. History of air pollution

Air pollution has been a major recognised problem for centuries. Since middle ages, the burning of coal, mainly in cities, has released increasing amounts of smoke and sulphur dioxide to the atmosphere. Well documented air pollution related works can be found as early as the late 16th century. However, it was since the middle of 18th century, with the British Industrial Revolution (*ca.* 1760 to 1840), that an escalation in pollutant emissions related to the use of coal in households and industry led to problematic levels of urban air pollution. Such historical event marks a major turning point in almost every aspect of daily life. The transition from hand-production methods to machines, the increasing use of steam power and the development of machine tools as well as the change from wood and other bio-fuels to coal and the use of new chemical manufacturing and iron production processes are probably the pinnacle of the Industrial Revolution features. Thus, side by side with technological and industrial development, the continuous growth of pollutant emissions was a reality. Culminating in the year of 1952, in its upmost catastrophic effect known as the Great London Smog [1], air pollution was responsible for around 4000 deaths in four days and further 8000 deaths in the following weeks. In a strategic attempt of reducing air pollution, the British Government introduced in 1956 its first Clean Air Act (CAA) with the aim to control domestic sources of smoke pollution by introducing smokeless zones. Though, it was the introduction of cleaner coals, the increased use of electricity and gas and the relocation of power stations to more rural areas that promoted a dramatically decreased in air pollution in cities. In 1968, assuming that higher chimneys would improve the dispersal of the air pollution, another Clean Air Act was introduced aiming the use of tall chimneys for burning coal, liquid or gaseous fuels industries.

In 1963, the United States government also deliberated the Clean Air Act (CAA) federal law to control air pollution on a national level and to protect the general public from airborne contaminants known to be hazardous to human health. The 1963 version of the legislation established a research program, further expanded in 1967. Major amendments to the law, requiring regulatory controls for air pollution, passed in 1970, 1977 and 1990. In 1969 it was also created the environmental law - National Environmental Policy Act (NEPA) [2], containing three sections: 1. the declaration of national environmental policies and goals; 2. the establishment of action-forcing provision for federal agencies to enforce those policies and goals; 3. the establishment of a Council on Environmental Quality (CEQ) in the Executive Office of the President.

United Kingdom also introduced further regulations after Clean Air Acts such as the 1974 Control of Air Pollution Act which included regulations for the composition of motor fuel

and limits for the sulphur content of industrial fuel oils.

Nowadays, pollution from motor vehicles has become the most recognised air quality issue. The number of cars around the world is now steadily increasing, and a speed up in environmental friendly technological development is required to tackle the pollution problem.

1.2. Indoor air: exposure to Volatile Organic Compounds (VOCs)

Although much attention has been directed towards poor air quality outdoors, people spend more than 90% of their time in an indoor environment such as home, office, car, and shopping centre [3]. Due to poor Indoor Air Quality (IAQ) and related health problems, the European Environmental Agency (EEA) identified IAQ as one of the worldwide priority concerns in children's health [4, 5]. Common indoor air pollutants include particles (such as dust and smoke), biological agents (moulds, spores), radon, asbestos, and gaseous contaminants such as CO, CO₂, NO_x, SO_x, aldehydes and volatile organic compounds (VOCs). These pollutants have a close relation with the sick building syndrome (SBS), which is one of many terms used by occupants to describe symptoms of reduced comfort or health (*e.g.* headache, fatigue, skin and eye irritations or respiratory illness) [6, 7]. It is worth noting that according to World Health Organization (WHO) fact sheet nr. 313/2014 [8] indoor air pollution causes 3.3 million deaths per year, while outdoors pollution induced mortality is 2.6 million. IAQ is also an important factor in work productivity as shown in Wargocki [9] work, where individuals exposed to a typical indoor pollution source (plastic carpet) typed 6.5 % less than a control group. Furthermore, empirical studies have shown that the use of ventilation rates lower than 25 L s⁻¹ per person in commercial and institutional buildings was correlated with an increase in the number of short-term sick leaves [10, 11].

According to the definition of the WHO, VOCs are referred as all carbon and hydrogen-containing chemicals in the boiling point range of 50 - 260 °C, excluding pesticides. Thus, there are thousands of different VOCs produced and present in our daily lives including those coming from cleaning and degreasing products, air fresheners, toilet bowl deodorants, tobacco smoke, furniture and building materials (*e.g.* wood products, adhesives, carpeting, paints, varnishes, vinyl floors, newspaper, upholstery, fabrics, sealing caulks), cosmetics, fuel oil, vehicle exhaust, cooking, photocopying, etc. Common VOCs include acetone, benzene, ethylene glycol, formaldehyde, methylene chloride, perchloroethylene, toluene, xylene, and 1,3-butadiene [3, 12, 13].

The concentration of indoor VOCs varies according to the total space volume, the

pollutant production and removal rates (the air exchange rate with the outside atmosphere) and the outdoor VOC concentrations. In a study conducted by Salthammer [14], 150 VOCs (mainly aliphatic and aromatic aldehydes, aromatic hydrocarbons, ketones, esters and glycols) from furniture coatings were identified in a test chamber air under dynamic condition. The Total VOC (TVOC) concentrations ranged from $4 \mu\text{g m}^{-3}$ up to $1288 \mu\text{g m}^{-3}$ being TVOC emission rates as high as $22280 \mu\text{g m}^{-2} \text{h}^{-1}$ [14]. Moulds and bacteria can also contribute significantly to the presence of particles (spores) and VOCs in indoor pollution [15]. Microbial development in buildings can also be found in places where humidity accumulates, such as defective heating and air conditioning systems, garbage disposal, bathrooms and water leaks, and they are responsible for toxic and allergenic responses [16]. Although the concentration of each contaminant is usually low ($\mu\text{g m}^{-3}$), several hundred contaminants can be found at the same time, resulting in significant TVOC levels. In a study conducted by Kostianen [17], the individual concentrations of selected pollutants were up to 1000 times higher in 38 finish sick-houses (where people experienced symptoms associated with SBS) than their individual mean concentrations found in 50 normal houses used as reference, with over 200 VOCs being simultaneously detected in 26 houses. The highest TVOC concentration found was $9538 \mu\text{g m}^{-3}$ in one sick house compared to the mean concentration of $121 \mu\text{g m}^{-3}$ for the normal houses. Daisey *et al.* [18] reported indoor TVOC concentrations of $230 - 7000 \mu\text{g m}^{-3}$ (geometric mean of $510 \mu\text{g m}^{-3}$) in 12 Californian office buildings. Although it is not an easy task to correlate the TVOC concentration with health effects, experience of eye, nose or mouth irritation has been reported for the range of $5000 - 25000 \mu\text{g}_{\text{TVOC}} \text{m}^{-3}$ [19].

1.3. Elimination of Volatile Organic Compounds (VOCs)

Generally, methods to improve the indoor air quality include a combination of actions such as removing/controlling the VOCs sources, increasing the ventilation rates and cleaning the indoor air. Source control/removal is only possible when the pollutants are known and when their control is technically or economically feasible, which scarcely happens. New substances are constantly detected and classified as hazardous, many sources can release compounds for years and many other air pollutants are yet to be discovered [20, 21]. Increasing ventilation rates by means of leaving doors or windows opened, is the easiest procedure to ensure indoor air quality above satisfactory levels. However due to outdoor weather, external pollution conditions or even issues related to security, safety in high buildings, climate control, or noise that is not always possible [18, 22]. Consequently, installing a forced ventilation system is one of the most common procedures used for air treatment [23]. Side by side with forced ventilation is the inherent energy consumption which has been strongly encouraged in the EU to be reduced. In this sense, purifying

indoor air seems the obvious procedure to ensure a good quality of the indoor air.

Current procedures for air purification can be divided in two main groups based on phase transfer or on destruction through oxidation of the pollutants. Phase transfer group includes processes such as filtration, adsorption and membrane separation [16]. Albeit the suitability for highly loaded streams of gas-phase pollutants such processes merely transfer pollutants from gaseous to liquid or solid phase without destroying the pollutants. For example, in membranes separation processes, the pollutants are passed through a membrane into another fluid by affinity separation. If the retained VOCs are not reused, the subsequently step should be the destruction of the membrane. In adsorption, air pollutants are typically adsorbed onto active carbon or zeolites which may be too specific or may saturate, and the pollutant is not destroyed.

Removing VOCs by oxidation reactions may be accomplished by means of biological or physicochemical processes. The former include enzymatic oxidation reactions (VOCs are transferred into an aqueous phase and degraded by suitable enzymes), botanical purification (air passes through a planted soil or directly on the plants being the VOCs degraded by microorganisms and/or plants) and biofilters or biotrickling filters (a packed bed of a solid support colonized by attached microorganisms will biodegrade VOCs as the air passes through). For instance, Wolverton *et al.* [24] reported the reduction of formaldehyde at 19000 - 46000 $\mu\text{g m}^{-3}$ to levels lower than 2500 $\mu\text{g m}^{-3}$ (detection limit) in a 24 h period by several plants. Orwell *et al.* [25] found that indoor plants were able to remove benzene (at a removal rate of 12 - 27 ppm day⁻¹) in a sealed chamber through microorganisms present in the plant rhizosphere. It was also found that benzene removal rate increased linearly with the dose concentration, suggesting that the system might be inefficient under typical indoor air conditions. Later on, the same research group demonstrated that plants could also significantly reduce toluene and xylene at indoor air concentrations [26] and even the TVOC concentration in office buildings during field testing under real conditions [27]. VOCs removal by biological oxidation is, in fact, widely used mainly due to the low cost and to the ability to treat highly loaded streams; however, the need to transfer VOC or other pollutants into an aqueous phase may be problematic [16, 28].

Physicochemical processes for VOCs removal mainly include thermal oxidation [29] and catalytic thermal oxidation [30]. Both techniques share the same principle of action: the oxidation of organic compounds into carbon dioxide (CO₂) and water (H₂O) in a combustion chamber. Thermal oxidation operates between 800 and 1400 °C in the presence of a methane fuelled flame which is suitable for pollutant concentrations ranging from 5 to 20 g m⁻³; catalytic thermal oxidation uses a catalyst consisting of refractory support of alumina, ceramic or metal type enabling the operation at lower temperatures in comparison to thermal oxidation. Both processes are, obviously, expensive due to energy requirements and economically unfeasible for low

pollutant concentrations.

In the recent decades, the application of a special class of oxidation techniques defined as Advanced Oxidation Processes (AOPs) to treat gas-phase pollutants has been a matter of intensive research.

1.4. Advanced Oxidation Processes (AOPs)

AOPs rely on the ability of making use of the high reactivity of hydroxyl radical ($\text{HO}^\bullet$) to drive oxidation processes suitable to achieve complete degradation and full mineralization of several organic pollutants. Hydroxyl radical is among all oxidant species the second most reactive after fluoride ($E^0(\text{HO}^\bullet/\text{H}_2\text{O}) = +2.8 \text{ V/SHE}$) and being non-selective it can attack any organic including those that make up living cells.

Oxidation processes involving hydroxyl radicals have been used since late 19th century, as for example in Fenton reaction. However, the concept of “Advanced Oxidation Processes” was only established after Glaze *et al.* [31] suggesting, for the first time, the generation of enough $\text{HO}^\bullet$ radicals which would affect the water purification.

AOPs can be divided in photochemical processes if radiation has a participation in the process or non-photochemical processes if no radiation is required as detailed in Table 1.1.

Table 1.1. Typical AOPs systems

<i>Photochemical</i>	<i>Non-photochemical</i>
O_3/UV	Ozonation at alkaline pH (> 8.5)
$\text{H}_2\text{O}_2/\text{UV}$	$\text{O}_3/\text{H}_2\text{O}_2$
$\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$	Ozone + catalyst
(Electro-) Photo-Fenton	Fenton system ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$)
TiO_2/UV (Heterogeneous photocatalysis)	Non-thermal plasma
Vacuum UV (VUV)	Ultrasonic cavitation
$\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$	
Photolysis	

Among all AOPs, only heterogeneous photocatalysis, homogeneous photo-Fenton and electro-photo-Fenton can take advantage of the sunlight as radiation source ($\lambda > 300 \text{ nm}$), out of which only heterogeneous photocatalysis can be employed for the removal of pollutants at gas-phase. In fact, heterogeneous photocatalysis or photocatalytic oxidation (PCO), has received increasing importance in the area of indoor air treatment as one of the most promising destructive technologies [32, 33].

1.5. Heterogeneous photocatalysis

Heterogeneous photocatalysis, or photocatalytic oxidation (PCO) is carried out when a semiconductor-based photocatalyst (TiO_2 , ZnO , SnO_2 ...) is irradiated by light photons that have energy equal to or higher than the photocatalyst band gap energy. When this happens, an electron (e_{cb}^-) is transferred from the valence band to the conduction band, leaving a hole (h_{vb}^+) in the valence band. The valence band hole can react directly with the pollutant molecule or can produce hydroxyl radicals, while the electron in the conduction band will react with water (H_2O) and oxygen (O_2) present in the surrounding air. Subsequently, hydroxyl ($\text{HO}^\bullet$) and superoxide ($\text{O}_2^{\bullet-}$) radicals are produced [34, 35].

1.5.1. General reaction mechanism

The mechanism of the photocatalytic reaction has been studied and described by several authors [36-38], briefly presented hereby:



First, conduction-band electrons $e_{\text{cb}}^-(\text{SC})$ and valence-band holes $h_{\text{vb}}^+(\text{SC})$, *i.e.* electron-hole pairs, are generated when light photons of energy $h\nu$ matching or exceeding the semiconductor band-gap energy are absorbed (eq. 1.1). Once at the surface of the semiconductor, and on the absence of any suitable acceptor (for e_{cb}^-) and donor (for h_{vb}^+) recombination will occur in a matter of nanoseconds avoiding any subsequent reaction [37, 39]. Hydroxyl anions and water molecules adsorbed on semiconductor surface, act as electron donors, while molecular oxygen acts as electron acceptor, leading to the formation of hydroxyl ($\text{HO}^\bullet$) and superoxide ($\text{O}_2^{\bullet-}$) radicals [40, 41] (eq. 1.2 - 1.4). If an organic molecule (RH) is adsorbed onto the semiconductor surface, the reaction with hydroxyl radical will occur, followed by structural breakdown into several intermediates until, eventually, total mineralization (eq. 1.5) [38, 42]. The photogenerated

holes, due to their high oxidation potential, can also participate in the direct oxidation of the organic pollutants (eq. 1.6) [43, 44]. Peroxide ($\text{HOO}^\bullet$) radical can also be generated from the protonation of $\text{O}_2^{\bullet-}$ radical and subsequently forms hydrogen peroxide (eq. 1.7, 1.8). Figure 1.1 schematizes the main steps of a photocatalytic reaction taking place in a solid semiconductor including recombination reactions.

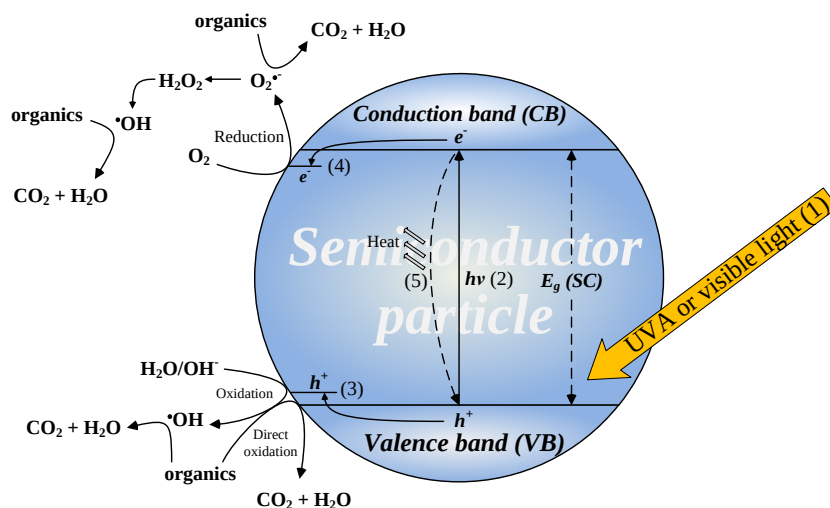


Figure 1.1. Steps of a photocatalytic reaction in a solid semiconductor particle: (1) light photons of energy $h\nu$ matching or exceeding the semiconductor band-gap energy; (2) excited electron, e_{cb}^- , migrates from valence band to conduction band leaving a hole, h_{vb}^+ , in the valence band; (3) h_{vb}^+ migrates to surface and initiates oxidation reactions; (4) e_{cb}^- migrates to surface and initiates reduction reactions; (5) charge carrier recombination liberating heat.

1.5.2. Air treatment applications

PCO is seen as a promising option for de-polluting purposes [38, 45-49], mainly because: *i)* can be operated at room temperature [37]; *ii)* uses air (through water vapour and molecular oxygen) as the source of oxidant [50], *iii)* degrades/mineralizes a wide range of organic and inorganic pollutants into harmless or easily neutralized final products (CO_2 , H_2O and mineral acids) [51]; *iv)* can take advantage of solar radiation for performing the charge separation at the semiconductor [52]. Also, the premise of low energy consumption, potentially long service life, and low maintenance are additional features that make PCO an attractive method for both indoor and outdoor applications. In Table 1.2 are summarized several PCO applications and main results obtained.

PCO can also be used to combat bioterrorism/agroterrorism, and maintain good IAQ in offices, buildings, homes, industrial premises, healthcare facilities and public transportations/vehicles (*i.e.* cars, ships and aircrafts). Back in the year of 2000, Anpo [68]

expected that using PCO with environmentally friendly photocatalysts would solve environmental pollution in a huge global scale.

Table 1.2. Current applications of PCO processes.

Author	Application	Remarks
Canela <i>et al.</i> [53][55]	Removal of malodorous S-containing compounds in sewages and WWTPs	99 % of C ₃ H ₆ S, C ₃ H ₆ S, C ₄ H ₄ S, C ₂ H ₆ S ₂ and H ₂ S removal
Ginestet <i>et al.</i> [54]	VOCs removal in aircrafts using a PCO air filter	Removals of 14 – 18 % for toluene, 41 – 49 % for ethanol and 21 – 28 % for acetone
Matsunaga <i>et al.</i> [55]	Inactivation of microorganisms in a photocatalyst aqueous suspension	<i>Lactobacillus acidophilus</i> (100 % inactivation after 60 min) <i>Saccharomyces cerevisiae</i> and <i>Escherichia coli</i> (respectively, 46 % and 80 % inactivation after 60 min and 100 % after 120 min) <i>Chlorella vulgaris</i> (15 % after 60 min; 45% after 120 min)
Maness <i>et al.</i> [56]	Inactivation of <i>Escherichia coli</i> in a photocatalyst aqueous suspension	Up to 93 % of inactivation after 30 min
Goswami <i>et al.</i> [57]	Inactivation of <i>Serratia marcescens</i> using photocatalyst-coated filters	100 % inactivation
Kozlov <i>et al.</i> [58]	Removal of diethyl sulfide (DES), a simulant for chemical agent mustard gas, using a gas-phase batch reactor.	Complete oxidation into CO ₂ , H ₂ O and sulphate species. Acetaldehyde and ethylene were detected as gaseous intermediates and diethylsulfone and carboxylates were detected as surface intermediate products
Grandcolas <i>et al.</i> [59]	Chemical warfare agents (CWA) removal over photocatalyst impregnated military textiles	Complete removal of the toxicity of the neurotoxic agent-simulating dimethylmethylphosphonate (DMMP) and yperite live agent within 7 and 20 min, respectively
Kau <i>et al.</i> [60]	Inactivation of <i>Bacillus anthracis</i> spores in mice	Significant viability reduction of anthrax spores and inactivation of lethal toxin. Photocatalyzed spores tenfold less potent to induce mortality.
Maneerat and Hayata [61]	Inactivation of fungal activity of <i>Penicillium expansum</i> <i>in vitro</i> and <i>in fruit</i>	Development of <i>Penicillium</i> rot in apple was significantly retarded
Cassar [62]	Photoabatement of airborne NO _x using photocatalyst incorporated cement	Approximately 40 % of NO was converted with 70 % of NO ₂ selectivity
Marcos <i>et al.</i> [63]	Removal of dye Orange II aqueous solution using ceramic glazed tiles with deposited photocatalyst layers	90 % of Orange II decolourisation efficiency although the unpleasant appearance, high degree of roughness and hard to clean
Matsubara <i>et al.</i> [64]	Removal of gaseous acetaldehyde over a photocatalyst-containing paper	90 % of acetaldehyde removal. Cellulosic fibre matrix of the paper can be easily damaged by the PCO process
Bygott <i>et al.</i> [65]		Daily NO _x removal equivalent to 4.5 g in about 10000 m ³ of air
Maggos <i>et al.</i> [66]	NO _x removal over photocatalyst containing paint	19 % and 20 % for NO and NO ₂ removal
Ângelo <i>et al.</i> [67]		95 % of NO conversion for an initial NO concentration of 100 ppb _v .

Canela *et al.* [53], [69] reported the use of heterogeneous photocatalysis in sewage and wastewater treatment plants (WWTPs) for the destruction of malodorous sulphur-containing compounds such as hydrogen sulfide (H_2S), trimethylene sulfide ($\text{C}_3\text{H}_6\text{S}$), propylene sulfide ($\text{C}_3\text{H}_6\text{S}$), thiophene ($\text{C}_4\text{H}_4\text{S}$) and methyl disulphide ($\text{C}_2\text{H}_6\text{S}_2$). Although observing the formation of intermediates and catalyst deactivation in their experiments, results showed that catalytic processes were efficient in decomposing those malodorous compounds.

PCO is also of great interest for improving air quality in aircraft cabins albeit the generally low VOC concentrations. Studies have confirmed that odour in aircraft cabins is a common problem especially in periods during and after boarding [54]. Ginestet *et al.* [54] developed a modular and regenerable PCO unit air filter, photocatalytically active under UV light illumination, to improve the quality of recirculated air entering the cabin. Despite the formation of intermediate reaction products found in their study, PCO process appears to be a promising solution to odour and IAQ problems in aircraft environments. Earlier, Hall *et al.* [70] developed a multi-stage honeycomb monolith PCO reactor and studied the destruction of VOCs and bioaerosols in airliner cabins. The study showed that PCO reactors for VOC control can replace HEPA filters for bioaerosol control. Moreover, the detailed life-cycle costs comparison made between PCO and carbon adsorption/HEPA showed that adsorption involves higher life cycle cost owing to the low adsorption capacity.

Airborne pathogenic organisms such as bacteria, fungi, viruses, as well as their spores can also be inactivated and destroyed by PCO. Matsunaga *et al.* [55] demonstrated in their pioneer research the microbicide effects of hydroxyl radicals and superoxide ions during PCO process. Furthermore, the extent of killing was found to be inversely proportional to the cell wall thickness [55]. The bactericidal activity and killing mechanism of photocatalytic TiO_2 towards *Escherichia coli* was explored by Maness *et al.* [56]. Huang *et al.* [71] found that the destruction of bacteria by PCO starts with the attack on the external cell wall followed by the oxidative damage of the underlying cytoplasmic membrane. The photocatalytic action goes deeper and deeper as the cell becomes more permeable and subsequently, inducing cell lysis and death. Huang *et al.* [71] ordered the sensitivity of microorganisms to TiO_2 -based photocatalysis as follow: virus > bacterial cells > bacterial spores. Comparative studies conducted by Goswami *et al.* [57] showed that PCO was more effective than ultraviolet germicidal radiation (UVC) in the destruction of *Serratia marcescens*.

Another worth dealing with PCO application is focused on the disposal of tons of confiscated chemical warfare agents (CWAs). Kozlov *et al.* [58] investigated the PCO of diethyl sulfide (DES), a simulant for chemical agent mustard gas. During the experiment, some intermediates were formed, but DES was still completely oxidized to yield CO_2 , water, sulfates

and carbonates as final products. In another study, Martyanov and Klabunde [72] reported the PCO of gaseous 2-chloroethyl ethyl sulfide, the main component of mustard gas. Oxidation of this compound resulted in the formation of intermediates of different toxicity levels with potential negative impact in human health. Nonetheless, such intermediates can undergo further oxidation leading to less toxic compounds. Smith [73] mentioned the possible incorporation of photocatalytic surfaces on protective garments and masks for the protection of emergency responders and Grandcolas *et al.* [59] reported the impregnation of photocatalyst in military textiles for CWA removal.

The above-mentioned ability to inactivate and kill bioaerosols such as bacteria, viruses, and spores makes PCO attractive in the mitigation of bioterrorism activities. For instances, Kau *et al.* [60] studied the inactivation of anthrax spores through PCO in mice over nitrogen or carbon doped TiO₂ under visible light illumination. Based on the obtained results, Kau *et al.* [60] suggested that PCO could directly inactivate the lethal toxin, the major virulence factor of *B. anthracis*.

PCO can also be employed as air cleaning technology for livestock buildings maintaining good air quality and preventing contamination and microbial spoilage of food and dairy products [74, 75]. In a study conducted by Cho *et al.* [74], PCO was used in the non-thermal disinfection of fresh vegetables through inactivation of foodborne pathogenic bacteria as *E. Coli*, *Salmonella Typhimurium* and *B cereus* in fresh carrots.

Maneerat and Hayata [61] also employed PCO towards the inactivation of fungal activity of *P. expansum*, an organism responsible for postharvest rot development in fruits such as tomatoes and lemons.

The incorporation of photocatalysts, specially TiO₂ (by far the most used photocatalyst [76]) into construction materials has also been an object of intense research not only for decontamination and de-polluting purposes but also for the development of self-cleaning and self-disinfecting materials. These construction materials include cement mortar [62, 77-79], tiles [63, 77, 80, 81], paving blocks [82-84], window glasses [85-87], composite sheets [88, 89], wall papers [64, 88, 90, 91] and paints [65-67, 92].

A pioneering work on cementitious materials with photocatalytic activity was performed by Murata *et al.* [79] evaluating the NO_x degradation over TiO₂ loaded concrete blocks. Later, in a similar study, Cassar [62] reported synergetic effects towards photoabatement of NO_x of the combined use of TiO₂ and cement: approximately 40 % of NO was converted with 70 % of NO₂ selectivity.

Marcos *et al.* [63] reported for the first time the deposition of TiO₂ layers on common ceramic glazed tiles using the screen-printing process, which is a low cost and common technique used for decoration in the ceramic industry. However, despite the good results achieved in terms of photocatalytic degradation of Orange II solution, the material's surface had an unpleasant appearance, a high degree of roughness and it was hard to clean.

Earlier, in 1995, Matsubara *et al.* [64] developed a TiO₂-containing paper presenting photocatalytic properties. These authors investigated its photocatalytic activity by measuring the decomposition of gaseous acetaldehyde under a weak UV light radiation. The highest quantum yield obtained with the TiO₂-containing paper was 90 %, *ca.* two times larger than that of commercial TiO₂. However, the cellulosic fibre matrix of the paper can be easily damaged by the process.

Considering the fact that almost all surfaces in urban areas can be painted, paint coatings are especially attractive as support for photocatalysts. For instances, Bygott *et al.* [65] reported a field trial in London, close to a school children playground, where an area of 300 m² of walls was painted with a silicate-based paint incorporating 7.5 wt.% of photocatalytic TiO₂. The results showed a daily NO_x abatement of *ca.* 4.5 g in about 10000 m³ of air around the school children playground [65]. Maggos *et al.* [66] reported NO_x depollution tests in an artificially closed parking area, which was polluted by a car exhaust during the testing period; they observed a reduction of 19 % and 20 % for NO and NO₂, respectively. Salthammer and Fuhrmannh [92] studied the photocatalytic efficiency of two different types of commercially available wall paints in a 1 m³ test chamber, with and without air exchange, using artificial daylight. The results showed that formaldehyde was photo-oxidised under static conditions, while for typical VOCs, under dynamic conditions, no significant photocatalytic activity was observed. In another real-outdoor conditions study, Ângelo *et al.* [67] determined the NO photoabatement efficiency of photocatalytic paints when irradiated by sunlight attaining *ca.* 95 % of NO conversion for an initial NO concentration of 100 ppb_v.

1.6. Common semiconductors used as photocatalysts

Semiconductors as metal oxides (TiO₂, ZnO, WO₃, SnO₂, Fe₂O₃) or metal chalcogenides (CdS, ZnS, WSe₂) are often employed as heterogeneous photocatalysts in photocatalytic processes [38, 93]. A semiconductor should fulfil the following characteristics to be considered efficient:

- i. Able to be activated by sunlight, *i.e.*, visible radiation or UVA;

- ii. Biologically and chemically inert;
- iii. Not prone to photocorrosion and resistant to the attack of reagents;
- iv. Insoluble in water;
- v. Low toxicity;
- vi. Availability at low cost.

Moreover, the redox potential of the photogenerated valence band hole must be positive enough to generate $\text{HO}^\bullet$ radicals in order to oxidize the contaminant and the redox potential of the conduction band electron should be negative enough to reduce oxygen to peroxide or other species [94]. The redox potential of some common semiconductors together with the band-gap energy is represented in Figure 1.2.

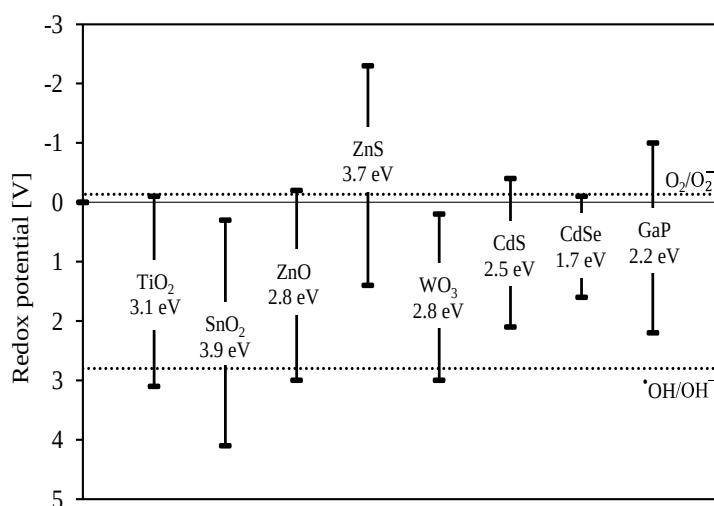


Figure 1.2. Band positions (top of valence band and bottom of conduction band) for several common semiconductors together with the band-gap energy [95].

However, some semiconductors present specific issues impairing their use in photocatalytic applications. For example, CdS and CdSe undergo photoanodic corrosion in aqueous media and show toxicity [36]. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) absorbs in the visible region, but shows much lower photocatalytic activity when compared to TiO_2 or ZnO , due to corrosion or formation of short-lived metal-to-ligand or ligand-to-metal charge transfer states [36]. ZnO and TiO_2 present similar bandgap energies; however, the former becomes unstable when illuminated in aqueous solutions, yielding $\text{Zn}(\text{OH})_2$ on the particle surface and leading to the deactivation of the catalyst [96]. WO_3 has also been investigated as photocatalyst but due to relatively low conduction band level (+ 0.5 V/SHE, standard hydrogen electrode) is generally less photocatalytic active than TiO_2 [97, 98]. TiO_2 (also known as titania), stands out as one of the most photoactive semiconductor-based catalyst, fulfilling all the referred criteria.

1.6.1. The preferred semiconductor: titanium dioxide (TiO₂)

TiO₂ exists in at least eleven different polymorphic forms, three of which are the well-known and abundant minerals rutile (auburn, bronze and black), anatase (black, blue, red, etc.) and brookite (bronze and black). Rutile (tetragonal, space group $P4_2/mnm$) is a crystallization product of igneous rocks whereas anatase (tetragonal, space group $I4_1/amd$) and brookite (orthorhombic, space group $Pbca$) occur as accessory minerals in alteration assemblages and sedimentary and metamorphic rocks [99-103]. There are also five high-pressure TiO₂ form materials: an orthorhombic α -PbO₂-like form TiO₂ (II) and a monoclinic baddeleyite-like form, both found at the Ries crater in Bavaria [104, 105]; the other three are orthorhombic cotunnite (PbCl₂)-like form TiO₂-OII [106], orthorhombic TiO₂-OI [107] and cubic TiO₂ form [108]. Other three forms that are metastable phases and can be produced synthetically are: monoclinic TiO₂(B) [109], tetragonal hollandite-like form TiO₂(H) [110] and orthorhombic ramsdellite-like form TiO₂(R) [111].

The base unit of the TiO₂ crystalline structure is an oxygen atoms-based octahedron centred on a titanium atom resulting in the molecular formula of (TiO₆)²⁻ as it is represented in Figure 1.3.

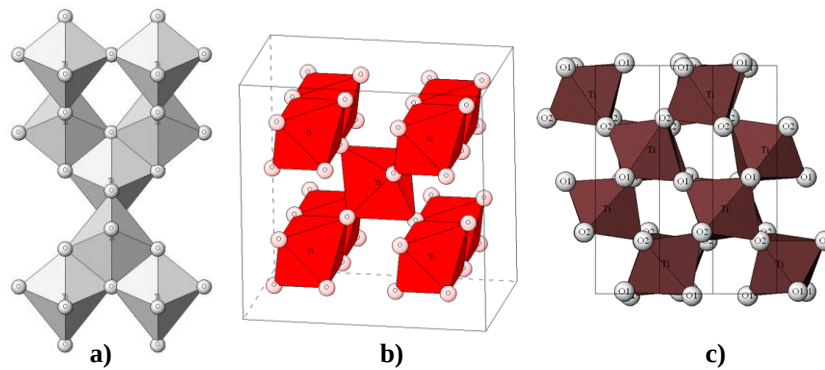


Figure 1.3. TiO₂ crystallographic phases of anatase (a), rutile (b) and brookite (c) (adapted from Carp *et al.* [112]).

Anatase and rutile share the same crystalline system (tetragonal system) but differ in the arrangement of the octahedrons and distortion. In anatase the octahedrons are connected by their vertices while in rutile the edges are connected. In both structures, Ti⁴⁺ species are surrounded in its first coordination sphere by six O²⁻ species in a distorted octahedral coordination. In anatase, Ti-Ti distances are longer than in rutile, whereas Ti-O distances are lower for anatase [113, 114]. These differences reflect on the electronic structure of both allotropic forms: the forbidden bandwidth of rutile is 2.8 - 3.0 eV while anatase is 3.2 eV. Rutile is the thermodynamically stable

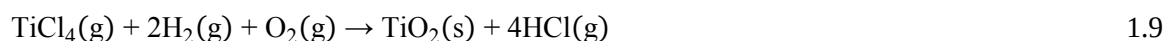
form of TiO_2 at any temperature and above $650\text{ }^\circ\text{C}$ brookite and anatase forms are converted into rutile [115]. Below $600\text{ }^\circ\text{C}$ the formation of anatase is kinetically favoured [116]. Notwithstanding, Zhang and Banfield [117] showed the superior stability of anatase form in comparison to rutile when the crystal size is smaller than 14 nm .

Brookite [118] has an orthorhombic structure which is more complex than anatase and rutile forms structures. The comparison of the volume occupied by the base unit of the TiO_2 crystalline structure of the three allotropic forms shows that the compactness of the TiO_2 structures decreases following the order: rutile > brookite > anatase. Moreover, both vertices and edges are connected.

Aside from the influence of the crystallographic structure of TiO_2 on the photocatalytic efficiency, other factors such as TiO_2 specific surface area, crystallinity and crystallite size may contribute to the photocatalytic properties of TiO_2 [119]. For instance, higher specific surface areas promote higher photocatalytic. Likewise, higher crystallinity suggests the possibility of lower density in surface defects increasing the charge recombination time. These two desired features are difficult to be obtained simultaneously since increasing crystallinity (as a result of, *e.g.*, higher heat treatment) is often achieved with a subsequent loss of specific surface area. In this sense, the anatase phase has usually the best photocatalytic performances, while the rutile phase is the most stable phase with crystallite sizes higher than 14 nm [117, 120]. There are already a number of commercial photocatalytic TiO_2 powders available on the market but that possessing better photoactivity in many reaction systems is TiO_2 Degussa P25 (commercial name Aeroxide[®] TiO_2 P25, after Evonik Industries taking over, in 2007, to be its Chemicals Business Area). This commercial TiO_2 material consists in a highly dispersed powder manufactured according to the patented Aerosil[®] process. It is composed by a mixture of 80 % of anatase and 20 % of rutile, with a specific surface area of $50\text{ m}^2\text{ g}^{-1}$ and an average particle size of 21 nm [121]. TiO_2 P25 has been used as a standard photocatalyst in several research works [122, 123].

The activity obtained for this type of material, in comparison to that of pure anatase, has been extensively studied [124-126]. Despite the fact that it is still subject of discussion, it is believed that its activity comes from the formation of heterojunctions between the two types of crystalline forms, anatase and rutile [127] when employed as photocatalytic films. Indeed, rutile, owing to its lower conduction band, may slightly absorb light in the visible range and thus serving as a photosensitizer to the TiO_2 particles of anatase structure. Also, the respective positions and the difference between the higher energy levels of the conduction bands of the two phases may produce a transfer of electrons from the anatase towards rutile. Due to their spatial charge separation, the transfer phenomenon of the photogenerated electrons from anatase conduction band towards the rutile conduction band of TiO_2 will prevent charge recombination [128].

Regarding the synthesis to the preparation conditions, TiO_2 can be prepared via two types of methods [129]: gas-phase and liquid-phase. Gas-phase methods include flame hydrolysis [130] or oxidation at high temperatures of TiCl_4 [131] and decomposition of titanium alkoxides (Ti(OR)_4) [132]. As example, TiO_2 P25 has been prepared by mixing gasified TiCl_4 with reactants gases (hydrogen and oxygen) and burning at high temperatures. The reaction is described in eq. 1.9:



Concerning liquid-phase methods, hydrolysis of TiCl_4 in liquid-phase has been explored to manufacture TiO_2 in a fine particulate form. Solvothermal and hydrothermal methods [133, 134], sol-gel [135, 136], water-in-oil microemulsion [137, 138], combustion and electrochemical synthesis [139, 140] and precipitation and co-precipitation [141, 142] have been the most popular techniques to synthesize TiO_2 materials.

1.6.2. Strategies to enhance the TiO_2 photocatalytic properties

TiO_2 has been for the last decades the most used and most efficient semiconductor in photocatalytic applications, particularly in the degradation of VOCs. However, this material presents three main limitations: (i) the threshold of absorption band does not allow visible light absorption, using only UV radiation which corresponds to 3 – 5 % of the solar spectrum reaching the Earth; (ii) the degradation process has a low quantum yield; (iii) the fast recombination of the charge carriers is in the order of nanoseconds. Chemical and physical modification of the TiO_2 by doping metal and non-metal ions into the TiO_2 lattice, deposition of transition metals, dye photosensitization or coupling with other semiconductors have been used over the recent years to overcome TiO_2 limitations.

1.6.2.1. Increasing the life time of charge carriers

The modification of TiO_2 surface with metals, the coupling of the TiO_2 with other semiconductors or the change over the morphology of the TiO_2 , are always to enhance the transfer and separation of photogenerated charges in TiO_2 and subsequently, the life time of charge carriers is increased.

Metal deposition onto TiO_2 surface: Schottky barrier

The addition of a metal to a semiconductor changes the semiconductor surface properties by creating a barrier between the metal and the semiconductor junction, known as Schottky barrier (Figure 1.4).

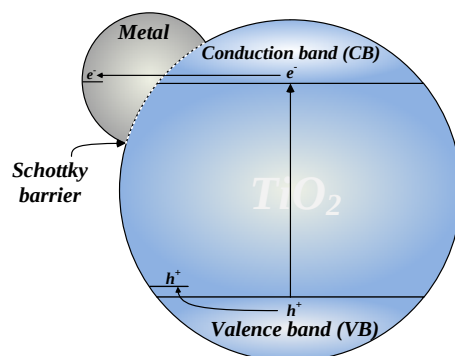


Figure 1.4. Photoexcitation and charge transfer in a metal-modified TiO₂ photocatalyst (adapted from Serpone *et al.* [143]).

The Schottky barrier promotes a better transfer of photogenerated electrons at TiO₂ surface towards electron acceptor species, such as oxygen leading to a decrease in the electron-hole recombination and, subsequently, to a more efficient charge separation [37]. Thus, the improved separation of charges by the presence of the metal increases the photocatalytic process efficiency [144-147], and ultimately increases the quantum yield. The positive effect of metal modification is highly dependent on the employed metal: the work function must be higher than the electron affinity of the semiconductor. Species like Ag, Pt, Pd, Au, Cr, among others are pointed out as very good doping metals for this purpose [142, 148-151]. The enhancement in TiO₂ reactivity was first observed for the photoconversion of H₂O to H₂ and O₂ through Pt/TiO₂ [148]. However, this type of modification has also shown negative effects such as the reduction of the TiO₂ bandgap energy resulting in a decrease in the energy threshold required to activate the photocatalyst [149]. It has also been reported an optimum metal content above which the metal acts as a charge recombination centre resulting in a reduction of the overall photocatalytic efficiency [37].

Coupling with other semiconductors: heterojunction

The coupling between TiO₂ and another semiconductor with different energy levels for their corresponding conduction and valence bands, leads to the formation of an interface between two semiconductor materials, called heterojunction. The existence of such interface will increase the photocatalytic process efficiency, reducing the probability of recombination of photogenerated charges through an irreversible spatial separation of the charge carriers. Besides the increase of the life time of the charge carriers, the structure of the interface (*i.e.* geometry of the particles, the

surface contact between particles and the particles size [152]) also represents an important feature to enhance the efficiency of the interfacial electron transfer. In this sense, several coupled semiconductors have been intensively used for the degradation of pollutants such as TiO_2/CdS , $\text{TiO}_2/\text{SnO}_2$, TiO_2/ZnO , $\text{Bi}_2\text{S}_3/\text{TiO}_2$ and TiO_2/WO_3 [152-155].

The evidence of a hole transfer between coupled semiconductors, together with a vectorial one-way displacement of both electrons and holes from one semiconductor to another, were first reported by Serpone *et al.* [152]. During the photocatalytic oxidation studies of several phenol-like molecules by using TiO_2/CdS coupled semiconductors, these authors concluded that the enhancement of the interfacial charge transfer to adsorbed substrates occurs via two mechanisms: in the first one, a photogenerated electron of the illuminated semiconductor with a more negative conduction band is injected into the less negative conduction band of the other semiconductor while the hole remains in the former; in the second mechanism both semiconductors are activated resulting in a simultaneous electron transfer from the first semiconductor to the second as well as hole transfer from the second semiconductor to the first one (Figure 1.5). As a result, electrons are accumulated at the lower lying conduction band of one semiconductor, while the holes accumulate at the higher valence band of the other semiconductor [152].

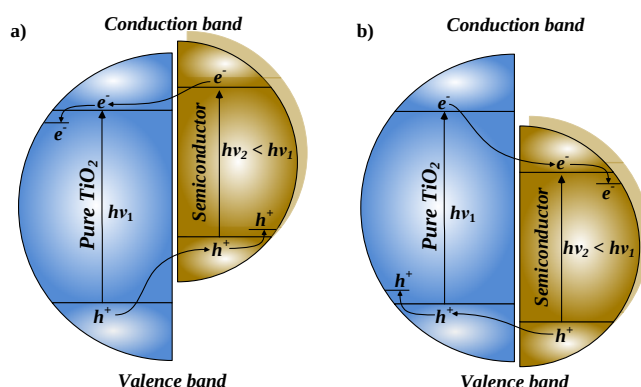


Figure 1.5. Photoexcitation and charge transfer between two light active semiconductors: (a) injection of an e^- in the TiO_2 conduction band and injection of a h^+ in the valence band of the other semiconductor; (b) injection of an e^- in the conduction band of the other semiconductor and injection of a h^+ in the TiO_2 valence band (adapted from Serpone *et al.* [152]).

Modifying TiO_2 morphology: specific surface area

As mentioned above the surface area of the photocatalyst is an important factor to be considered in the design of efficient photocatalysts. Successful attempts were made at synthesizing different forms of TiO_2 -based nanostructures with increased surface areas [118, 156, 157]. These include one dimensional nanotubes, nanorods, and two dimensional nanosheets, as

shown in Figure 1.6. Titania nanotubes are one of the widely studied forms of titanium dioxide and have shown promising results over the past few years [158-162]. A detailed overviewing regarding this particular topic will be made further ahead in this introduction.

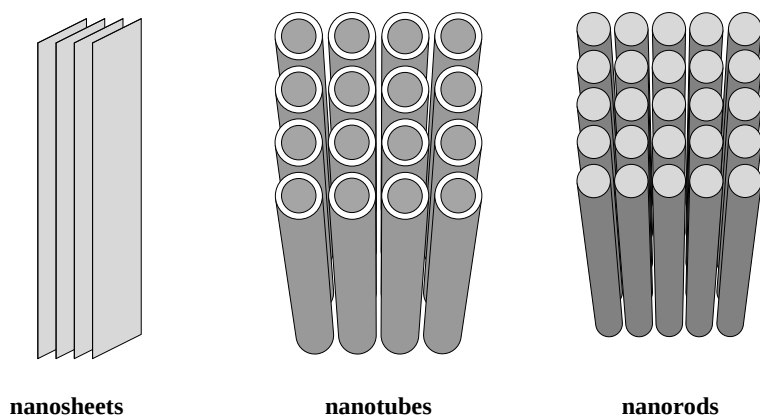


Figure 1.6. Different morphologies of TiO₂ nanostructures.

1.6.2.2. Red shifting of TiO₂ absorption: towards solar applications

Due to the rather large bandgap energy of TiO₂ (~3.2 eV), photocatalytic-related processes are limited to the UV radiation ($\lambda < 400$ nm). Considering the natural sunlight, the UV radiation fraction represents only 3–5 % of the solar spectrum [163]. Shifting the TiO₂ absorption spectrum into the visible light range, where the exploitable fraction of the solar spectrum is near 42 % seems to be advantageous from an energetic and economic point of view. In fact, over the recent years, several approaches have been presented in the literature to shift the absorption onset of TiO₂ to the visible region: metal [164-182] and non-metal doping of TiO₂ [183-194], reduction of TiO₂ with plasma treatments [195, 196], and sensitization with organic dyes [197, 198].

Metal and non-metal ion doping

In recent years an extensive research focused on visible-light induced photocatalysis by metal ion-doped semiconductors since some of these materials have shown a stretched absorption spectra into visible-light region. This phenomenon has been explained by the excitation of electrons of dopant ions to the conduction band of the semiconductor, *i.e.*, a metal to conduction band charge transfer. Alkaline Earth metal ions (magnesium and barium) [164-166], transition metal ions (*e.g.* chromium, iron, cobalt, nickel, niobium, vanadium, ruthenium, platinum and gold) [167-173], post transition metal ions (tin, bismuth, indium, ...) [174-177] and rare earth metal ions (*e.g.* lanthanum, cerium, ytterbium, praseodymium, ...) [178-182], have been

investigated as potential dopants for visible-light induced photocatalysis. However, metal ion dopant can also serve as a recombination centre, resulting in decreased photocatalytic activities as already explained previously [37, 149, 169, 175].

First reports of anion-doped TiO_2 began to appear since the mid-1980s to early 1990s [183, 184, 199], but it was only in 2001 that anion-doping was considered a prelude to produce second generation materials in the study reported by Asahi *et al.* [190] dealing with visible-light active nitrogen (N) -doped TiO_2 . N-doping has the potential to increase the photoactivity under UV radiation and, more importantly, under visible-light in comparison to the pure TiO_2 (Figure 1.7a). Subsequent studies reported several other visible-light active N-doped TiO_2 materials [185-189], together with carbon (C) -doped TiO_2 [190-192] and sulphur (S) -doped TiO_2 [193, 194]. It was originally proposed that N-doping of TiO_2 can shift its photo-response into the visible region by mixing p states of nitrogen with $2p$ states of lattice oxygen and, thus, increasing the photocatalytic activity by narrowing the TiO_2 bandgap as shown in (Figure 1.7b) [190, 193, 200].

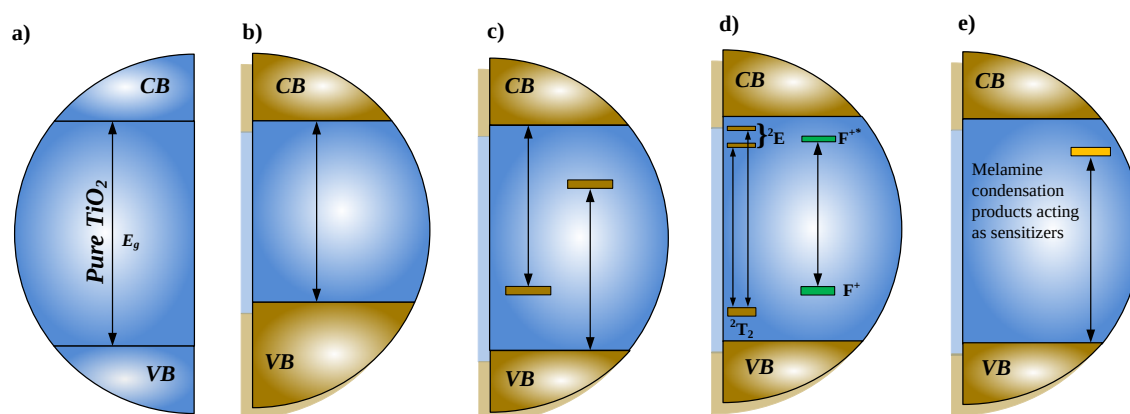


Figure 1.7. Mechanisms proposals for the changes that may occur to the bandgap electronic structure of N-doped TiO_2 : (a) undoped TiO_2 ; (b) bandgap narrowing as a result of VB broadening; (c) introduction of localized states above VB or below CB; (d) electronic transitions from localized states near VB to the corresponding excited states for Ti^{3+} (Jahn-Teller split ${}^2\text{T}_2 \rightarrow {}^2\text{E}$) and F^+ (equivalent to a single electron associated with the O vacancy) centres; (e) sensitization by compounds containing nitrogen species (adapted from Serpone [163]).

However, other studies proposed different ideas for the visible light absorption of N-doped TiO_2 . One is that the nitrogen species originate localized $\text{N}2p$ states above the valence band and the electronic transitions from localized $\text{N}2p$ state to the conduction band (Figure 1.7c) [187]. Another hypothesis is that the visible-light absorption band of N-doped TiO_2 is ascribed to the localized states of the oxygen deficiencies caused by nitrogen doping instead of the dopant itself (Figure 1.7c) [201]. In 2006, Serpone [163] proposed that the visible-light absorption band was originated by the formation of colour centres in the bandgap, resulting from the heat treatment or the photostimulation process (Figure 1.7d). In addition, Mitoraj and Kisch [202] suggested a

sensitization mechanism in which melamine condensation products would act as visible light sensitizers (Figure 1.7e).

Despite the general agreement found in the literature regarding the improvement of the TiO_2 photocatalytic activity driven by the incorporation of nitrogen, the mechanism on what such enhancement is reported is still unclear. The photocatalytic activity of N-doped TiO_2 materials depends on several factors, such as the preparation methods and precursors employed playing unequivocally a critical role on the resulting photocatalytic properties [203].

Sensitizing with organic dyes

Figure 1.8 represents the mechanism of sensitizing TiO_2 surface with organic dyes, where the visible light excited electrons from the dye molecule can be injected to the conduction band of the semiconductor to initiate the photocatalytic reactions [197, 204, 205]. However, the stability of such dyes may not be ensured as gradual photooxidation in oxidizing media can occur [206, 207].

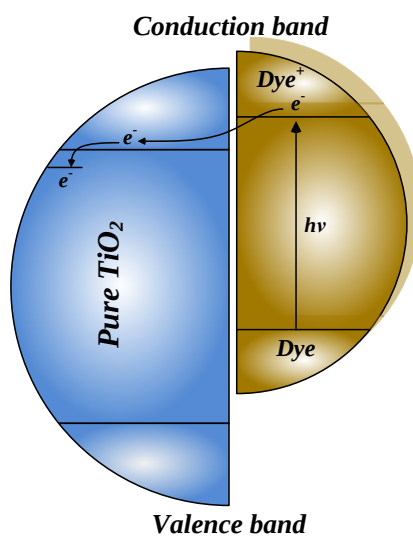


Figure 1.8. Photoexcitation and charge transfer of TiO_2 using dye molecule sensitizer (adapted from [197]).

Besides the application in photocatalytic processes, TiO_2 dye sensitization has a preponderant role [198, 208-210] in the field of energy production due to their high incident solar light-to-electricity conversion efficiency, colourful and decorative natures, and low cost of production. At present, state-of-the-art dye sensitized solar cells based on ruthenium(II)-polypyridyl complexes as the active materials have overall power conversion efficiencies over 11% under standard (Global AirMass 1.5) illumination [211, 212]. The high efficiencies of the ruthenium(II)-polypyridyl DSSCs can be attributed to their wide absorption range from the visible

to the near infrared (NIR) regime [208].

1.6.2.3. Increasing the oxidizing potential: quantum size effect (QSE)

Using TiO₂ crystal sizes in the order of nanometres is advantageous for photocatalytic purposes since the specific surface area increases as the particle size decreases. For example, Anpo and Takeuchi [213] and Yu *et al.* [214] obtained a specific surface area of 350 m² g⁻¹ for 10 nm crystals. The nanometric scale effect on the TiO₂ electronic structure has also a positive influence [215, 216]. Reducing the size of semiconductors particles to a few nanometres, often leads to a conduction band delocalization to upper levels increasing the bandgap energy, known as quantum size effect (QSE) [37]. This phenomenon results in an increase of the oxidizing potential as absorption band shifts to lower wavelengths (blue-shift). However, such influence has not been observed for the TiO₂ crystal sizes typically used in photocatalysis [215, 217]. According to Anpo *et al.* [218], only particles with a size lower than 6.5 nm would promote an enhancement of the quantum efficiency. On the other hand, reducing TiO₂ particles size to the order of a few nanometres will increase the amount of defects due to the loss of crystallinity; this leads to an increase in the bandgap energy by displacement of the conduction band reducing visible-drive photocatalytic efficiency. All the above suggests that an optimum size for the crystal size of TiO₂ is around 5 – 6 nm.

1.7. Titania nanotubes (TNTs)

Over the past decades, nanosized TiO₂-based materials have extensively been investigated for a wide range of applications, including solar cells/batteries, electroluminescent hybrid devices, and photocatalysis, owing to their peculiar chemical and physical behaviours. Moreover, the discovery of carbon nanotubes intrigued the intensive researches of one-dimensional nanostructures, such as nanotubes, nanorods, nanowires or nanobelts [219]. Due to the large specific surface area, ion-changeable ability, and photocatalytic performances, TiO₂-based nanotubes have attracted extensive interest, and despite the still controversial crystalline structure this type of material has been considered for extensive applications [160, 219, 220].

Several methods of fabricating TiO₂-based nanotubes can be found in literature surveys such as assisted-template [221-223], sol-gel [158, 224], electrochemical anodic oxidation [225-227] and hydrothermal treatment [159, 228-231] methods. Synthesis of a nanotubular form of titania was first reported in 1996 by Hoyer [221] via the template-assisted method. Thereafter, in 1998 and 1999, Kasuga and colleagues [158, 228] developed, respectively, for the first time the

sol-gel process and hydrothermal treatment towards titania nanotubes fabrication. Later, in 2001, Gong *et al.* [226] employed electrochemical anodic oxidation to synthesize titania nanotubes (TNTs).

The template-assisted method consists in the use of a known material – template – to prepare materials with similar morphology. In other words, adjusting the morphology of the template material it is possible to produce new materials with a regular and controlled morphology on the nano- and microscale. The production of TNTs involves controlled sol-gel hydrolysis of titanium-containing compounds solutions in the presence of templating agents. Then, the templating agent is selectively removed and the newly formed material is calcined. Due to the dependence on the pre- and post-synthesis treatment, this method may become expensive and susceptible of appearing impurities in the resulting materials. Surfactant organic molecules, such as 11-aminocarbonylundecylpyridinium [232] and hydrochloride laurylamine [233], are often used as templates. Tobacco mosaic viruses [234] or precipitated platinum salts [235] are other examples of templating agents. Another material widely used as template is the anodic aluminum oxide (AAO) nanoporous membrane. The internal surface of cylindrical pores of anodic alumina is used for the deposition of TiO_2 thin films from many different precursors [236, 237].

The electrochemical anodic oxidation is a method based on the anodization of titanium foil to obtain nanoporous titanium oxide films [225]. Grimes work group [226] showed that it is possible to obtain self-assembled TNTs ($\pi\text{-TiO}_2$) in the form of highly ordered arrays. Furthermore, comprehensive reviews associated with the fabrication, characterization, formation mechanism, and corresponding applications of TiO_2 -based nanotubes arrays have been also reported by the same group [238].

The fabrication of TNTs can also be made via hydrothermal treatment. Its cost-effectiveness, easy route of fabrication and the feasibility/availability of widespread applications has been the allure for several research groups.

Kasuga *et al.* [158] were the first authors to report the synthesis of anatase phase TiO_2 -based nanotubes, with a specific surface area of $400 \text{ m}^2 \text{ g}^{-1}$ and 8 nm in diameter. Their later published research also demonstrated the formation mechanism of these nanotubes [228]. Since then, many studies concerning the optimization of the synthesis, as well as the understanding for the mechanisms of nanotubes formation have been carried out [239-241]. TiO_2 -based nanotubes can be classified according to the crystal structure: anatase TiO_2 [228, 242, 243]; lepidocrocite $\text{H}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4$ ($x \sim 0.7$, $\square$: vacancy) [244, 245]; $\text{H}_2\text{Ti}_3\text{O}_7/\text{Na}_2\text{Ti}_3\text{O}_7/\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ [239, 240, 246]; $\text{H}_2\text{Ti}_2\text{O}_4(\text{OH})_2/\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2/\text{Na}_x\text{H}_{2-x}\text{Ti}_2\text{O}_5(\text{H}_2\text{O})$ [230, 247]; $\text{H}_2\text{Ti}_4\text{O}_9$ (H_2O) [248] structures.

Among these chemical structures, $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ and $\text{Na}_x\text{H}_{2-x}\text{Ti}_2\text{O}_4(\text{OH})$ are more acceptable due to the exclusive dependence on the replacement rate of Na^+ by H^+ in the interstitial plans of the nanosheets. This issue will be briefly addressed in the following sub-section.

1.7.1. Synthesis of TNTs by hydrothermal method

Zhang *et al.* [249] reported two possible $\text{H}_2\text{Ti}_3\text{O}_7$ formation mechanisms: *i)* TiO_2 reacts with NaOH forming nanosheets of sodium trititanate, $\text{Na}_2\text{Ti}_3\text{O}_7$. Progressively, sodium titanates will peel TiO_2 nanocrystals off forming independent nanosheets which will be more or less stable according to the intercalated ions in the sheets vicinity. Rinsing and neutralizing this material by hydrochloric acid will step-by-step replace Na^+ ions by H^+ ions which will create ionic asymmetry between the nanosheets. Subsequently, required surface tensions will arise curling the nanosheets into the tubular form [239, 250]. Moreover, this mechanism, which seems to be most well-accepted, explain the term “titanate nanotube” and suggests that the rinsing step has a vital role in the formation of the nanotubes; *ii)* the second mechanism is more controversial: TiO_2 reacts with a strong alkaline solution (NaOH) forming a highly distorted phase, which will recrystallize into $\text{H}_2\text{Ti}_3\text{O}_7$ -like phase as long plates or nanoribbons. According to the authors studies [240, 250], the hydrogen-deficiency on the surface of $(\text{Ti}_3\text{O}_7)^{2-}$ plates can provide the driving force (surface tension) for the peeling-off of $(\text{Ti}_3\text{O}_7)^{2-}$ plates and therefore resulting in the formation of layers bent to form the tube morphology. In Figure 1.9 is schematized a possible experimental procedure to synthesise TNTs.

On the other hand and based on the idea that $\text{H}_2\text{Ti}_3\text{O}_7$ could not exist in concentrated NaOH , Yang *et al.* [247] postulated that TNT structure would be assigned for the $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ phase and the formation mechanism includes TiO_2 particles swelling as the initial stage. The shorter $\text{Ti}-\text{O}$ bonds within TiO_6 units are expected to break under the concentrated NaOH solution, resulting in irregular swelling. The linear fragments would bond to each other in the form of $\text{O}^--\text{Na}^+-\text{O}^-$ to produce flexible planar fragments. Thus, nanotubes could be obtained through the covalent bonding of ending groups [251]. Tsai and Teng [252] also stated that the replacement of Na^+ by H^+ would cause a peeling-off of individual layers from TiO_2 particles owing to the variation of the surface charge.

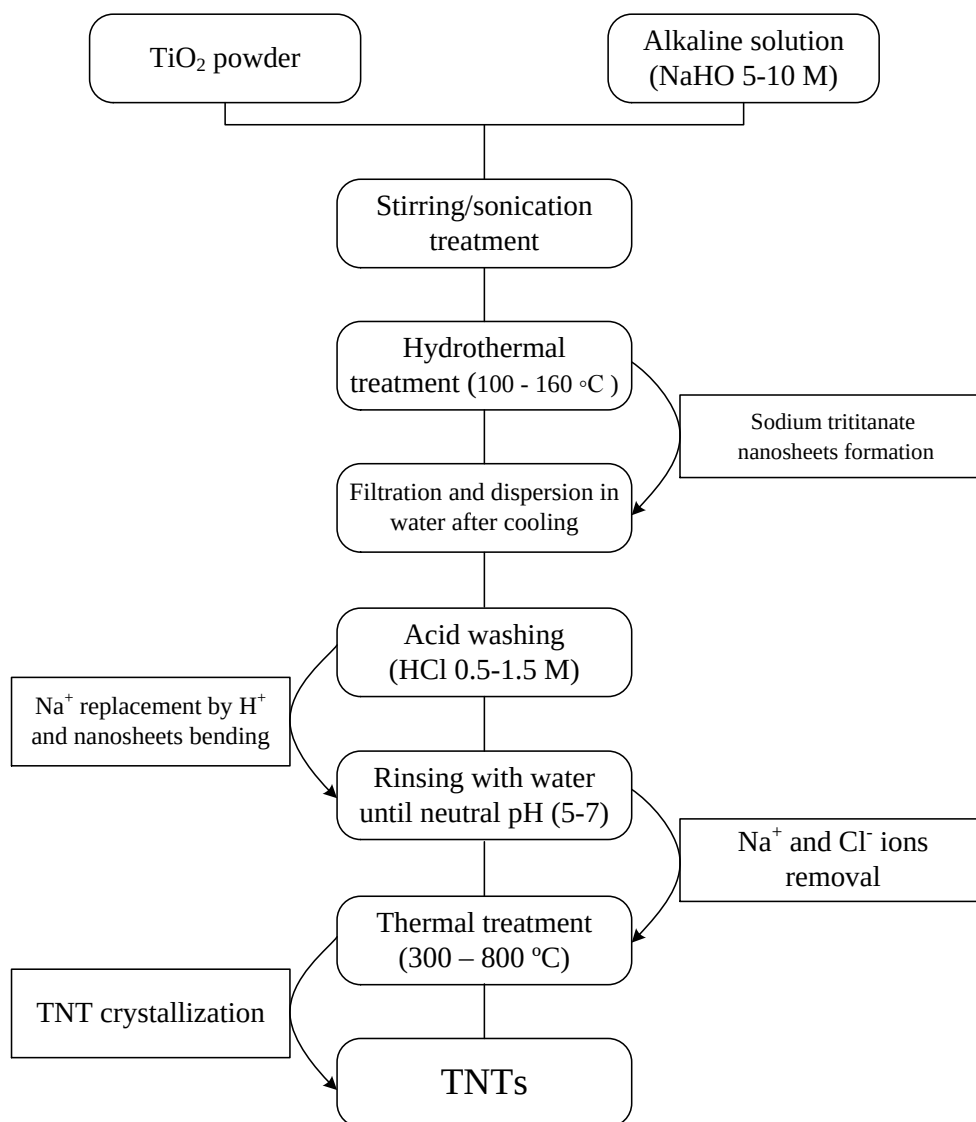


Figure 1.9. Schematic representation of TNTs synthesis by hydrothermal method.

Kukovecz *et al.* [253] used $\text{Na}_2\text{Ti}_3\text{O}_7$ directly as a precursor (instead of TiO_2) for the hydrothermal reaction, producing nanosheets instead of nanotubes. These sheets subsequently curved into nanoloops, which was thought to be the trigger in the formation process of TNTs. The curvature of the loops determines the morphology of the nanotube cross sections, giving rise to spiral, onion, and multiplespiral types.

In a different study, Ma *et al.* [254] reported the rolling mechanism from nanosheets into nanotubes, indicating that the de-intercalation of Na^+ ions caused by H_3O^+ substitution would reduce the interaction between layered sheets. The outer layer would peel off due to a reduction in electrostatic interaction with the underlying substrates and gradually curl up into tube structure.

1.7.2. Main parameters influencing TNT synthesis

The morphology and properties of TiO₂ nanotubes have a strong dependence on the hydrothermal conditions. The Ti precursor, sonication pre-treatment, temperature and time of treatment, the type and concentration of alkali solution, the acid washing and the TiO₂ nanotubes post-treatment (calcination) are found to be the predominant factors influencing the formation of the above mentioned nanotubes.

The effects of NaOH concentration, temperature and type of precursor (anatase, rutile, amorphous, titanates among others) on the nanotubes formation were investigated by several groups [252, 255, 256]. For example, Yuan and Su [255] established that hydrothermal treatment at 100 - 160 °C, nanotubes and nanofibers would be obtained using amorphous TiO₂ as precursor; nanoribbons were produced using 5 - 15 M NaOH solution at 180 – 250 °C and nanowires would be formed exclusively using a KOH solution. Tsai and Teng [252], Lan *et al.* [256] stated that using rutile phase as the precursor of TNTs, the increasing hydrothermal temperature and duration can result in single-crystalline nanorods with excellent thermal stability [47].

The sonication treatment plays an important role in TNTs formation; *i.e.* speeds up the dispersion of nanoparticles, breaking the intermolecular interactions between TiO₂ particles and concentrated NaOH solution in the hydrothermal process. When the samples are irradiated with ultrasound waves, the milky mixture becomes a smoother and more uniform starting material. Sonication may also be used to provide energy and sustain several chemical reactions. Viriyampikul *et al.* [257, 258] found that the BET areas and average nominal lengths of the titanate nanotubes obtained with sonication pre-treatment were, respectively, about 1.4 and 8 – 9 times higher than those of the titanate nanotubes obtained without the sonication pre-treatment. Also, Ma *et al.* [259] stated that using sonication pre-treatment longer TNTs with smaller diameters were produced. At 100 and 280 W, sheet and fibre-like structures were observed, respectively, whereas tube-like structures of 9 – 14 nm of diameter and 100 - 600 nm of length were obtained with 380 W. According to the same authors, the sonication treatment promoted intercalating Na⁺ ions into lattices of titania by breaking the Ti-O -Ti bonds [259]. The spherical shaped titania were transformed into nanorods during the treatment and the subsequent growth of the nanorods led to the formation of longer nanotubes.

Owing to the relative amount of Na and H atoms in the nanotube structure, the acid washing process has an important influence on the attributes of TiO₂ nanotubes. An optimal acid concentration (usually hydrochloric acid) is thought to be between 0.5 and 1.5 M. Below 0.5 M HCl, washing seems ineffective for removing sodium ions, whereas above 2 M, destruction of tubular structure is expected [260, 261].

Different investigations oriented to post-synthesis thermal treatments have been reported as these treatments have a strong influence on crystallinity, morphology, specific surface area and porosity of the nanotubes. According to the temperature of calcination, it has been demonstrated the formation of different crystal phases including brookite, anatase, rutile, $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{Na}_2\text{Ti}_6\text{O}_{13}$. Suzuki and Yoshikawa [262] and Armstrong *et al.* [263] found the existence of monoclinic TiO_2 (B) free of anatase, respectively, after the thermal treatment at 800 °C of TNTs and 400 – 600 °C of nanowires. Poudel *et al.* [264] indicated that the rutile phase begins to crystallize at 800 °C, well below the transformation temperature of 925 °C for bulk anatase TiO_2 nanopowder but well above the transformation temperature of 580 °C reported by Varghese *et al.* [265] for TNTs prepared by anodization. Also, a change from nanotubes to nanowire morphology was observed at 650 °C of annealing temperature. It is also for this range of calcination temperature that was observed the total transformation of the tubular structure in TiO_2 nanoparticles, although some authors reported a similar phenomenon at temperatures of 300 °C [266]. This deterioration of the morphology was attributed to removal of hydroxyl groups with the inter-sheets temperature.

Despite the general beneficial effects of TiO_2 nanotubes thermal treatment on the photocatalytic efficiencies, it is also reported that such treatment may impair physical aspects as BET surface area and pore volume. In this sense, other post-synthesis treatments have been explored to increase the TiO_2 nanotubes activity without the undesirable effects of pore blockage, elimination of surface OH groups and of unstable tube morphology. Bavykin *et al.* [246] reported the formation of a stable rutile phase TiO_2 nanotubes after a series of acid-immersed treatment periods. They ascribed this phenomenon to the low rate phase change. Nian and Teng [267] performed a similar study finding that only anatase phase appears at pH 2.2 while anatase along with brookite can be observed at pH 8.2; at pH 5.6 rod morphology was obtained. Yu *et al.* [268] revealed the formation of fibre-like structures with anatase phase after a similar post-hydrothermal treatment.

1.7.3. Enhancing titania nanotube photocatalysts

Despite the excellent morphologic properties of TNT, they share the same limitations of TiO_2 nanoparticles. Several approaches similar to those found for TiO_2 nanoparticles have been attempted to limit the recombination of the photogenerated electron-hole pairs and to broaden the photocatalytic activity from the ultra-violet region to the visible region. Metal and non-metal ion doping, coupling with other semiconductors are among other approaches used for enhancing TNTs attributes. Kukovecz's group [269, 270] and Hsu *et al.* [271] reported the synthesis of CdS/TNTs by modifying the precursor as a mixing solution of $\text{Na}_2\text{S}/\text{NaOH}$. They stated that the uniform particle size and extensive tube coverage by CdS nanoparticles attributed to the

homogeneous solution phase of the Cd–EDTA complex [270].

Colmenares *et al.* [272], in previous studies, used a series of metal and non-metal dopants, including chromium (Cr), iron (Fe), manganese (Mn), nickel (Ni), platinum (Pt) and vanadium (V), to dope TNTs for photocatalysis applications. The results showed that the new materials have higher activity and efficiency in the photooxidation of pollutants under visible light, but only up to certain level of doping. Beyond the optimum doping level, the photocatalytic activity of TNTs decreased [272].

Kim *et al.* [273] produced open-ended Ni-doped titanate nanotubes by hydrothermal treatment with several hundred nanometres of length and 5 – 6 nm of inner diameter and 10–11 nm of outer diameter. Hsieh *et al.* [274] reported the photocatalytic degradation of basic violet 10 (BV10) using cobalt-doped titanate nanotubes. They also pointed out that the band gap of Co-TNTs (2.14 eV) is much lower than that of the commercial Degussa P25 photocatalyst (3.20 eV). Dong *et al.* [275] synthesized highly ordered N-doped TNTs by annealing anodized TNTs with ammonia at 500 °C. The nanotubes diameter ranged between 60 - 80 nm and the wall thickness was around 20 nm. Detailed analysis of the nanotubes structure revealed that the phase transformation temperature from anatase to rutile decreases after nitrogen doping.

1.7.4. Applications

Some recent research works where TNTs and their derived materials were used in photocatalytic applications are listed in Table 1.3.

Although the development of TNTs have been mostly directed towards photocatalytic applications, several other applications can be found in literature surveys. Supported TNTs for water-shift gas (WGS) reactions and CO₂ hydrogenation, ion-exchange/adsorption, DSSCs, among others, have been the focus of several researchers.

The first successful photoactivation of TNTs was accomplished by Hodos *et al.* [269] through supporting CdS particles in these TNTs. Idakieva *et al.* [287] used gold particles supported on TNTs and performed the water–gas shift (WGS) reaction. This reaction was four times more efficient over Au/TNTs than over Au/Al₂O₃. Pt/Au nanosized particles supported on TNTs were also used in a study conducted by Chien *et al.* [288] dealing with CO₂ hydrogenation and CO oxidation. TNTs impregnated with copper were employed in a study where NO conversion was evaluated [289]. Wang *et al.* [290] disclosed that after dispersing a monolayer of benzoic acid molecules onto the TNTs surface, *i.e.* acting as a carrier agent, these molecules can react with the hydroxyl groups of TNTs forming carboxylic species.

Table 1.3. Photocatalytic applications of TNTs and their derived materials.

<i>Authors</i>	<i>Photocatalyst</i>	<i>Model pollutant (physical state)</i>	<i>Photocatalytic performance (Type of radiation)</i>
Zhang <i>et al.</i> [230]	TNTs	Propylene (gaseous)	TNTs < P25 TiO ₂ (UVA)
Nakahira <i>et al.</i> [248]	TNTs	Formaldehyde (aqueous)	TNTs > P25 TiO ₂ (UV)
Štengl <i>et al.</i> [276]	TNTs	4-Chlorophenol (aqueous)	TNTs < P25 TiO ₂ (UVA)
Jing <i>et al.</i> [277]	TNTs	<i>Escherichia Coli</i> (aqueous)	TNTs < TiO ₂ (UV)
Xu <i>et al.</i> [278]	Zn-TNTs	Methyl orange (aqueous)	Zn-TNTs > TiO ₂ (UV)
Hsieh <i>et al.</i> [274]	Co-TNTs	Basic violet 10 (aqueous)	Co-TNTs > P25 TiO ₂ (Visible)
Zhao <i>et al.</i> [279]	Au or Pt-TNTs	Methyl orange (aqueous)	Au (or Pt)-TNTs > P25 TiO ₂ (UVA)
Song <i>et al.</i> [280]	I- TNTs	Phenol (aqueous)	I-TNTs > I-TiO ₂ , TNTs, P25 TiO ₂ (Solar)
Asapu <i>et al.</i> [281]	P-TNTs	Rhodamine B (aqueous)	P-TNTs > TNTs and TiO ₂ P25 (UV)
Zhang <i>et al.</i> [282]	S-TNTs	Glyphosate (aqueous)	S-TNTs > TNTs (UV)
Geng <i>et al.</i> [283]	N-TNTs	Methylene blue (aqueous)	N-TNTs > TNTs (Solar)
Shen <i>et al.</i> [284]	N-TNTs	Methylene blue Sulfosalicylic acid (aqueous)	N-TNTs > P25 TiO ₂ (Visible)
Xu <i>et al.</i> [285]	N-TNTs	Phenol Methyl orange (aqueous)	N-TNTs > P25 TiO ₂ (Visible).
Yamin <i>et al.</i> [286]	WO ₃ -TNTs	Butanone (gaseous)	WO ₃ -TNTs > TNT (UVA) WO ₃ -TNTs > TNT (Solar)

Sun and Li [291] were the first authors reporting the influence of the intercalation of transition metals in metal-substituted TNTs for ion-exchange. This phenomenon was ascribed to the electrostatic interactions between the negatively charged host lattice of the nanotube and the positively charged cationic ions. Also, Umek *et al.* [292] indicated that Na atoms along with the hydrolysed surface of nanoribbons can transform adsorbed NO₂ into NO₃ and NO.

The anatase phase TNTs can also be applied in lithium-ion batteries, as reported by Zhang's group [293, 294]. During their investigations on TNTs electrochemical properties, these authors found that such structure provides an excellent cycling stability for lithium intercalation. In another study, Yu and Zhang [295] determined the electrochemical capacitance and voltammetric current of vanadium oxide/titanate composite nanorods, revealing better results with the composites than with pure V₂O₅. Furthermore, in a study conducted by Hu *et al.* [296], it was demonstrated that carbonized TNTs could significantly improve the performance of Pd-based electrocatalysts for ethanol oxidation in alkaline media. They have suggested that the open

mesoporous lattices of TNTs can make the Pd/TiO₂C electrocatalyst structure loose and porous increasing the surface active sites and, consequently, the activity for ethanol oxidation.

Another promising application was reported by Kim *et al.* [297], where TNTs films were fabricated on F-SnO₂ coated glass (FTO) via electrophoretic deposition. The photocurrent densities of the DSSCs gradually increased with the annealing temperature (450 – 500 °C). Above 500 °C the photocurrent densities are lower due to the thermal limitation of the FTO substrate, as well as due to the decrease of the TNTs surface area.

In the field of biocompatibility studies, Kubota *et al.* [298] applied TNTs to bone repair in filling defective areas of bones. They observed a newly formed bone of Ca-TNTs after a week of being implanted in the femur of a Wistar rat. The study also revealed that Ca-TNTs induced a fast acquisition and development of osteoblast and bone tissues and a better bone regeneration ability in comparison with other clinically-used biomaterials, like hydroxyapatite and β -tricalcium phosphate.

As regards smart windows, displays, and optical memories, Miao *et al.* [299] used modified Ag/AgCl-TNTs as photochromism materials exhibiting multicolour photochromism corresponding to that of incident light.

1.8. Substrates for immobilization of photocatalyst powders

Photocatalyst suspended powders are often used in aqueous media photocatalysis owing to an efficient contact between the catalyst and the organic pollutant. Immobilization of photocatalysts on an adequate substrate is mandatory in air treatment due to the problems associated with catalyst fluidization [300] and separation/recovery [301-303]. However, increased difficulty in structured catalyst preparation and decreased photocatalytic efficiency, mainly due to a less exposed area per catalyst weight unit, are typical resulting disadvantages [304]. Various substrates already used as photocatalyst supports for air and water treatment are listed in Table 1.4, together with the respective configurations.

Table 1.4. Substrates and configurations used as photocatalyst supports.

Substrate material	Configuration	Reference
Glass	Deposited on reactor wall/lamp ^{*#}	[305-307]
	Raschig rings/Beads [#]	[50, 308-310]
	Fibre mesh ^{*#}	[308, 311, 312]
	Plate [*]	[313, 314]
Quartz	Plate [#]	[315, 316]
	Sand [#]	[317, 318]
	Optical fibre ^{*#}	[319, 320]
Silica	Monolith [*]	[321]
	Gel [#]	[322, 323]
	Plate [#]	[324]
Silicon	Plate [#]	[324, 325]
	Wafer [#]	[326]
Metal	Stainless steel plate [#]	[315, 327]
	Anodized iron plate [#]	[328]
	Foam [#]	[329]
	Optical fibre [*]	[330]
Polymer	Poly(ethylene terephthalate) (PET), acrylic resin (AC), polycarbonate (PC) wafers [#]	[325]
	Tedlar [®] , parylene and PE (polyethylene) stripes [#]	[331]
	Cellulose microspheres [#]	[332]
	PS (polystyrene) micro-capsules [#]	[333]
	Polyurethane foam ^{*#}	[334, 335]
	Monoliths [*]	[336, 337]
Paper	Sheets ^{*#}	[51, 64]
Cotton	Fabric [#]	[59, 338]
Ceramic	Monoliths [*]	[339-341]
	Foam [#]	[342]
	Membranes [#]	[343, 344]
	Zeolites [#]	[168, 345]
Activated carbon	Powder [#]	[346]
	Fibres [#]	[347, 348]

* for air treatment applications

for water treatment applications

Although several investigations have been conducted over the recent years, the pursuit for an optimum substrate to support the photocatalyst has not met yet an end. Choosing the substrate is not a trivial task in photocatalysis and the material structure, dimension and optical properties are important features in order to achieve high photocatalytic activity. Based on Pozzo *et al.* [349] concepts, the ideal substrate to support a given photocatalyst should have the following properties:

- i. promote good photocatalyst adherence;
- ii. chemically inert, photo, chemical and mechanical-resistant;
- iii. transparent to UV radiation;

- iv. low pressure drop, promoting a turbulent regime avoiding the formation of dead volumes and the limitations to mass transfer;
- v. high surface area;
- vi. light weight and easy handling;
- vii. low cost.

Considering the above-mentioned features, quartz/glass and polymers have stood out as supporting materials for photocatalytic applications. Affixing the powders to the reactor internal walls [306] or to flat plates [313] are interesting procedures at lab-scale, but low mass transfer limits the flow rates. Raschig rings [50, 309], small glass tube pieces, and massive glass beads are the most common materials used for supporting the photocatalysts. Possessing high area/volume ratio and random distribution, Raschig rings and glass beads ensure a turbulent flow regime and subsequently a good contact between the gas stream and the photocatalyst. However, high pressure drop and dead volumes are the main disadvantages that are faced by this type of supports. On the other hand, monolith-like form polymers (Figure 1.10) cause low pressure drop, do not promote the occurrence of dead volumes and are UV-transparent contrarily to the ceramic or metal ones which are opaque to radiation [340, 341]. Moreover, this type of material is cheap, light-weighted and easy to handle, attracting a great interest for photocatalytic applications. Thin-walled honeycomb or monolithic structures of polyethylene terephthalate (PET) and cellulose acetate (CA), which are commercially available, are some alternatives. High thermal sensitivity, low adherence and low resistance to photooxidation are the main disadvantages of these materials.

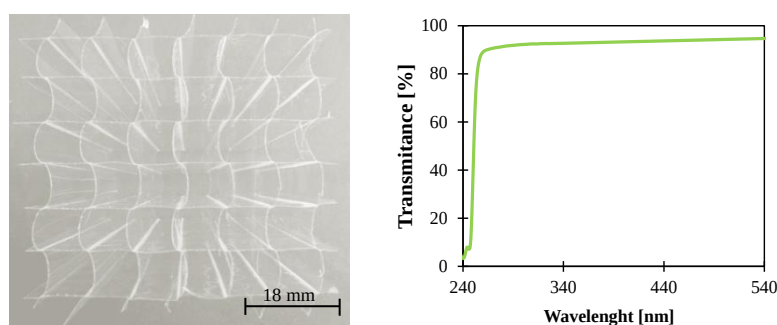


Figure 1.10. Cellulose acetate polymer: (a) commercially available monolith-like structure – TIMAX CA50-9/S, Wacotech GmbH & Co. K.G.; (b) transmittance in the UV-Vis range.

1.8.1. Routes for photocatalyst immobilization

Two main routes have been explored to immobilize the photocatalyst on any supporting substrate [308, 349]: i) manipulating a previously made photocatalyst powder in a suitable

dispersing agent [307, 308, 330] or *ii*) in situ synthesis of the photocatalyst during the deposition process. The former is the simplest way to obtain a support coating and the latter is the result of a combined series of physical and chemical transformations of a precursor, such as a titanium salt (usually an alkoxide), in an adequate solvent and/or controlling acid-base conditions. The main techniques are:

- i*) *Chemical vapour deposition (CVD)* [350, 351] – the substrate is exposed to volatile precursors which react at the substrate surface producing a thin film of the photocatalyst. This process can be performed under atmospheric pressure (APCVD), low pressure (LPCVD) or ultrahigh vacuum (UHCVD);
- ii*) *Physical vapour deposition (PVD)* [352-355] – a vaporized form of the photocatalyst is condensated at the surface of the substrate under high-temperature vacuum or plasma sputter bombardment; As the sputtered material is not in its thermodynamic equilibrium state, tend to affix on the substrate material;
- iii*) *Spray pyrolysis deposition* [356, 357] – a thin photocatalytic film is deposited by spraying a solution on a heated surface. The mechanism behind this technique is similar to that of CVD;
- iv*) Liquid-phase sol-gel, hydrothermal, solvothermal, etc., methods.

Other techniques based on vapour-phase deposition have also been used, such as ion implantation [358], molecular beam epitaxy [359] and dynamic ion beam mixing [360]. However, despite of providing an efficient control in the film growth (resulting in high purity materials), the very high energy consumption of such techniques is considered a great disadvantage from the economical point of view. Therefore, simple routes of synthesis such as sol-gel and hydrothermal/solvothermal methods solution routes are the most commonly employed techniques not only for the materials synthesis but also for affixing the catalyst onto the substrate surface or matrix. In this sense, different methods can be carried out to accomplish the deposition of the catalyst onto the surface of a substrate such as:

- i*) *Dip-coating* - the substrate is immersed and emerged into a liquid solution containing the coating precursor at a constant rate;
- ii*) *Spin-coating* – a small amount of the aqueous-phase coating material is added on the centre of the substrate while the substrate is rotated at high speed in order to spread the coating material by centrifugal force;
- iii*) *Spray* – the coating material is sprayed onto the substrate surface;
- iv*) *Electrophoresis* – developed for ceramic coatings, this technique can be used if the substrate is conductive: a potential is applied between a counter-electrode and the

substrate (both with the same size, shape and inside the coating material) forming a thin film at the substrate surface. In this case, the substrate acts as a cathode.

1.9. Photocatalytic reactors

Over the years, different reactor geometries and configurations have been used in photocatalytic applications. A categorization based on the *modus operandi* (batch, with or without recirculation, and one-pass continuous flow) or based on their geometry (the most representative are the flat plate, tubular and annular) will help distinguishing the reactors employed for air treatment [361, 362]. They can also be categorized based on the radiation source or by the way the photocatalyst is introduced into the reactor. Choosing a reactor predicates a hard task since entails several considerations that have to be taken into account in order to enhance the photocatalytic efficiency, and at the same time, to obtain comparable and repeatable measurements.

Batch reactors are an interesting choice for lab-scale applications when seeking repeatable results in controlled conditions, of relevance to study the fundamentals of the process. Most of the batch reactors operate with recirculation of gas flow providing, in this way, an uniform concentration of reactants and products and, thus, enabling kinetic studies and comparison of newly produced photocatalysts [58, 363]. Alternatively, one-pass continuous flow reactors are suitable for applications where a continuous source of pollutants is available, specially indicated for industrial facilities where large amounts of gases have to be handled. Albeit the application on industrial context, continuous flow reactors can also be employed at lab-scale where gaseous inlet and outlet streams are constantly monitored by techniques such as CG-MS, GC-FID, GC-TCD or FT-IR. [364, 365].

1.9.1. Flat plate reactors (FPRs)

Flat plate reactors are suitable for lab-scale applications and, in particular, for kinetic studies [313, 366]. Consisting of a thin layer of photocatalyst-coated on a flat substrate (usually made of glass or metal), the polluted gas stream flows parallel and on the top of the photocatalyst (Figure 1.11).

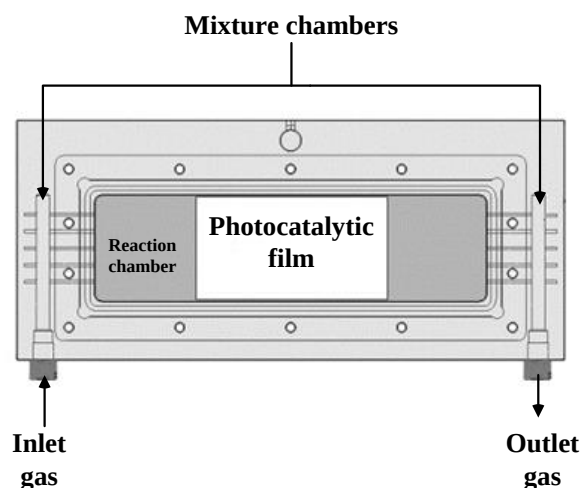


Figure 1.11. Schematic representation of a FPR (adapted from Águia *et al.* [367])

The light source can be either placed within the embodiment of the reactor, or outside the reactor where the photocatalyst is irradiated through a glass window. However, a high ratio between the photocatalyst surface and the flow rate is mandatory in order to avoid mass transfer limitations resulting from a faulty contact between the photocatalyst and the pollutants. A possible and interesting approach to overcome this limitation is to employ a multi-flat plate reactor as described by Leung *et al.* [314] – Figure 1.12.

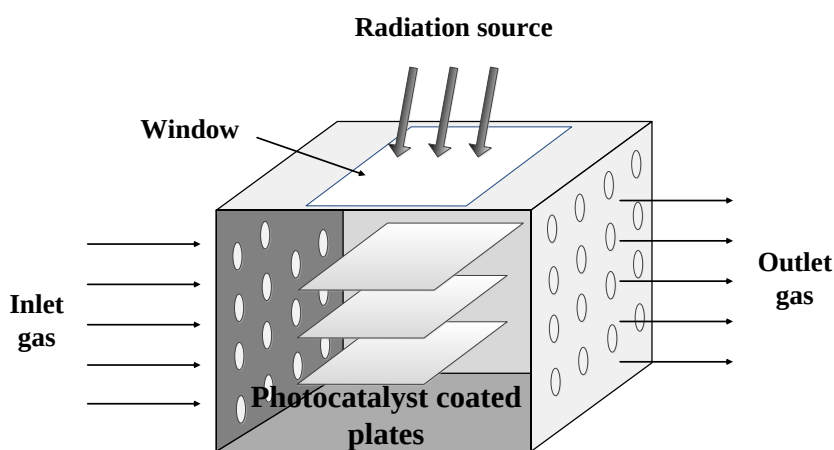


Figure 1.12. Schematic representation of a multi-parallel FPR (adapted from Leung *et al.* [314]).

1.9.2. Tubular reactors

Due to the simplicity of assembling and handling, tubular reactors are probably the most common in photocatalytic processes. Consisting of one – single tubular reactor – or more than one glass tube – multitubular reactor – the gas stream flows along the axis, the photocatalyst can

be employed under several forms such as thin coated film on its inner wall, fluidized particles, or coated on supporting substrate. The light sources are located outside the tube, in a parallel configuration relative to its axis.

Powder layered tubular reactor (PLR)

One of the first types of photocatalytic reactors employed for air treatment was the powder layer tubular reactor (PLR), in the seventies and beginning of the eighties, by Formenti *et al.* [368] for partial oxidation of isobutene. Albeit its simplicity and easy catalyst replacement, avoiding mass transfer limitations, Lewandowski and Ollis [369] pointed out that the PLR was not suitable for full scale commercial applications. Due to high flow rates usually employed in industrial/commercial applications the catalyst particles may be displaced into the gas stream.

Fluidized bed reactor (FBR)

The fluidized bed tubular reactor (FBR) was also one of the first reactors to be used in air treatment [300], besides the liquid-solid slurry reactors for water treatment (Figure 1.13). They are characterized by an upward stream which will lift and suspend the photocatalyst particles, enhancing the contact between the surface of the photocatalyst and the pollutant.

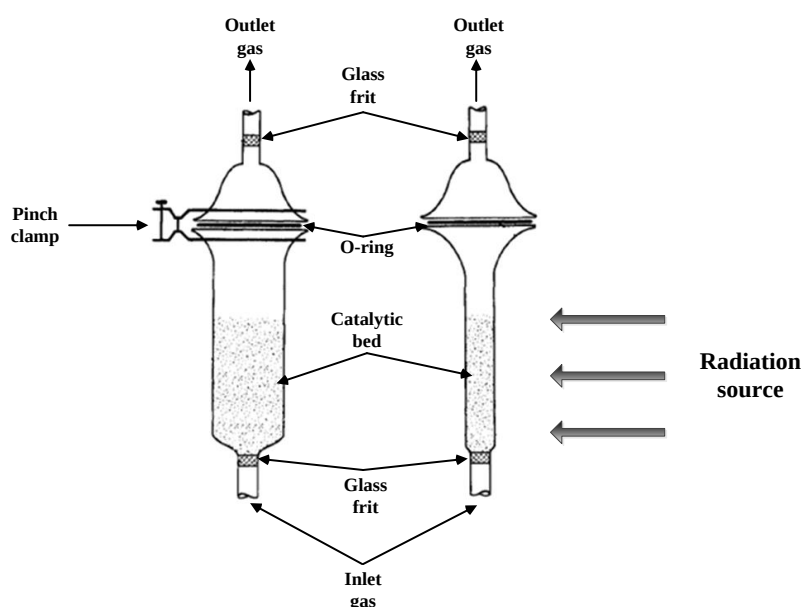


Figure 1.13. Schematic representation of a FBR (adapted from Dibble and Raupp [300]).

Packed bed reactor (PBR)

One of most used reactors in industrial context is the packed bed tubular reactor (PBR) [361, 362]. Consisting of tubes filled with photocatalyst pellets with reactants entering at one end and products exiting at the other, the gas stream flows in the space-between the pellets and reacts on the surface of the pellets (Figure 1.14). The main disadvantage of this family of reactors stems from the need of introducing the radiation source into the packed bed, since an external light source will only illuminate the outer part of the flow cross section whereas the inner pellets will remain in the dark [370-372].

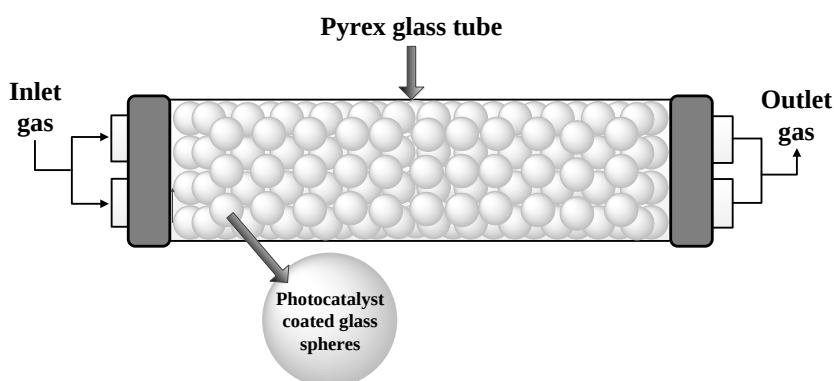


Figure 1.14. Schematic representation of a PBR with glass spheres coated with the photocatalyst (adapted from Tsoukleris *et al.* [372]).

Plasma-driven catalytic packed bed reactor (PDC)

A very promising reactor configuration for airborne VOCs removal is the combination of a packed bed tubular reactor with non-thermal plasma (NTP) features [373-377]. Such combination is divided into single-stage and two-stages processes. In the latter system, NTP aims to partially convert the pollutants or producing ozone will facilitate catalytic reactions over suitable heterogeneous catalysts located downstream of the plasma reactor [377, 378]. This process is known as post-plasma catalysis (PPC). In single-stage process, the catalysts are exposed to the active plasma which are activated by high energy particles (electron, excited molecules) and photons produced by the NTP [375, 377, 378]. Typical working temperature range of this process is below 473 K, in which the NTP alone reactions would not take place. In this sense, single-stage plasma-catalyst hybrid system is also referred to as a plasma-driven catalyst (PDC) process [375].

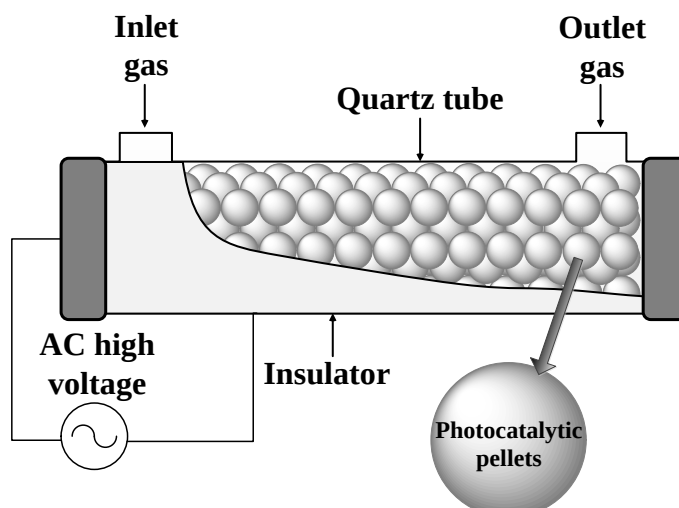


Figure 1.15. Schematic diagram of a PDC reactor packed with photocatalytic pellets (adapted from Kim *et al.* [377]).

Figure 1.15 schematizes a possible configuration of a PDC reactor. PDC synergistic effects are claimed to be beneficial as they improve the oxidation kinetic rates and the mass balance of mineralized carbon and reduce the ratio between the production rate of carbon monoxide and that of carbon dioxide [379]. Several configurations have been widely used, where the photocatalyst is either affixed into a supporting material or into the reactors walls [339, 371, 380-383].

Monolithic tubular reactor

The monolithic configuration is commonly used in automotive emission control systems [381]. In these reactors the photocatalyst is supported in a porous solid monolithic structure (usually made of metal or oxide) pierced by parallel channels enhancing the distribution of the polluted air flow (Figure 1.16). Alternatively, the photocatalyst can be incorporated as part of the matrix of the structure. The channels are usually wide enough to reduce the pressure drop which is an advantage in comparison with powdered reactors. The large external surface allows a higher exposed area to radiation thus making them a good candidate for commercial use. However, these type of reactors would be more expensive than the simple powdered reactors [339, 381, 382, 384].

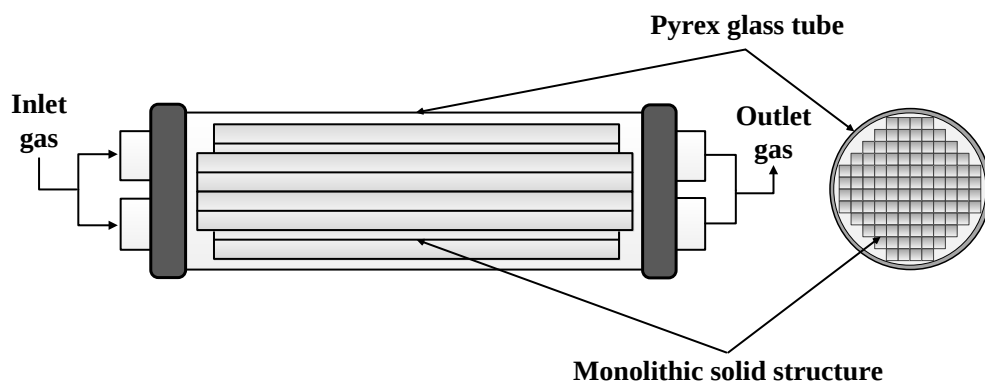


Figure 1.16. Schematic representation of a tubular reactor filled with a monolithic solid structure.

Permeable layer tubular reactor

Supporting the active material in a permeable layer confers another interesting configuration – Permeable layer tubular reactor. In this case, a thin porous metal or ceramic substrate is coated with photocatalyst. The flow can be either perpendicular to the surface of the substrate or combining both parallel and perpendicular flows [383, 385, 386].

Optical fibre tubular reactor (OFR)

Another conceptual photocatalytic reactor is the optical fibre tubular reactor – OFR – and it was introduced by Marinangeli and Ollis [387] and further developed by other authors [319, 320, 388, 389]. The photocatalyst is coated onto the optical fibres, ensuring promoting a large irradiated surface (Figure 1.17). Although, this configuration suggests high quantum yield owed to an apparent superior radial light distribution, the short light propagating length, significantly limits the efficient use of fibers [320].

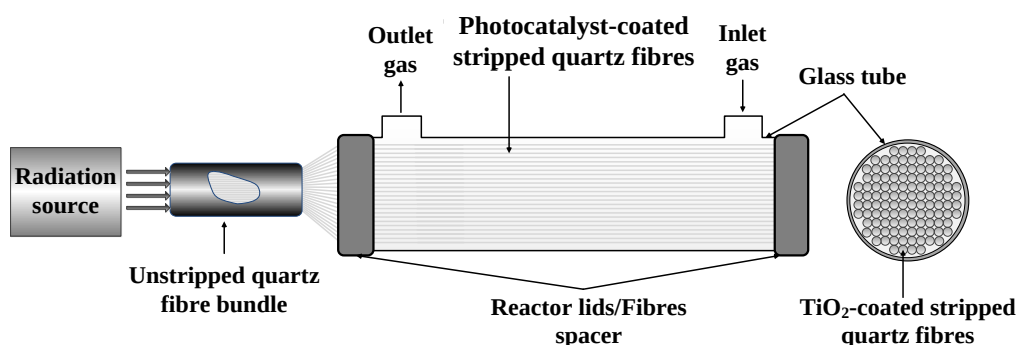


Figure 1.17. Schematic representation of an OFR filled with photocatalyst-coated fibres.

Coated wall tubular reactor (CWR)

An easy way of supporting the photocatalyst can be found in a coated wall tubular reactor (CWR). Here, the inner wall of the reactor is coated with the photocatalyst, where the polluted gas stream flows as represented in Figure 1.18. The thickness of the film should ensure that almost all non-reflected photons are absorbed. Otherwise may impair the photocatalytic efficiency as the number of photogenerated charge carriers is reduced [371, 380, 390].

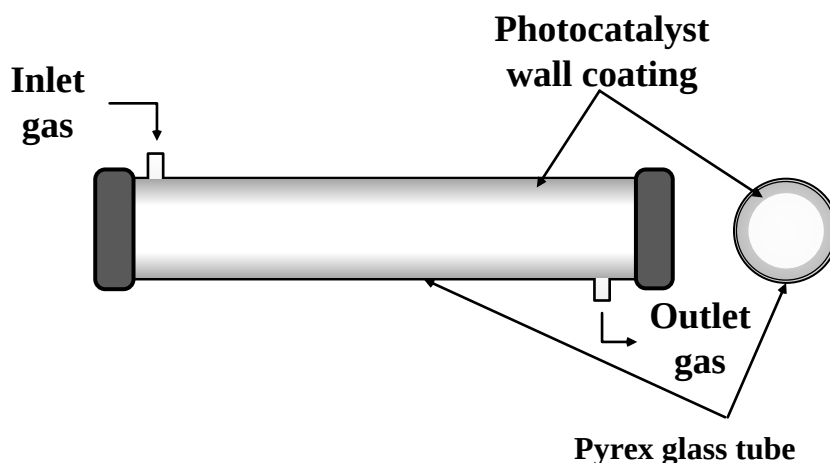


Figure 1.18. Schematic representation of a CWR.

1.9.3. Annular reactors

Annular reactors comprise a tube lamp surrounded by two concentric tubes with a photocatalyst located in-between the tubes, as show in Figure 1.19. It is also between the tubes that the polluted gas stream flows. Although the light source is generally positioned inside the inner tube, Jacoby *et al.* [391] used the tube light lamp as itself as the inner surface of the annular reactor. Likewise the tubular reactors, the photocatalytic material can be employed under different reactor configurations: fluidized bed [392, 393], packed bed [394, 395], plasma-driven [396, 397], affixed to a supporting material [336, 397] or coated on the inner wall or the outer wall of the external tube or internal tube, respectively [286, 306]. An internal radiation source ensures that the photocatalytic material is irradiated in deeper layers which are usually in the dark in a tubular configuration. Moreover, if the reactor outer tube is transparent to radiation, it is also possible to externally irradiate the photocatalytic material. In this way, and using an external reflector, the whole photocatalytic material can be irradiated, greatly improving the quantum yield [392].

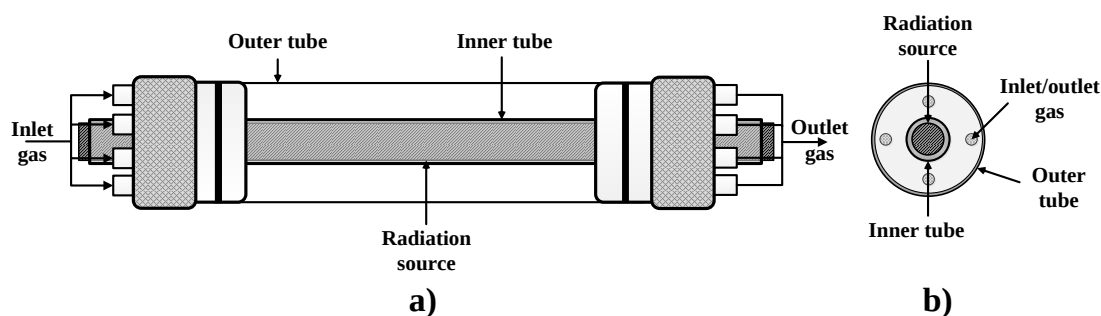


Figure 1.19. Schematic representation of an annular reactor: a) side and b) cross section point of view.

Based on an annular reactor, Imoberdorf *et al.* [398] studied the performance of a multi-annular reactor towards perchloroethylene elimination. According to these authors, such reactor configuration improves the radiative energy absorption, because the radiation transmitted through the two photocatalyst films of the inner annulus can be absorbed by the photocatalyst films of the middle and outer annuli. Furthermore, a multi-annular reactor with its annuli interconnected in a way that the gas stream is forced to revert its direction when passing from one annulus to the next, in order to achieve high photocatalytic activities. Figure 1.20 shows a multi-annular reactor based on that used by Imoberdorf *et al.* [398].

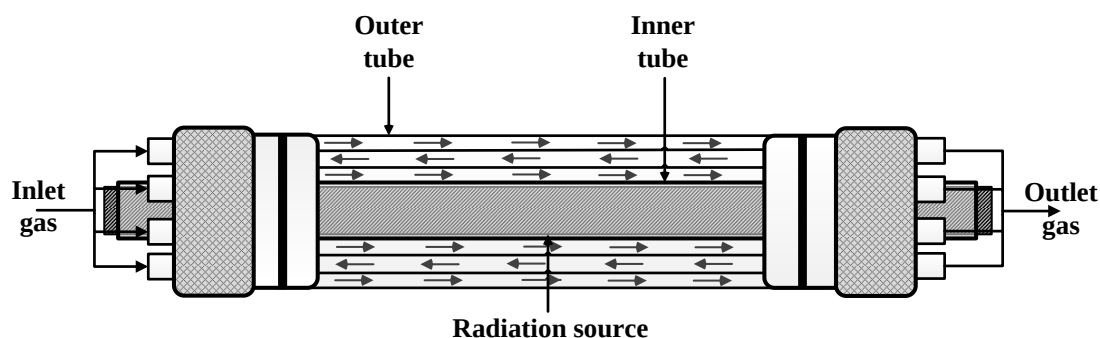


Figure 1.20. Schematic representation of a multi-annular reactor (adapted from Imoberdorf *et al.* [398]).

1.9.4. Radiation reflective collectors

In what concerns air or water treatment through solar photocatalytic processes, an efficient use of the sunlight is a great advantage. Regardless the employed reactor or its geometry or configuration, using a radiation collector with reflective properties enhances the photonic yield. Although the different configurations already discussed previously, the most suitable configurations for air treatment solar photocatalysis are the tubular and annular ones. Considering a 24 hours air pollutant emission process, the annular configuration will provide a non-stop photoabatement as through this configuration will be possible to use the sunlight during the day and a tubular lamp (UVA, visible or solar light emitting radiation) during the night.

Collectors can be categorized based on the temperatures reached by the receptor of the radiation and three systems can be defined: non- or low concentrating collectors (temperatures up to 150 °C), medium concentrating collectors (from 150 °C up to 400 °C) and high concentrating collectors (above 400 °C). The reached temperature results from the relation between the wingspan area and the surface area of the collector.

Parabolic trough concentrators, PTCs, are a type of concentrating collectors and are rather suitable to collect radiation to the receiver (focus); however they have to follow the sun and only make use of the direct radiation. Non- or low concentrating collectors are based on PTCs, yet do not concentrate the radiation, *i.e.* the focus is diffuse allowing, therefore, the use of both diffuse and direct radiation without the need of following the sun. Subsequently, this system becomes less expensive, with lower maintenance cost and longer service life. Moreover, most of photocatalysts require UV radiation which is mainly present in diffuse radiation and therefore cannot be collected by concentrating collectors as PTCs. From the above-stated, non-concentrating collectors seems to be much more suitable for solar photocatalytic applications [399, 400]. Figure 1.21 shows the different geometries of non-concentrating collectors:

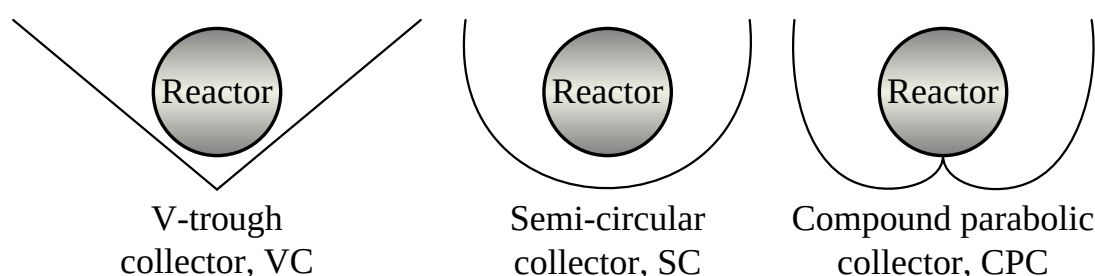


Figure 1.21. Schematic representation of three non-concentrating reflective collectors' geometries.

Among these collectors' configurations, the compound parabolic collectors (CPCs) type features some advantages. Owing to its reflective surface shape, almost all the incident radiation reaches the reactor [401]. Although CPCs have a more complex manufacturing details and, therefore, they are more expensive than V-trough (VC) and semi-circular (SC) collectors' configurations, the large scale production of CPCs would reduce the costs of their fabrication [402, 403]. According to Bandala *et al.* [404, 405], the photocatalytic results obtained towards water treatment with CPCs are generally better than those with SCs and VCs.

1.10. Aim of the work and thesis outline

Although semiconductor-based photocatalysis has a huge potential to air and water remediation, several limitations can jeopardize its full and world wide application. The low

photonic yield, low efficiency under visible light ($380 < \lambda < 740$ nm) and the requirement of a substrate to support the photoactive catalyst are the main challenges that this work will try to tackle and overcome.

The main objective of this thesis is to evaluate the efficiency of solar gas-phase heterogeneous photocatalysis towards the elimination of pollutants such as VOCs present mainly in indoor air atmospheres. For this purpose, a lab- and a pilot-scale, single-pass, continuous-flow annular photocatalytic reactors are proposed. To accomplish the main objective, several partial objectives must be addressed:

- i. Synthesis and characterization of TiO_2 nanotubes as well as nitrogen modified TiO_2 nanotubes and nanoparticles;
- ii. Preparation of TiO_2 -based materials and their immobilization as thin films on different supports using the *dip-coating* technique;
- iii. Evaluation of photocatalytic activity of the prepared photocatalysts and its dependence on different operational conditions (flow rate – Q_{feed} ; pollutant concentration – $C_{\text{voc, feed}}$; relative humidity – RH , irradiance – I ; presence/absence oxygen concentration) using a lab-scale single-pass continuous-flow annular photoreactor;
- iv. Description of the photocatalytic oxidation mechanisms;
- v. Evaluation of the photocatalytic activity of selected photocatalysts in a pilot-scale photoreactor for continuous removal of volatile organic compounds.

Considering the extent of the objectives, the present thesis was organized in five parts. Part I includes this chapter which is an introductory section, wherein the problematic of volatile organic compounds present in both indoor and outdoor air, as well as current and potential decontamination procedures, are discussed. The main concepts of gas-phase heterogeneous photocatalysis are presented and complemented with an extensive literature survey. Part II contains Chapter 2 and 3 where it is reported the photocatalytic conversion of perchloroethylene and *n*-decane over different commercially available TiO_2 . Chapter 4 and 5 deal with construction materials (paint) as TiO_2 supporting matrix for the removal of PCE and *n*-decane and are both included in Part III. Part IV reports the photocatalytic activity of titania nanoparticles (Chapter 6) and titania nanotubes (Chapter 7) both modified with nitrogen towards the elimination of pollutants whether present in water or in air. Finally Part V deals with the application of heterogeneous photocatalysis in a pilot-scale towards a continuous photo-oxidation of VOCs (Chapter 8) and suggestions of future work and conclusions (Chapter 9). A detailed description of each chapter is given in the following.

In Chapter 2 is reported the rate of PCE photocatalytic oxidation with UV-TiO₂ using a single-pass continuous flow annular reactor under UVC radiation. The effects of PCE concentration, feed flow rate, and water vapour content on the rate of PCO were investigated and several kinetic models were tested. Also, by-products formation was weighed; according to the isolated intermediates, a reaction mechanism was proposed for PCE gas-phase photocatalytic oxidation.

In Chapter 3 the influence of the feed flow rate, pollutant concentration, relative humidity, presence or absence of gas-phase molecular oxygen and incident irradiance on photocatalytic conversions of PCE and *n*-decane was evaluated. Within this chapter the continuous-flow annular photoreactor was assembled with monolithic structure made of cellulose acetate coated with different commercially available photoactive powders and exposed to simulated solar radiation. A comparison in terms of photocatalytic efficiency between the photoactive powders tested was also assessed.

In Chapter 4 the photooxidation of PCE was studied in the annular photoreactor under simulated solar radiation employing two different configurations of a monolithic structure of cellulose acetate coated with an active TiO₂-based paint. The influence of the structure configuration and different experimental conditions, namely feed flow rate, PCE concentration, relative humidity in the system, absence of oxygen and incident irradiance on the PCE conversion was evaluated. Also, based on the intermediates identified, a reaction mechanism was proposed for PCE gas-phase photooxidation.

Chapter 5 reports the *n*-decane photocatalytic oxidation carried out in the annular photoreactor under simulated solar irradiation and employing the cellulose acetate monoliths coated with a water-based exterior vinyl paint with photocatalytic properties as the catalytic bed. The influence of the feed flow rate, *n*-decane concentration, relative humidity, and incident irradiance on the *n*-decane degradation kinetics was assessed. Also, a phenomenological reaction rate model of the *n*-decane photocatalytic oxidation was proposed and assessed. Finally, reaction by-products were identified and, based on those compounds, a reaction mechanism was formulated.

Chapter 6 reports a study where nitrogen modified TiO₂ powders were modified with different urea amounts and calcined at different temperatures, in order to optimize the method for the synthesis of an active photocatalyst. Several characterizations techniques were performed on the prepared materials. The photocatalytic activity of these nitrogen (N) modified TiO₂ materials was evaluated in the gas-phase perchloroethylene PCO under simulated solar radiation. The photocatalytic activity of these N modified TiO₂ materials was also evaluated in the degradation

of diphenhydramine, an emerging water pollutant under visible light illumination ($\lambda = 430$ nm) and in the inactivation of *Escherichia coli* bacteria under UVA radiation.

In Chapter 7 high aspect ratio titanate nanotubes (TiNT) synthesized with an alkaline hydrothermal treatment and the modification of the TiNT with nitrogen are reported. The effect of calcination temperature and nitrogen content on the structure of the nanotubes was also assessed. The photocatalytic efficiency of the prepared materials was evaluated for degradation of methylethylketone (MEK) and hydrogen sulfide (H_2S) under UVA and solar light radiation. These gas-phase PCO reactions were performed in a single-pass continuous annular photoreactor.

Chapter 8 reports the design and construction of a low-cost pilot-scale continuous-flow annular photoreactor. The photochemical and photocatalytic oxidation of *n*-decane was evaluated as a function of the radiation source: sunlight or UVA illumination.

Chapter 9 is dedicated to the final remarks where the main conclusions are discussed and subsequent suggestions for future work are presented.

1.11. References

- [1] M.L. Bell, D.L. Davis, T. Fletcher, *Environ. Health Persp.* 112 (2004) 6-8.
- [2] C.H. Eccleston, *NEPA and Environmental Planning: Tools, Techniques, and Approaches for Practitioners*, CRC Press, Richland, Washington, USA, 2008.
- [3] S. Wang, H.M. Ang, M.O. Tade, *Environ. Int.* 33 (2007) 694-705.
- [4] M.S. Zuraimi, C.-A. Roulet, K.W. Tham, S.C. Sekhar, K.W. David Cheong, N.H. Wong, K.H. Lee, *Build. Environ.* 41 (2006) 316-329.
- [5] J. Zhang, K.R. Smith, *Br. Med. J.* 68 (2003) 209-225.
- [6] P.S. Burge, *Occup. Environ. Med.* 61 (2004) 185-190.
- [7] L.A. Wallace, *Annu. Rev. Energ. Env.* 26 (2001) 269-301.
- [8] WHO, Ambient (outdoor) air quality and health - <http://www.who.int/mediacentre/factsheets/fs313/en/> Last access 14th April 2014.
- [9] P. Wargocki, *Indoor Air* 9 (1999) 165-179.
- [10] J. Sundell, B. Anderson, K. Anderson, T. Lindvall, *Indoor Air* 3 (1993) 82-93.
- [11] J. Sundell, *Indoor Air* 14 (2004) 51-58.
- [12] P. Wolkoff, G.D. Nielsen, *Atmos. Environ.* 35 (2001) 4407-4417.
- [13] C. Yu, D. Crump, *Build. Environ.* 33 (1998) 357-374.
- [14] T. Salthammer, *Indoor Air* 7 (1997) 189-197.
- [15] H. Schleibinger, R. Keller, H. Rüdén, *The handbook of environmental chemistry - indoor air pollution by microorganisms and their metabolites* (2004) 149-177.
- [16] B. Guieysse, C. Hort, V. Platel, R. Munoz, M. Ondarts, S. Revah, *Biotechnol. Adv.* 26 (2008) 398-410.
- [17] R. Kostianinen, *Atmos. Environ.* 29 (1995) 693-702.
- [18] J.M. Daisey, A.T. Hodgson, W.J. Fisk, M.J. Mendell, J. Ten Brinke, *Atmos. Environ.* 28 (1994) 3557-3562.
- [19] K. Andersson, *Indoor Air* 7 (1997) 78-91.
- [20] T. Otake, J. Yoshinaga, Y. Yanagisawa, *Environ. Sci. Technol.* 35 (2001) 3099-3102.
- [21] D.C.G. Muir, P.H. Howard, *Environ. Sci. Technol.* 40 (2006) 7157-7166.
- [22] L.E. Ekberg, *Atmos. Environ.* 28 (1994) 3571-3575.
- [23] P. Wargocki, J. Sundell, W. Bischof, G. Brundrett, P.O. Fanger, F. Gyntelberg, S.O. Hanssen, P. Harrison, A. Pickering, O. Seppänen, P. Wouters, *Indoor Air* 12 (2002) 113-128.
- [24] B.C. Wolvertson, R. McDonald, E.A. Watkins, *Econ. Bot.* 38 (1984) 224-228.
- [25] R. Orwell, R. Wood, J. Tarran, F. Torpy, M. Burchett, *Water Air Soil Pollut.* 157 (2004) 193-207.
- [26] R.L. Orwell, R.A. Wood, M.D. Burchett, J. Tarran, F. Torpy, *Water Air Soil Pollut.* 177 (2006) 59-80.
- [27] R. Wood, M. Burchett, R. Alquezar, R. Orwell, J. Tarran, F. Torpy, *Water Air Soil Pollut.* 175 (2006) 163-180.
- [28] R. Muñoz, S. Villaverde, B. Guieysse, S. Revah, *Biotechnol. Adv.* 25 (2007) 410-422.
- [29] D.W. Park, S.W. Chun, J.Y. Jang, H.S. Kim, H.C. Woo, J.S. Chung, *Catal. Today* 44 (1998) 73-79.

- [30] J. Hermia, S. Vigneron, *Catal. Today* 17 (1993) 349-358.
- [31] W.H. Glaze, J.-W. Kang, D.H. Chapin, *Ozone-Sci. Eng.* 9 (1987) 335-352.
- [32] J. Zhao, X. Yang, *Build. Environ.* 38 (2003) 645-654.
- [33] W.J. Kowalski, *Immune building systems technology*, McGraw-Hill, Michigan University 2003.
- [34] W.A. Jacoby, D.M. Blake, J.A. Fennell, J.E. Boulter, L.M. Vargo, M.C. George, S.K. Dolberg, J. *Air Waste Manage. Assoc.* 46 (1996) 891-898.
- [35] M. Schiavello, *Electrochim. Acta* 38 (1993) 11-14.
- [36] M.A. Fox, M.T. Dulay, *Chem. Rev.* 93 (1993) 341-357.
- [37] A.L. Linsebigler, G. Lu, J.T. Yates, *Chem. Rev.* 95 (1995) 735-758.
- [38] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69-96.
- [39] A. Furube, T. Asahi, H. Masuhara, H. Yamashita, M. Anpo, *Chem. Phys. Lett.* 336 (2001) 424-430.
- [40] V. Augugliaro, S. Coluccia, V. Loddo, L. Marchese, G. Martra, L. Palmisano, M. Schiavello, *Appl. Catal. B: Environ.* 20 (1999) 15-27.
- [41] E. Pelizzetti, C. Minero, *Electrochim. Acta* 38 (1993) 47-55.
- [42] Y.V. Kolen'ko, K.A. Kovnir, A.I. Gavrilo, A.V. Garshev, P.E. Meskin, B.R. Churagulov, M. Bouchard, C. Colbeau-Justin, O.I. Lebedev, G. Van Tendeloo, M. Yoshimura, *J. Phys. Chem. B* 109 (2005) 20303-20309.
- [43] F. Benoit-Marquié, U. Wilkenhöner, V. Simon, A.M. Braun, E. Oliveros, M.-T. Maurette, J. *Photochem. Photobiol. A* 132 (2000) 225-232.
- [44] L. Cermenati, P. Pichat, C. Guillard, A. Albini, *J. Phys. Chem. B* 101 (1997) 2650-2658.
- [45] D.Y. Goswami, *J. Sol. Energy Eng.* 119 (1997) 101-107.
- [46] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, *J. Chem. Technol. Biotechnol.* 77 (2002) 102-116.
- [47] C. McCullagh, J. Robertson, D. Bahnemann, P. Robertson, *Res. Chem. Intermed.* 33 (2007) 359-375.
- [48] D. Bahnemann, *Sol. Energy* 77 (2004) 445-459.
- [49] J.-M. Herrmann, *Top. Catal.* 34 (2005) 49-65.
- [50] M. Hernandez-Alonso, I. Tejedor-Tejedor, J. Coronado, J. Soria, M. Anderson, *Thin Solid Films* 502 (2006) 125-131.
- [51] C. Guillard, J. Disdier, C. Monnet, J. Dussaud, S. Malato, J. Blanco, M.I. Maldonado, J.-M. Herrmann, *Appl. Catal. B: Environ.* 46 (2003) 319-332.
- [52] M.L. Satuf, R.J. Brandi, A.E. Cassano, O.M. Alfano, *Appl. Catal. B: Environ.* 82 (2008) 37-49.
- [53] M.C. Canela, R.M. Alberici, W.F. Jardim, *J. Photochem. Photobiol. A* 112 (1998) 73-80.
- [54] A. Ginestet, D. Pugnet, J. Rowley, K. Bull, H. Yeomans, *Indoor Air* 15 (2005) 326-334.
- [55] T. Matsunaga, R. Tomoda, T. Nakajima, H. Wake, *FEMS Microbiology Letters* 29 (1985) 211-214.
- [56] P. Maness, S. Smolinski, D.M. Blake, Z. Huang, E.J. Wolfrum, W.A. Jacoby, *Appl. Environ. Microbiol.* 65 (1999) 4094-4098.
- [57] D.Y. Goswami, D.M. Trivedi, S.S. Block, *Journal of Solar Energy Engineering, Transactions of the ASME* 119 (1997) 92-96.
- [58] D.V. Kozlov, A.V. Vorontsov, P.G. Smirniotis, E.N. Savinov, *Appl. Catal. B: Environ.* 42 (2003)

- 77-87.
- [59] M. Grandcolas, L. Sinault, F. Mosset, A. Louvet, N. Keller, V. Keller, *Appl. Catal. A: Gen.* 391 (2011) 455-467.
 - [60] J.-H. Kau, D.-S. Sun, H.-H. Huang, M.-S. Wong, H.-C. Lin, H.-H. Chang, *PLoS ONE* 4 (2009) e4167.
 - [61] C. Maneerat, Y. Hayata, *Int. J. Food Microbiol.* 107 (2006) 99-103.
 - [62] L. Cassar, *MRS Bull.* 29 (2004) 328-331.
 - [63] P.S. Marcos, J. Marto, T. Trindade, J.A. Labrincha, J. *Photochem. Photobiol. A* 197 (2008) 125-131.
 - [64] H. Matsubara, M. Takada, S. Koyama, K. Hashimoto, A. Fujishima, *Chem. Lett.* 24 (1995) 767-768.
 - [65] C.E. Bygott, J.E. Maltby, J.L. Stratton, R. McIntyre, Photocatalytic coatings for the construction industry International RILEM Symposium on Photocatalysis, Environment and Construction Materials, 8-9 October, Florence, Italy, 2007, pp. 251-258.
 - [66] T. Maggos, J.G. Bartzis, M. Liakou, C. Gobin, J. Hazard. Mater. 146 (2007) 668-673.
 - [67] J. Ângelo, L. Andrade, A. Mendes, Manuscript submitted for publication (2014).
 - [68] M. Anpo, *Pure Appl. Chem.* 72 (2000) 1265-1270.
 - [69] M.C. Canela, R.M. Alberici, R.C.R. Sofia, M.N. Eberlin, W.F. Jardim, *Environ. Sci. Technol.* 33 (1999) 2788-2792.
 - [70] J. Hall, J.J. Sangiovanni, H.H. Hollick, T.N. Obee, S.O. Hay, in: N.L. Nagda (Ed.), *Air Quality and Comfort in Airliner Cabins*, ASTM STP 1393, ASTM, West Conshohocken, USA, 2000, p. 294.
 - [71] Z. Huang, P.C. Maness, D.M. Blake, E.J. Wolfrum, S.L. Smolinski, W.A. Jacoby, J. *Photochem. Photobiol. A* 130 (2000) 163-170.
 - [72] I.N. Martyanov, K.J. Klabunde, *Environ. Sci. Technol.* 37 (2003) 3448-3453.
 - [73] B.M. Smith, *Chem. Soc. Rev.* 37 (2008) 470-478.
 - [74] M. Cho, Y. Choi, H. Park, K. Kim, G.J. Woo, J. Park, *J. Food Protect.* 70 (2007) 97-101.
 - [75] Y. Kim, Y. Choi, S. Kim, J. Park, M. Chung, K.B. Song, I. Hwang, K. Kwon, J. Park, *J. Food Protect.* 72 (2009) 1916-1922.
 - [76] C.O. Robichaud, A.E. Uyar, M.R. Darby, L.G. Zucker, M.R. Wiesner, *Environ. Sci. Technol.* 43 (2009) 4227-4233.
 - [77] K. Demeestere, J. Dewulf, B. De Witte, A. Beeldens, H. Van Langenhove, *Build. Environ.* 43 (2008) 406-414.
 - [78] A.M. Ramirez, K. Demeestere, N. De Belie, T. Mäntylä, E. Levänen, *Build. Environ.* 45 (2010) 832-838.
 - [79] Y. Murata, H. Tawara, H. Obata, K. Takeuchi, J. *Adv. Oxid. Technol.* 4 (1999) 227-230.
 - [80] K. Murugan, R. Subasri, T.N. Rao, A.S. Gandhi, B.S. Murty, *Prog. Org. Coat.* 76 (2013) 1756-1760.
 - [81] M.P. Seabra, R.R. Pires, J.A. Labrincha, *Chem. Eng. J.* 171 (2011) 692-702.
 - [82] C.S. Poon, E. Cheung, *Constr. Build. Mater.* 21 (2007) 1746-1753.
 - [83] C.S. Poon, E. Cheung, Performance of photo-catalytic paving blocks made from waste, *Proceedings of the ICE - Waste and Resource Management*, 2006, pp. 165-171.
 - [84] A. Beeldens, Air purification by pavement blocks: final results of the research at the BRRC, Transport Research Arena Europe, Ljubljana, 2008.

- [85] J.M. Langridge, R.J. Gustafsson, P.T. Griffiths, R.A. Cox, R.M. Lambert, R.L. Jones, *Atmos. Environ.* 43 (2009) 5128-5131.
- [86] D. Byun, Y. Jin, B. Kim, J. Kee Lee, D. Park, *J. Hazard. Mater.* 73 (2000) 199-206.
- [87] Y. Paz, Z. Luo, L. Rabenberg, A. Heller, *J. Mater. Res.* 10 (1995) 2842-2848.
- [88] H. Ichiura, T. Kitaoka, H. Tanaka, *Chemosphere* 50 (2003) 79-83.
- [89] H. Ichiura, T. Kitaoka, H. Tanaka, *J. Mater. Sci.* 37 (2002) 2937-2941.
- [90] J. Zhang, W. Liu, P. Wang, K. Qian, *J. Environ. Chem. Eng.* 1 (2013) 175-182.
- [91] H. Taoda, M. Fukaya, E. Watanabe, K. Tanaka, *Mater. Sci. Forum* 510-511 (2006) 22-25.
- [92] T. Salthammer, F. Fuhrmann, *Environ. Sci. Technol.* 41 (2007) 6573-6578.
- [93] P. Pichat, J.M. Herrmann, J. Disdier, M.N. Mozzanega, *J. Phys. Chem.* 83 (1979) 3122-3126.
- [94] A. Mills, R.H. Davies, D. Worsley, *Chem. Soc. Rev.* 22 (1993) 417-425.
- [95] M. Gratzel, *Nature* 414 (2001) 338-344.
- [96] D.W. Bahnemann, C. Kormann, M.R. Hoffmann, *J. Phys. Chem.* 91 (1987) 3789-3798.
- [97] I.M. Szilágyi, B. Fórizs, O. Rosseler, Á. Szegedi, P. Németh, P. Király, G. Tárkányi, B. Vajna, K. Varga-Josepovits, K. László, A.L. Tóth, P. Baranyai, M. Leskelä, *J. Catal.* 294 (2012) 119-127.
- [98] M.S. Bazarjani, M. Hojamberdiev, K. Morita, G. Zhu, G. Cherkashinin, C. Fasel, T. Herrmann, H. Breitzke, A. Gurlo, R. Riedel, *J. Am. Chem. Soc.* 135 (2013) 4467-4475.
- [99] J.F. Banfield, D.R. Veblen, D.J. Smith, *Am. Mineral.* 76 (1991) 343-353.
- [100] J.F. Banfield, D.R. Veblen, *Am. Mineral.* 76 (1991) 113-127.
- [101] J.F. Banfield, D.R. Veblen, *Am. Mineral.* 77 (1992) 545-557.
- [102] S. Bakardjieva, V. Stengl, L. Szatmary, J. Subrt, J. Lukac, N. Murafa, D. Niznansky, K. Cizek, J. Jirkovsky, N. Petrova, *J. Mater. Chem.* 16 (2006) 1709-1716.
- [103] Z. Zheng, H. Liu, J. Ye, J. Zhao, E.R. Waclawik, H. Zhu, *J. Mol. Catal. A-Chem.* 316 (2010) 75-82.
- [104] A.E. Goresy, M. Chen, L. Dubrovinsky, P. Gillet, G. Graup, *Science* 293 (2001) 1467-1470.
- [105] A.E. Goresy, M. Chen, P. Gillet, L. Dubrovinsky, G. Graup, R. Ahuja, *Earth Planet. Sc. Lett.* 192 (2001) 485-495.
- [106] L.S. Dubrovinsky, N.A. Dubrovinskaia, V. Swamy, J. Muscat, N.M. Harrison, R. Ahuja, B. Holm, B. Johansson, *Nature* 410 (2001).
- [107] N.A. Dubrovinskaia, L.S. Dubrovinsky, R. Ahuja, V.B. Prokopenko, V. Dmitriev, H.P. Weber, J.M. Osorio-Guillen, B. Johansson, *Phys. Rev. Lett.* 87 (2001) 275501.
- [108] M. Mattesini, J.S. de Almeida, L. Dubrovinsky, N. Dubrovinskaia, B. Johansson, R. Ahuja, *Phys. Rev. B* 70 (2004) 212101.
- [109] R. Marchand, L. Brohan, M. Tournoux, *Mater. Res. Bull.* 15 (1980) 1129-1133.
- [110] M. Latroche, L. Brohan, R. Marchand, M. Tournoux, *J. Solid State Chem.* 81 (1989) 78-82.
- [111] J. Akimoto, Y. Gotoh, Y. Oosawa, N. Nonose, T. Kumagai, K. Aoki, H. Takei, *J. Solid State Chem.* 113 (1994) 27-36.
- [112] O. Carp, C.L. Huisman, A. Reller, *Prog. Solid State Ch.* 32 (2004) 33-177.
- [113] D.T. Cromer, K. Herrington, *J. Am. Chem. Soc.* 77 (1955) 4708-4709.
- [114] S. Andersson, A.D. Wadsley, *Nature* 211 (1966) 581.
- [115] S. Sankar, K.G. Gopchandran, P. Kuppusami, S. Murugesan, *Ceram. Int.* 37 (2011) 3307-3315.

-
- [116] F. Thevenet, O. Guañtella, J.M. Herrmann, A. Rousseau, C. Guillard, *Appl. Catal. B: Environ.* 61 (2005) 58-68.
- [117] H. Zhang, J.F. Banfield, *J. Mater. Chem.* 8 (1998) 2073-2076.
- [118] U. Diebold, *Surf. Sci. Rep.* 48 (2003) 53-229.
- [119] X. Wang, L. Sør, R. Su, S. Wendt, P. Hald, A. Mamakhel, C. Yang, Y. Huang, B.B. Iversen, F. Besenbacher, *J. Catal.* 310 (2014) 100-108.
- [120] K. Tanaka, M.F.V. Capule, T. Hisanaga, *Chem. Phys. Lett.* 187 (1991) 73-76.
- [121] Evonik Industries (www.aerosil.com, accessed February 2014).
- [122] M. Hussain, R. Ceccarelli, D.L. Marchisio, D. Fino, N. Russo, F. Geobaldo, *Chem. Eng. J.* 157 (2010) 45-51.
- [123] B. Abramović, D. Šojić, V. Despotović, D. Vione, M. Pazzi, J. Csanádi, *Appl. Catal. B: Environ.* 105 (2011) 191-198.
- [124] A.G. Agrios, K.A. Gray, E. Weitz, *Langmuir* 19 (2003) 1402-1409.
- [125] A.G. Agrios, K.A. Gray, E. Weitz, *Langmuir* 20 (2004) 5911-5917.
- [126] D.C. Hurum, K.A. Gray, T. Rajh, M.C. Thurnauer, *J. Phys. Chem. B* 108 (2004) 16483-16487.
- [127] D.C. Hurum, A.G. Agrios, K.A. Gray, T. Rajh, M.C. Thurnauer, *J. Phys. Chem. B* 107 (2003) 4545-4549.
- [128] R.I. Bickley, T. Gonzalez-Carreno, J.S. Lees, L. Palmisano, R.J.D. Tilley, *J. Solid State Chem.* 92 (1991) 178-190.
- [129] J. Mo, Y. Zhang, Q. Xu, J.J. Lamson, R. Zhao, *Atmos. Environ.* 43 (2009) 2229-2246.
- [130] A.J. Maira, K.L. Yeung, C.Y. Lee, P.L. Yue, C.K. Chan, *J. Catal.* 192 (2000) 185-196.
- [131] L.y. Zeatoun, D. Feke, *Part. Part. Syst. Char.* 22 (2005) 276-281.
- [132] J. Rubio, J. Oteo, M. Villegas, P. Duran, *J. Mater. Sci.* 32 (1997) 643-652.
- [133] H. Cheng, J. Ma, Z. Zhao, L. Qi, *Chem. Mater.* 7 (1995) 663-671.
- [134] R.-C. Xie, J. Shang, *J. Mater. Sci.* 42 (2007) 6583-6589.
- [135] J. Yu, X. Zhao, J. Du, W. Chen, *J. Sol-Gel Sci. Technol.* 17 (2000) 163-171.
- [136] Y.V. Kolen'ko, A.V. Garshev, B.R. Churagulov, S. Boujday, P. Portes, C. Colbeau-Justin, J. Photochem. Photobiol. A 172 (2005) 19-26.
- [137] P. Monnoyer, A. Fonseca, J.B. Nagy, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 100 (1995) 233-243.
- [138] M. Andersson, A. Kiselev, L. Österlund, A.E.C. Palmqvist, *J. Phys. Chem.* 111 (2007) 6789-6797.
- [139] B.R. Sankapal, S.D. Sartale, M.C. Lux-Steiner, A. Ennaoui, C. R. Chim. 9 (2006) 702-707.
- [140] Y. Kitamura, N. Okinaka, T. Shibayama, O.O.P. Mahaney, D. Kusano, B. Ohtani, T. Akiyama, *Powder Technol.* 176 (2007) 93-98.
- [141] J.H. Lee, Y.S. Yang, *Mater. Chem. Phys.* 93 (2005) 237-242.
- [142] M. Bellardita, M. Addamo, A. Di Paola, L. Palmisano, *Chem. Phys.* 339 (2007) 94-103.
- [143] N. Serpone, A.V. Emeline, S. Horikoshi, V.N. Kuznetsov, V.K. Ryabchuk, *Photochem. Photobiol. Sci.* 11 (2012) 1121-1150.
- [144] C.M. Wang, A. Heller, H. Gerischer, *J. Am. Chem. Soc.* 114 (1992) 5230-5234.
- [145] H. Kobayashi, K. Kishimoto, Y. Nakato, *Surf. Sci.* 306 (1994) 393-405.
-

- [146] V. Subramanian, E. Wolf, P.V. Kamat, *J. Phys. Chem. B* 105 (2001) 11439-11446.
- [147] W. Chen, J.S. Zhang, *Build. Environ.* 43 (2008) 246-252.
- [148] S. Sato, J.M. White, *Chem. Phys. Lett.* 72 (1980) 83-86.
- [149] A. Di Paola, G. Marci, L. Palmisano, M. Schiavello, K. Uosaki, S. Ikeda, B. Ohtani, *J. Phys. Chem. B* 106 (2001) 637-645.
- [150] J. Araña, *J. Mol. Catal. A-Chem.* 215 (2004) 153-160.
- [151] J.C. Colmenares, A. Magdziarz, D. Łomot, O. Chernyayeva, D. Lisovytskiy, *Appl. Catal. B: Environ.* 147 (2014) 624-632.
- [152] N. Serpone, P. Maruthamuthu, P. Pichat, E. Pelizzetti, H. Hidaka, *J. Photochem. Photobiol. A* 85 (1995) 247-255.
- [153] Y. Bessekhoud, D. Robert, J.V. Weber, *J. Photochem. Photobiol. A* 163 (2004) 569-580.
- [154] Y. Bessekhoud, N. Chaoui, M. Trzpit, N. Ghazzal, D. Robert, J.V. Weber, *J. Photochem. Photobiol. A* 183 (2006) 218-224.
- [155] C.F. Lin, C.H. Wu, Z.N. Onn, *J. Hazard. Mater.* 154 (2008) 1033-1039.
- [156] T. Rajh, J.M. Nedeljkovic, L.X. Chen, O. Poluektov, M.C. Thurnauer, *J. Phys. Chem. B* 103 (1999) 3515-3519.
- [157] T. Tachikawa, M. Fujitsuka, T. Majima, *J. Phys. Chem.* 111 (2007) 5259-5275.
- [158] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Langmuir* 14 (1998) 3160-3163.
- [159] B.D. Yao, Y.F. Chan, X.Y. Zhang, W.F. Zhang, Z.Y. Yang, N. Wang, *Appl. Phys. Lett.* 82 (2003) 281-283.
- [160] H. Ou, S. Lo, *Sep. Purif. Technol.* 58 (2007) 179-191.
- [161] M. Qamar, C.R. Yoon, H.J. Oh, N.H. Lee, K. Park, D.H. Kim, K.S. Lee, W.J. Lee, S.J. Kim, *Catal. Today* 131 (2008) 3-14.
- [162] C.L. Wong, Y.N. Tan, A.R. Mohamed, *J. Environ. Manage.* 92 (2011) 1669-1680.
- [163] N. Serpone, *J. Phys. Chem. B* 110 (2006) 24287-24293.
- [164] M. Zamora, T. López, R. Gómez, M. Asomoza, R. Melendrez, *Catal. Today* 107-108 (2005) 289-293.
- [165] J.E. Son, J. Chattopadhyay, D. Pak, *Int. J. Hydrogen Energy* 35 (2010) 420-427.
- [166] H. Feng, L.E. Yu, M.-H. Zhang, *Mater. Res. Bull.* 48 (2013) 672-681.
- [167] E. Borgarello, N. Serpone, G. Emo, R. Harris, E. Pelizzetti, C. Minero, *Inorg. Chem.* 25 (1986) 4499-4503.
- [168] L. Davydov, E.P. Reddy, P. France, P.G. Smirniotis, *J. Catal.* 203 (2001) 157-167.
- [169] F.B. Li, X.Z. Li, *Appl. Catal. A: Gen.* 228 (2002) 15-27.
- [170] Z. Du, C. Feng, Q. Li, Y. Zhao, X. Tai, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 315 (2008) 254-258.
- [171] Y.-H. Peng, G.-F. Huang, W.-Q. Huang, *Adv. Powder Technol.* 23 (2012) 8-12.
- [172] J.C. Rooke, T. Barakat, M.F. Finol, P. Billemon, G. De Weireld, Y. Li, R. Cousin, J.M. Giraudon, S. Siffert, J.F. Lamonier, B.L. Su, *Appl. Catal. B: Environ.* 142-143 (2013) 149-160.
- [173] S.N.R. Inturi, T. Boningari, M. Suidan, P.G. Smirniotis, *Appl. Catal. B: Environ.* 144 (2014) 333-342.

-
- [174] W.-J. Hong, M. Kang, *Mater. Lett.* 60 (2006) 1296-1305.
- [175] J. Yu, S. Liu, Z. Xiu, W. Yu, G. Feng, *J. Alloys Compd.* 461 (2008) L17-L19.
- [176] Y. Duan, N. Fu, Q. Zhang, Y. Fang, X. Zhou, Y. Lin, *Electrochim. Acta* 107 (2013) 473-480.
- [177] C.S. Chua, O.K. Tan, M.S. Tse, X. Ding, *Thin Solid Films* 544 (2013) 571-575.
- [178] S. Zhang, Z. Zheng, J. Wang, J. Chen, *Chemosphere* 65 (2006) 2282-2288.
- [179] S. Forissier, H. Roussel, C. Jimenez, O. Chaix, A. Pereira, A. Bensalah-Ledoux, J.L. Deschanvres, B. Moine, *Energy Procedia* 10 (2011) 192-196.
- [180] M. Boutinguiza, J. del Val, A. Riveiro, F. Lusquiños, F. Quintero, R. Comesaña, J. Pou, *Phys. Procedia* 41 (2013) 787-793.
- [181] C. Zhan, F. Chen, J. Yang, D. Dai, X. Cao, M. Zhong, *J. Hazard. Mater.* 267 (2014) 88-97.
- [182] L. Zheng, R. Lisiecki, W. Ryba-Romanowski, G. Aka, J. Di, D. Li, X. Xu, J. Xu, *J. Lumin.* 145 (2014) 547-552.
- [183] S. Sato, *Chem. Phys. Lett.* 123 (1986) 126-128.
- [184] N.C. Saha, H.G. Tompkins, *J. Appl. Phys.* 72 (1992) 3072-3079.
- [185] T. Morikawa, R. Asahi, T. Ohwaki, K. Aoki, Y. Taga, *Jpn. J. Appl. Phys.* 40 (2001) L561-L563.
- [186] T. Lindgren, J.M. Mwabora, E. Avendaño, J. Jonsson, A. Hoel, C.-G. Granqvist, S.-E. Lindquist, *J. Phys. Chem. B* 107 (2003) 5709-5716.
- [187] H. Irie, Y. Watanabe, K. Hashimoto, *J. Phys. Chem. B* 107 (2003) 5483-5486.
- [188] C. Di Valentin, G. Pacchioni, A. Selloni, *Phys. Rev. B* 70 (2004) 085116.
- [189] O. Diwald, T.L. Thompson, T. Zubkov, S.D. Walck, J.T. Yates, *J. Phys. Chem. B* 108 (2004) 6004-6008.
- [190] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* 293 (2001) 269-271.
- [191] S. Sakthivel, H. Kisch, *Angew. Chem., Int. Ed.* 42 (2003) 4908-4911.
- [192] H. Irie, Y. Watanabe, K. Hashimoto, *Chem. Lett.* 32 (2003) 772-773.
- [193] T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, *Appl. Phys. Lett.* 81 (2002) 454.
- [194] T. Umebayashi, T. Yamaki, S. Yamamoto, A. Miyashita, S. Tanaka, T. Sumita, K. Asai, *J. Appl. Phys.* 93 (2003) 5156-5160.
- [195] K. Takeuchi, I. Nakamura, O. Matsumoto, S. Sugihara, M. Ando, T. Ihara, *Chem. Lett.* 29 (2000) 1354-1355.
- [196] T. Ihara, M. Miyoshi, M. Ando, S. Sugihara, Y. Iriyama, *J. Mater. Sci.* 36 (2001) 4201-4207.
- [197] J. Moon, C.Y. Yun, K.-W. Chung, M.-S. Kang, J. Yi, *Catal. Today* 87 (2003) 77-86.
- [198] C. Li, X. Yang, R. Chen, J. Pan, H. Tian, H. Zhu, X. Wang, A. Hagfeldt, L. Sun, *Sol. Energ. Mat. Sol. C.* 91 (2007) 1863-1871.
- [199] D.H. Lee, Y.S. Cho, W.I. Yi, T.S. Kim, J.K. Lee, H. Jin Jung, *Appl. Phys. Lett.* 66 (1995) 815-816.
- [200] T. Umebayashi, T. Yamaki, S. Tanaka, K. Asai, *Chem. Lett.* 32 (2003) 330.
- [201] T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto, S. Sugihara, *Appl. Catal. B: Environ.* 42 (2003) 403-409.
- [202] D. Mitoraj, H. Kisch, *Angew. Chem., Int. Ed.* 47 (2008) 9975-9978.
- [203] C. Pastravanu, I.F. Alexa, I. Cretescu, E. Popovici, Photocatalytic properties of N-doped TiO₂. The effect of the synthesis procedure, 2010, pp. 533-536.
-

- [204] M.M.T. Khan, D. Chatterjee, M. Krishnaratnam, M. Bala, *J. Mol. Catal.* 72 (1992) 13-18.
- [205] W. Ho, J.C. Yu, J. Lin, J. Yu, P. Li, *Langmuir* 20 (2004) 5865-5869.
- [206] G. Mele, R. Del Sole, G. Vasapollo, G. Marci, E. García-López, L. Palmisano, J.M. Coronado, M.D. Hernández-Alonso, C. Malitesta, M.R. Guascito, *J. Phys. Chem. B* 109 (2005) 12347-12352.
- [207] G. Mele, E. García-López, L. Palmisano, G. Dyrda, R. Słota, *J. Phys. Chem.* 111 (2007) 6581-6588.
- [208] Y. Qin, Q. Peng, *Int. J. Photoenergy* 2012 (2012) 21.
- [209] J. He, J. Hua, G. Hu, X.J. Yin, H. Gong, C. Li, *Dyes Pigments* 104 (2014) 75-82.
- [210] X. Yu, Z. Ci, T. Liu, X. Feng, C. Wang, T. Ma, M. Bao, *Dyes Pigments* 102 (2014) 126-132.
- [211] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Mueller, P. Liska, N. Vlachopoulos, M. Graetzel, *J. Am. Chem. Soc.* 115 (1993) 6382-6390.
- [212] M.K. Nazeeruddin, P. Péchy, T. Renouard, S.M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G.B. Deacon, C.A. Bignozzi, M. Grätzel, *J. Am. Chem. Soc.* 123 (2001) 1613-1624.
- [213] M. Anpo, M. Takeuchi, *J. Catal.* 216 (2003) 505-516.
- [214] J. Yu, J.C. Yu, M.K.P. Leung, W. Ho, B. Cheng, X. Zhao, J. Zhao, *J. Catal.* 217 (2003) 69-78.
- [215] S. Monticone, R. Tufeu, A.V. Kanaev, E. Scolan, C. Sanchez, *Appl. Surf. Sci.* 162-163 (2000) 565-570.
- [216] J.C. Yu, J. Yu, H.Y. Tang, L. Zhang, *J. Mater. Chem.* 12 (2002) 81-85.
- [217] N. Serpone, D. Lawless, R. Khairutdinov, *J. Phys. Chem.* 99 (1995) 16646-16654.
- [218] M. Anpo, T. Shima, S. Kodama, Y. Kubokawa, *J. Phys. Chem.* 91 (1987) 4305-4310.
- [219] D.V. Bavykin, J.M. Friedrich, F.C. Walsh, *Adv. Mater.* 18 (2006) 2807-2824.
- [220] H. Yu, J. Yu, B. Cheng, J. Lin, *J. Hazard. Mater.* 147 (2007) 581-587.
- [221] P. Hoyer, *Langmuir* 12 (1996) 1411-1413.
- [222] J.H. Jung, H. Kobayashi, K.J.C. van Bommel, S. Shinkai, T. Shimizu, *Chem. Mater.* 14 (2002) 1445-1447.
- [223] J.-H. Lee, I.-C. Leu, M.-C. Hsu, Y.-W. Chung, M.-H. Hon, *J. Phys. Chem. B* 109 (2005) 13056-13059.
- [224] J. Wang, J. Hou, M.W. Ellis, A.S. Nain, *New J. Chem.* 37 (2013) 571-574.
- [225] V. Zwillling, E. Darque-Ceretti, A. Boutry-Forveille, D. David, M.Y. Perrin, M. Aucouturier, *Surf. Interface Anal.* 27 (1999) 629-637.
- [226] D. Gong, C.A. Grimes, O.K. Varghese, W. Hu, R.S. Singh, Z. Chen, E.C. Dickey, *J. Mater. Res.* 16 (2001) 3331-3334.
- [227] D.-J. Yang, H.-G. Kim, C. Seong-Je, C. Won-Youl, *IEEE T. Nanotechnol.* 7 (2008) 131-134.
- [228] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihar, *Adv. Mater.* 11 (1999) 1307-1311.
- [229] S. Zhang, L.M. Peng, Q. Chen, G.H. Du, G. Dawson, W.Z. Zhou, *Phys. Rev. Lett.* 91 (2003) 256103.
- [230] M. Zhang, Z. Jin, J. Zhang, X. Guo, J. Yang, W. Li, X. Wang, Z. Zhang, *J. Mol. Catal. A-Chem.* 217 (2004) 203-210.
- [231] Y. Guo, N.-H. Lee, H.-J. Oh, C.-R. Yoon, K.-S. Park, W.-H. Lee, Y. Li, H.-G. Lee, K.-S. Lee, S.-J. Kim, *Thin Solid Films* 516 (2008) 8363-8371.

-
- [232] S. Kobayashi, K. Hanabusa, N. Hamasaki, M. Kimura, H. Shirai, S. Shinkai, *Chem. Mater.* 12 (2000) 1523-1525.
- [233] T. Peng, A. Hasegawa, J. Qiu, K. Hirao, *Chem. Mater.* 15 (2003) 2011-2016.
- [234] C. Hippe, M. Wark, E. Lork, G. Schulz-Ekloff, *Micropor. Mesopor. Mat.* 31 (1999) 235-239.
- [235] S. Fujikawa, T. Kunitake, *Langmuir* 19 (2003) 6545-6552.
- [236] A. Michailowski, D. AlMawlawi, G. Cheng, M. Moskovits, *Chem. Phys. Lett.* 349 (2001) 1-5.
- [237] S.-Z. Chu, K. Wada, S. Inoue, S.-i. Todoroki, *Chem. Mater.* 14 (2002) 266-272.
- [238] G.K. Mor, O.K. Varghese, M. Paulose, K. Shankar, C.A. Grimes, *Sol. Energ. Mat. Sol. C.* 90 (2006) 2011-2075.
- [239] G.H. Du, Q. Chen, R.C. Che, Z.Y. Yuan, L.-M. Peng, *Appl. Phys. Lett.* 79 (2001) 3702-3704.
- [240] Q. Chen, W. Zhou, G.H. Du, L.M. Peng, *Adv. Mater.* 14 (2002) 1208-1211.
- [241] W. Wang, O.K. Varghese, M. Paulose, C.A. Grimes, Q. Wang, E.C. Dickey, *J. Mater. Res.* 19 (2004) 417-422.
- [242] Y.Q. Wang, G.Q. Hu, X.F. Duan, H.L. Sun, Q.K. Xue, *Chem. Phys. Lett.* 365 (2002) 427-431.
- [243] X. Wu, Q.-Z. Jiang, Z.-F. Ma, M. Fu, W.-F. Shangguan, *Solid State Commun.* 136 (2005) 513-517.
- [244] R. Ma, Y. Bando, T. Sasaki, *Chem. Phys. Lett.* 380 (2003) 577-582.
- [245] R. Ma, K. Fukuda, T. Sasaki, M. Osada, Y. Bando, *J. Phys. Chem. B* 109 (2005) 6210-6214.
- [246] D.V. Bavykin, J.M. Friedrich, A.A. Lapkin, F.C. Walsh, *Chem. Mater.* 18 (2006) 1124-1129.
- [247] J. Yang, Z. Jin, X. Wang, W. Li, J. Zhang, S. Zhang, X. Guo, Z. Zhang, *Dalton T.* (2003) 3898-3901.
- [248] A. Nakahira, W. Kato, M. Tamai, T. Isshiki, K. Nishio, H. Aritani, *J. Mater. Sci.* 39 (2004) 4239-4245.
- [249] S. Zhang, Q. Chen, L.M. Peng, *Phys. Rev. B* 71 (2005) 014104.
- [250] Q. Chen, G.H. Du, S. Zhang, L.-M. Peng, *Acta Crystallogr. B* 58 (2002) 587-593.
- [251] S. Zhang, W. Li, Z. Jin, J. Yang, J. Zhang, Z. Du, Z. Zhang, *J. Solid State Chem.* 177 (2004) 1365-1371.
- [252] C.-C. Tsai, H. Teng, *Chem. Mater.* 18 (2005) 367-373.
- [253] Á. Kukovecz, M. Hodos, E. Horváth, G. Radnóczy, Z. Kónya, I. Kiricsi, *J. Phys. Chem. B* 109 (2005) 17781-17783.
- [254] R. Ma, Y. Bando, T. Sasaki, *J. Phys. Chem. B* 108 (2004) 2115-2119.
- [255] Z.-Y. Yuan, B.-L. Su, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 241 (2004) 173-183.
- [256] Y. Lan, X.P. Gao, H.Y. Zhu, Z.F. Zheng, T.Y. Yan, F. Wu, S.P. Ringer, D.Y. Song, *Adv. Funct. Mater.* 15 (2005) 1310-1318.
- [257] N. Viriya-empikul, N. Sano, T. Charinpanitkul, T. Kikuchi, W. Tanthapanichakoon, *Nanotechnology* 19 (2008) 035601.
- [258] N. Viriya-empikul, T. Charinpanitkul, N. Sano, A. Sootitawatwat, T. Kikuchi, K. Faungnawakij, W. Tanthapanichakoon, *Mater. Chem. Phys.* 118 (2009) 254-258.
- [259] Y. Ma, Y. Lin, X. Xiao, X. Zhou, X. Li, *Mater. Res. Bull.* 41 (2006) 237-243.
- [260] C.-K. Lee, C.-C. Wang, M.-D. Lyu, L.-C. Juang, S.-S. Liu, S.-H. Hung, *J. Colloid Interface Sci.* 316 (2007) 562-569.
-

- [261] W.V. Prescott, A.I. Schwartz, Nanorods, Nanotubes, and Nanomaterials Research Progress, Nova Science, New York, 2008.
- [262] Y. Suzuki, S. Yoshikawa, *J. Mater. Res.* 19 (2004) 982-985.
- [263] A.R. Armstrong, G. Armstrong, J. Canales, P.G. Bruce, *Angew. Chem., Int. Ed.* 43 (2004) 2286-2288.
- [264] B. Poudel, W.Z. Wang, C. Dames, J.Y. Huang, S. Kunwar, D.Z. Wang, D. Banerjee, G. Chen, Z.F. Ren, *Nanotechnology* 16 (2005) 1935-1940.
- [265] O.K. Varghese, D. Gong, M. Paulose, C.A. Grimes, E.C. Dickey, *J. Mater. Res.* 18 (2003) 156-165.
- [266] S. Sreekantan, L.C. Wei, *J. Alloys Compd.* 490 (2010) 436-442.
- [267] J.-N. Nian, H. Teng, *J. Phys. Chem. B* 110 (2006) 4193-4198.
- [268] J. Yu, H. Yu, B. Cheng, X. Zhao, Q. Zhang, *J. Photochem. Photobiol. A* 182 (2006) 121-127.
- [269] M. Hodos, E. Horváth, H. Haspel, Á. Kukovecz, Z. Kónya, I. Kiricsi, *Chem. Phys. Lett.* 399 (2004) 512-515.
- [270] Á. Kukovecz, M. Hodos, Z. Kónya, I. Kiricsi, *Chem. Phys. Lett.* 411 (2005) 445-449.
- [271] M.-C. Hsu, I.-C. Leu, Y.-M. Sun, M.-H. Hon, *J. Cryst. Growth* 285 (2005) 642-648.
- [272] J.C. Colmenares, R. Luque, J.M. Campelo, F. Colmenares, Z. Karpinski, A.A. Romero, *Materials* 2 (2009) 2228-2258.
- [273] D.H. Kim, J.S. Jang, N.H. Goo, M.S. Kwon, J.W. Lee, S.H. Choi, D.W. Shin, S.-J. Kim, K.S. Lee, *Catal. Today* 146 (2009) 230-233.
- [274] C.-T. Hsieh, W.-S. Fan, W.-Y. Chen, J.-Y. Lin, *Sep. Purif. Technol.* 67 (2009) 312-318.
- [275] L. Dong, Y. Ma, Y. Wang, Y. Tian, G. Ye, X. Jia, G. Cao, *Mater. Lett.* 63 (2009) 1598-1600.
- [276] V. Štengl, S. Bakardjieva, J. Šubrt, E. Večerníková, L. Szatmary, M. Klementová, V. Balek, *Appl. Catal. B: Environ.* 63 (2006) 20-30.
- [277] Z. Jing, D. Guo, W. Wang, S. Zhang, W. Qi, B. Ling, *Solid State Sci.* 13 (2011) 1797-1803.
- [278] J.-C. Xu, M. Lu, X.-Y. Guo, H.-L. Li, *J. Mol. Catal. A-Chem.* 226 (2005) 123-127.
- [279] Q. Zhao, M. Li, J. Chu, T. Jiang, H. Yin, *Appl. Surf. Sci.* 255 (2009) 3773-3778.
- [280] S. Song, J. Tu, Z. He, F. Hong, W. Liu, J. Chen, *Appl. Catal. A: Gen.* 378 (2010) 169-174.
- [281] R. Asapu, V.M. Palla, B. Wang, Z. Guo, R. Sadu, D.H. Chen, *J. Photochem. Photobiol. A* 225 (2011) 81-87.
- [282] G.-W. Zhang, G.-H. He, W.-L. Xue, X.-F. Xu, D.-N. Liu, Y.-H. Xu, *J. Mol. Catal. A-Chem.* 363-364 (2012) 423-429.
- [283] J. Geng, D. Yang, J. Zhu, D. Chen, Z. Jiang, *Mater. Res. Bull.* 44 (2009) 146-150.
- [284] Y. Shen, J. Wu, Y. Tao, M. Li, H. Jin, T. Xiong, *Mater. Sci. Forum* 694 (2011) 37-41.
- [285] J.-h. Xu, W.-L. Dai, J. Li, Y. Cao, H. Li, H. He, K. Fan, *Catal. Commun.* 9 (2008) 146-152.
- [286] Y. Yamin, N. Keller, V. Keller, *J. Photochem. Photobiol. A* 245 (2012) 43-57.
- [287] V. Idakieva, Z.-Y. Yuanb, T. Tabakovaa, B.-L. Sub, *Appl. Catal. A: Gen.* 281 (2005) 149-155.
- [288] S.-H. Chien, Y.-C. Liou, M.-C. Kuo, *Synthetic Met.* 152 (2005) 333-336.
- [289] C.-C. Tsai, H. Teng, *Chem. Mater.* 16 (2004) 4352-4358.
- [290] W. Wang, J. Zhang, H. Huang, Z. Wu, Z. Zhang, *Appl. Surf. Sci.* 253 (2007) 5393-5399.
- [291] X. Sun, Y. Li, *Chem-Eur. J.* 9 (2003) 2229-2238.

-
- [292] P. Umek, P. Cevc, A. Jesih, A. Gloter, C.P. Ewels, D. Arčon, *Chem. Mater.* 17 (2005) 5945-5950.
- [293] J. Li, Z. Tang, Z. Zhang, *Electrochem. Commun.* 7 (2005) 62-67.
- [294] J. Li, Z. Tang, Z. Zhang, *Chem. Phys. Lett.* 418 (2006) 506-510.
- [295] L. Yu, X. Zhang, *Mater. Chem. Phys.* 87 (2004) 168-172.
- [296] F. Hu, F. Ding, S. Song, P.K. Shen, *J. Power Sources* 163 (2006) 415-419.
- [297] G.-S. Kim, H.-K. Seo, V.P. Godble, Y.-S. Kim, O.B. Yang, H.-S. Shin, *Electrochem. Commun.* 8 (2006) 961-966.
- [298] S. Kubota, K. Johkura, K. Asanuma, Y. Okouchi, N. Ogiwara, K. Sasaki, T. Kasuga, *J. Mater. Sci. - Mater. Med.* 15 (2004) 1031-1035.
- [299] L. Miao, Y. Ina, S. Tanemura, T. Jiang, M. Tanemura, K. Kaneko, S. Toh, Y. Mori, *Surf. Sci.* 601 (2007) 2792-2799.
- [300] L.A. Dibble, G.B. Raupp, *Environ. Sci. Technol.* 26 (1992) 492-495.
- [301] F. Chen, J. Zhao, *Catal. Lett.* 58 (1999) 246-247.
- [302] P. Fernández-Ibáñez, J. Blanco, S. Malato, F.J.d.l. Nieves, *Water Res.* 37 (2003) 3180-3188.
- [303] K. Azrague, P. Aimar, F. Benoit-Marquié, M.T. Maurette, *Appl. Catal. B: Environ.* 72 (2007) 197-204.
- [304] J. Sabate, M.A. Anderson, M.A. Aguado, J. Giménez, S. Cervera-March, C.G. Hill, *J. Mol. Catal.* 71 (1992) 57-68.
- [305] G. Imoberdorf, H. Irazoqui, O. Alfano, A. Cassano, *Chem. Eng. Sci.* 62 (2007) 793-804.
- [306] C.P. Chang, J.N. Chen, M.C. Lu, H.Y. Yang, *Chemosphere* 58 (2005) 1071-1078.
- [307] A.K. Ray, *Catal. Today* 44 (1998) 357-368.
- [308] M. Bideau, B. Claudel, C. Dubien, L. Faure, H. Kazouan, *J. Photochem. Photobiol. A* 91 (1995) 137-144.
- [309] E. Piera, M.I. Tejedor-Tejedor, M.E. Zorn, M.A. Anderson, *Appl. Catal. B: Environ.* 46 (2003) 671-685.
- [310] M.J. Sampaio, C.G. Silva, A.M.T. Silva, V.J.P. Vilar, R.A.R. Boaventura, J.L. Faria, *Chem. Eng. J.* 224 (2013) 32-38.
- [311] K.C. Pugh, D. Kiserow, J., J.M. Sullivan, J.H. Grinstead, *Emerging Technologies in Hazardous Waste Management V*, American Chemical Society, 1995, pp. 174-194.
- [312] G. Vincent, A. Queffeuilou, P.M. Marquaire, O. Zahraa, *J. Photochem. Photobiol. A* 191 (2007) 42-50.
- [313] G. Imoberdorf, H. Irazoqui, A. Cassano, O. Alfano, *Ind. Eng. Chem. Res.* 44 (2005) 6075-6085.
- [314] M.K.H. Leung, S.M. Tang, R.C.W. Lam, D.Y.C. Leung, W.C. Yam, S.P. Ng, L.L.P. Vrijmoed, *Sol. Energy* 80 (2006) 949-955.
- [315] A. Fernandez, G. Lassaletta, V.M. Jiménez, A. Justo, A.R. González-Elipé, J.-M. Herrmann, H. Tahiri, Y. Ait-Ichou, *Appl. Catal. B: Environ.* 7 (1995) 49-63.
- [316] W.-Y. Wang, Y. Ku, *Water Res.* 40 (2006) 2249-2258.
- [317] A. Haarstrick, O.M. Kut, E. Heinzle, *Environ. Sci. Technol.* 30 (1996) 817-824.
- [318] R.L. Pozzo, J.L. Giombi, M.A. Baltanás, A.E. Cassano, *Catal. Today* 62 (2000) 175-187.
- [319] N.J. Peill, M.R. Hoffmann, *Environ. Sci. Technol.* 29 (1995) 2974-2981.
-

- [320] W. Choi, J.Y. Ko, H. Park, J.S. Chung, *Appl. Catal. B: Environ.* 31 (2001) 209-220.
- [321] P. Ávila, B. Sánchez, A.I. Cardona, M. Rebollar, R. Candal, *Catal. Today* 76 (2002) 271-278.
- [322] J.C. Crittenden, Y. Zhang, D.W. Hand, D.L. Perram, E.G. Marchand, *Water Environ. Res.* 68 (1996) 270-278.
- [323] Y. Zhang, J.C. Crittenden, D.W. Hand, D.L. Perram, *J. Sol. Energy Eng.* 118 (1996) 123-129.
- [324] Y.M. Gao, H.S. Shen, K. Dwight, A. Wold, *Mater. Res. Bull.* 27 (1992) 1023-1030.
- [325] A. Matsuda, T. Matoda, T. Kogure, K. Tadanaga, T. Minami, M. Tatsumisago, *J. Sol-Gel Sci. Technol.* 27 (2003) 61-69.
- [326] S.-H. Lee, M. Kang, S.M. Cho, G.Y. Han, B.-W. Kim, K.J. Yoon, C.-H. Chung, *J. Photochem. Photobiol. A* 146 (2001) 121-128.
- [327] Y. Chen, D.D. Dionysiou, *Appl. Catal. B: Environ.* 62 (2006) 255-264.
- [328] N.Z. Muradov, *Sol. Energy* 52 (1994) 283-288.
- [329] G. Plantard, V. Goetz, D. Sacco, *Mater. Res. Bull.* 46 (2011) 231-234.
- [330] H. Joo, H. Jeong, M. Jeon, I. Moon, *Sol. Energ. Mat. Sol. C.* 79 (2003) 93-101.
- [331] Y. Zhiyong, D. Laub, M. Bensimon, J. Kiwi, *Inorg. Chim. Acta* 361 (2008) 589-594.
- [332] S. Nagaoka, Y. Hamasaki, S.-i. Ishihara, M. Nagata, K. Iio, C. Nagasawa, H. Ihara, *J. Mol. Catal. A-Chem.* 177 (2002) 255-263.
- [333] R. Naik, P. Joshi, R.K. Deshpande, *J. Mol. Catal. A-Chem.* 238 (2005) 46-50.
- [334] S. Josset, S. Hajiesmaili, D. Begin, D. Edouard, C. Pham-Huu, M.-C. Lett, N. Keller, V. Keller, *J. Hazard. Mater.* 175 (2010) 372-381.
- [335] A.N. Kouamé, R. Masson, D. Robert, N. Keller, V. Keller, *Catal. Today* 209 (2013) 13-20.
- [336] B. Sanchez, J. Coronado, R. Candal, R. Portela, I. Tejedor, M. Anderson, D. Tompkins, T. Lee, *Appl. Catal. B: Environ.* 66 (2006) 295-301.
- [337] R. Portela, S. Suárez, R.F. Tessinari, M.D. Hernández-Alonso, M.C. Canela, B. Sánchez, *Appl. Catal. B: Environ.* 105 (2011) 95-102.
- [338] W.A. Daoud, J.H. Xin, *J. Am. Ceram. Soc.* 87 (2004) 953-955.
- [339] J. Blanco, P. Avila, A. Bahamonde, E. Alvarez, B. Sánchez, M. Romero, *Catal. Today* 29 (1996) 437-442.
- [340] B. Sánchez, A.I. Cardona, M. Romero, P. Avila, A. Bahamonde, *Catal. Today* 54 (1999) 369-377.
- [341] M.M. Hossain, G.B. Raupp, S.O. Hay, T.N. Obee, *AIChE J.* 45 (1999) 1309-1321.
- [342] S. Kato, Y. Hirano, M. Iwata, T. Sano, K. Takeuchi, S. Matsuzawa, *Appl. Catal. B: Environ.* 57 (2005) 109-115.
- [343] M.A. Anderson, M.J. Gieselmann, Q. Xu, *J. Membrane Sci.* 39 (1988) 243-258.
- [344] S. Tunesi, M. Anderson, *J. Phys. Chem.* 95 (1991) 3399-3405.
- [345] Y. Xu, C.H. Langford, *J. Phys. Chem. B* 101 (1997) 3115-3121.
- [346] H. Yoneyama, T. Torimoto, *Catal. Today* 58 (2000) 133-140.
- [347] B. Herbig, P. Löbmann, *J. Photochem. Photobiol. A* 163 (2004) 359-365.
- [348] E. Carpio, P. Zúñiga, S. Ponce, J. Solis, J. Rodriguez, W. Estrada, *J. Mol. Catal. A-Chem.* 228 (2005) 293-298.
- [349] R.L. Pozzo, M.A. Baltanás, A.E. Cassano, *Catal. Today* 39 (1997) 219-231.

-
- [350] D.M. Dobkin, M.K. Zuraw, *Principles of chemical vapor deposition: what's going on inside the reactor*, Kluwer Academic ed., Kluwer Academic Publishers, The Netherlands, 2003.
- [351] H.M. Yates, M.G. Nolan, D.W. Sheel, M.E. Pemble, J. Photochem. Photobiol. A 179 (2006) 213-223.
- [352] C.-C. Ting, S.-Y. Chen, D.-M. Liu, J. Appl. Phys. 88 (2000) 4628-4633.
- [353] R. Dannenberg, P. Greene, Thin Solid Films 360 (2000) 122-127.
- [354] I. Turkevych, Y. Pihosh, M. Goto, A. Kasahara, M. Tosa, S. Kato, K. Takehana, T. Takamasu, G. Kido, N. Koguchi, Thin Solid Films 516 (2008) 2387-2391.
- [355] P. Sigmund, Nucl. Instrum. Meth. B 27 (1987) 1-20.
- [356] I. Oja, A. Mere, M. Krunk, R. Nisumaa, C.H. Solterbeck, M. Es-Souni, Thin Solid Films 515 (2006) 674-677.
- [357] R.R. Chamberlin, J.S. Skarman, J. Electrochem. Soc. 113 (1966) 86-89.
- [358] X. Zhao, X. Liu, C. Ding, P.K. Chu, Surf. Coat. Tech. 201 (2007) 6878-6881.
- [359] X. Weng, P. Fisher, M. Skowronski, P.A. Salvador, O. Maksimov, J. Cryst. Growth 310 (2008) 545-550.
- [360] N.K. Huang, D.Z. Wang, Z. Lu, L.B. Lin, Surf. Coat. Tech. 70 (1994) 69-71.
- [361] Y. Paz, in: I.d.L. Hugo, R. Benito Serrano (Eds.), *Advances in Chemical Engineering Photocatalytic Technologies*, Academic Press, 2009, pp. 289-336.
- [362] Y. Paz, Appl. Catal. B: Environ. 99 (2010) 448-460.
- [363] K. Demeestere, J. Dewulf, T. Ohno, P.H. Salgado, H. Van Langenhove, Appl. Catal. B: Environ. 61 (2005) 140-149.
- [364] F.V.S. Lopes, R.A.R. Monteiro, A.M.T. Silva, G.V. Silva, J.L. Faria, A.M. Mendes, V.J.P. Vilar, R.A.R. Boaventura, Chem. Eng. J. 204-206 (2012) 244-257.
- [365] O. Debono, F. Thévenet, P. Gravejat, V. Héquet, C. Raillard, L. Le Coq, N. Locoge, J. Photochem. Photobiol. A 258 (2013) 17-29.
- [366] R.J. Brandi, O.M. Alfano, A.E. Cassano, Chem. Eng. Sci. 54 (1999) 2817-2827.
- [367] C. Águia, J. Ângelo, L.M. Madeira, A. Mendes, J. Environ. Manage. 92 (2011) 1724-1732.
- [368] M. Formenti, F. Juillet, P. Meriaudeau, S.J. Teichner, Chem. Technol. 1 (1971) 680-686.
- [369] M. Lewandowski, D. Ollis, in: V. Ramamurthy, K.S. Schanze (Eds.), *Semiconductor photochemistry and photophysics*, Marce Dekker, New York, 2003, p. 249.
- [370] S. Yamazaki-Nishida, X. Fu, M.A. Anderson, K. Hori, J. Photochem. Photobiol. A 97 (1996) 175-179.
- [371] J. Araña, A. Peña Alonso, J.M. Doña Rodríguez, J.A. Herrera Melián, O. González Díaz, J. Pérez Peña, Appl. Catal. B: Environ. 78 (2008) 355-363.
- [372] D. Tsoukleris, T. Maggos, C. Vassilakos, P. Falaras, Catal. Today 129 (2007) 96-101.
- [373] T. Oda, Journal of Electrostatics 57 (2003) 293-311.
- [374] T. Oda, R. Yamashita, I. Haga, T. Takahashi, S. Masuda, IEEE Trans. Ind. Appl. 32 (1996) 118-124.
- [375] H.-H. Kim, K. Tsunoda, S. Katsura, A. Mizuno, IEEE Trans. Ind. Appl. 35 (1999) 1306-1310.
- [376] R.-B. Sun, Z.-G. Xi, F.-H. Chao, W. Zhang, H.-S. Zhang, D.-F. Yang, Atmos. Environ. 41 (2007) 6853-6859.
-

- [377] H.-H. Kim, S.-M. Oh, A. Ogata, S. Futamura, *Appl. Catal. B: Environ.* 56 (2005) 213-220.
- [378] A.M. Vandenbroucke, R. Morent, N. De Geyter, C. Leys, J. Hazard. Mater. 195 (2011) 30-54.
- [379] F. Thevenet, O. Guaitella, E. Puzeat, J.M. Herrmann, A. Rousseau, C. Guillard, *Catal. Today* 122 (2007) 186-194.
- [380] N. Doucet, F. Bocquillon, O. Zahraa, M. Bouchy, *Chemosphere* 65 (2006) 1188-1196.
- [381] C. Nicolella, M. Rovatti, *Chem. Eng. J.* 69 (1998) 119-126.
- [382] M.R. Nimlos, W.A. Jacoby, D.M. Blake, T.A. Milne, *Environ. Sci. Technol.* 27 (1993) 732-740.
- [383] T. Tsuru, T. Kan-no, T. Yoshioka, M. Asaeda, *J. Membrane Sci.* 280 (2006) 156-162.
- [384] M.L. Sauer, D.F. Ollis, *J. Catal.* 149 (1994) 81-91.
- [385] T. Tsuru, T. Kan-no, T. Yoshioka, M. Asaeda, *Catal. Today* 82 (2003) 41-48.
- [386] S.S. Chin, K. Chiang, A.G. Fane, *J. Membrane Sci.* 275 (2006) 202-211.
- [387] R.E. Marinangeli, D.F. Ollis, *AIChE J.* 23 (1977) 415-426.
- [388] N.J. Peill, M.R. Hoffmann, *Environ. Sci. Technol.* 30 (1996) 2806-2812.
- [389] N.J. Peill, M.R. Hoffmann, *Environ. Sci. Technol.* 32 (1998) 398-404.
- [390] A.V. Vorontsov, V.P. Dubovitskaya, *J. Catal.* 221 (2004) 102-109.
- [391] W.A. Jacoby, D. Blake, R.D. Noble, C.A. Koval, *J. Catal.* 157 (1995) 87-96.
- [392] T.H.K. Lim, S. D. , *Chemosphere* 54 (2004) 305-312.
- [393] A. Collin, K.E. Wirth, M. Stroeder, *Powder Technol.* 190 (2009) 31-35.
- [394] G.B. Raupp, J.A. Nico, S. Annangi, R. Changrani, R. Annapragada, *AIChE J.* 43 (1997) 792-801.
- [395] J.-F. Wu, C.-H. Hung, C.-S. Yuan, *J. Photochem. Photobiol. A* 170 (2005) 299-306.
- [396] A.A. Assadi, A. Bouzaza, C. Vallet, D. Wolbert, *Chem. Eng. J.*
- [397] H.Q. Trinh, Y.S. Mok, *Chem. Eng. J.* 251 (2014) 199-206.
- [398] G. Imoberdorf, A. Cassano, H. Irazoqui, O. Alfano, *Catal. Today* 129 (2007) 118-126.
- [399] D. Bockelmann, D. Weichgrebe, R. Goslich, D. Bahnmann, *Sol. Energ. Mat. Sol. C.* 38 (1995) 441-451.
- [400] D. Curcó, S. Malato, J. Blanco, J. Giménez, P. Marco, *Sol. Energy* 56 (1996) 387-400.
- [401] J. Blanco, S. Malato, P. Fernandez, A. Vidal, A. Morales, P. Trincado, J.C. Oliveira, C. Minero, M. Musci, C. Casalle, M. Brunotte, S. Tratzky, N. Dischinger, K.-H. Funken, C. Sattler, M. Vincent, M. Collares-Pereira, J.F. Mendes, C.M. Rangel, *Sol. Energy* 67 (1999) 317-330.
- [402] J.I. Ajona, A. Vidal, *Sol. Energy* 68 (2000) 109-120.
- [403] S.M. Rodríguez, J.B. Gálvez, M.I.M. Rubio, P.F. Ibáñez, D.A. Padilla, M.C. Pereira, J.F. Mendes, J.C.d. Oliveira, *Sol. Energy* 77 (2004) 513-524.
- [404] E.R. Bandala, C.A. Arancibia-Bulnes, S.L. Orozco, C.A. Estrada, *Sol. Energy* 77 (2004) 503-512.
- [405] E.R. Bandala, C. Estrada, *J. Sol. Energy Eng.* 129 (2005) 22-26.

Part II

Chapter 2. Gas-phase UV TiO₂ photocatalysis of PCE using a lab-scale packed bed annular photoreactor

Chapter 3. Gas-phase solar photocatalysis of PCE and n-decane over different TiO₂ photocatalysts using a lab-scale fixed bed annular photoreactor

2. Gas-phase UV TiO₂ photocatalysis of PCE using a lab-scale packed bed annular photoreactor

In this chapter, gas-phase photocatalytic oxidation (PCO) of PCE (574 – 2442 ppm) was carried out in a single-pass continuous-flow annular packed bed photoreactor under non-catalytic (UV) and catalytic (UV-TiO₂) conditions. Under UVC radiation, PCE conversion was dependent on the photoreactor inner tube: conversion was negligible (~ 0 %) with a concentric soda-lime glass inner tube placed inside the photoreactor outer tube, or almost complete (98 %) with a concentric quartz filter. The PCE PCO under UV-TiO₂ was studied using the photoreactor with the glass inner tube (mimicking solar radiation). Effects of PCE concentration, feed flow rate, and water vapour content on the PCE conversion through PCO were investigated. A complete mathematical model able to describe the effects of these operating parameters on the process performance was disclosed; six different kinetic rate equations were tested, suggesting that PCE and H₂O molecules have to be considered in association with different specific active sites of the surface. Under steady-state conditions, by-products formation was also weighed; according to the isolated intermediates, a reaction mechanism was proposed for PCE gas-phase PCO.

This chapter is based on the research article “Lopes, F.V.S., Monteiro, R.A.R., Silva, A.M.T., Silva, G.V., Faria, J.L., Mendes, A.M., Vilar, V.J.P., Boaventura, R.A.R., *Insights into UV TiO₂ Photocatalytic Degradation of PCE for Air Decontamination Systems*, Chemical Engineering Journal, 204 (2012) 244-257, DOI: 10.1016/j.cej.2012.07.079”.

2.1. Introduction

Several chlorinated volatile organic compounds (VOCs), such as perchloroethylene (PCE), have been widely used as solvents at industrial scale in dry cleaning factories, metal degreasing facilities, and plastic and fumigant manufacturing industries [1-3]. These extensive uses lead to water and air pollution, particularly in indoor environments [4, 5]. Due to its high toxicity and volatility and since it is suspected to be carcinogenic to humans and extremely persistent in the environment, PCE present in water and/or air must be removed. Instead of conventional techniques, such as adsorption or air stripping processes which only transfer the pollutants between phases, photocatalytic oxidation (PCO) in gas phase has become a well-established process for air decontamination [1, 2, 6-9], capable of complete PCE conversion/mineralization.

Many reactor configurations have been used for the treatment of PCE in air streams by UV-TiO₂ photocatalytic processes. Among the several types of reactors designed, honeycomb, monolith, plate, fluidized bed, packed bed, and annular tube flow reactors are the most representative [6, 8]. For the last decade, it has become clear that the reactor design should be consistent with the use of a photocatalyst of high specific surface area, and consider small pass-through channels, low air velocity, and direct irradiance of UV light on catalyst surface, allowing a large contact area and reducing mass transfer limitations [8]. However, the photocatalytic oxidation reaction can be influenced, not only by the catalyst nature, structure and morphology, reactor configuration, and radiation source but also by temperature, oxygen and pollutant concentration, water vapour content, flow rate (residence time) and surface velocity [4, 6, 8, 10, 11].

Within this chapter, a wide set of experimental conditions using a lab-scale facility consisting of a single-pass continuous-flow packed-bed annular photoreactor for air decontamination systems is tested in photochemical and photocatalytic oxidation of PCE. Ideally, for the analysis of an effective industrial application process, high volumes of polluted air must be treated, at different continuous feed stream conditions, and for fast and efficient gas-phase treatment (with a contact time of seconds) [12]. Therefore, PCE conversion through PCO was studied for the same reaction temperature as a function of three parameters: (a) pollutant concentration, (b) flow rate (residence time/surface velocity), and (c) humidity content. High concentrations of PCE (between 574 and 2442 ppm) were employed to test the efficiency of the photocatalytic material in extreme conditions of pollutant concentration. Moreover, the effect of these parameters on PCE conversion was assessed for a large range of air stream flow rates contaminated with PCE (59 - 300 cm³ min⁻¹, measured at 298 K and 1 bar) as well as for different

water vapour contents (12 – 40 %, measured at 298 K and 1 bar). A complete mathematical model for air decontamination systems using a single-pass continuous-flow annular UV-photoreactor (glass spheres and TiO₂ photocatalytic packed bed) was presented and different kinetic rate expressions were combined with the mathematical model to study the kinetics through PCO. It should be mentioned that, prior to the PCO experiments, the photochemical reaction of PCE was estimated under UVC radiation. In addition, two different inner tubes were tested (glass and quartz) with the aim of evaluating how important is the effect of the higher transmittance of quartz, when compared with glass, on the global process. By-products of VOC type formed on PCE conversion were analysed by GC/MSD. Finally, a reaction mechanism covering the formation of all identified by-products was proposed for both UV and UV-TiO₂ conversion processes of PCE. All the operating parameters assessed within this work as well as the theoretical/experimental considerations for kinetic modelling and reaction mechanism will contribute for the better understanding of the photocatalytic PCE conversion process.

2.2. Experimental

2.2.1. Materials and chemicals

The benchmark TiO₂ photocatalyst (TiO₂ P25 from Evonik®) was employed in the gas-phase photocatalytic experiments. This material consists of 80 % anatase and 20 % rutile crystalline phases, an average particle size of 30 nm, a BET specific surface area of 50 m² g⁻¹, and a band-gap energy of ~3.00 - 3.15 eV. The perchloroethylene analytical reagent (PCE; 99.5 %) used for the generation of contaminated air streams was purchased from Panreac Química S.A.U. and used without further purification (HCl: < 0.005 %; H₂O: < 0.02 %; non-volatile matter: < 0.005 %). Deionized water was used for the generation of the water vapour content in the feed stream. All gases employed in this work were provided by Air Liquide: helium N50, nitrogen N50, and air K N50 (O₂: 20 ± 1 %; H₂O: < 3 ppm; C_nH_m: < 0.1 ppm; CO₂: < 1 ppm; CO: < 1 ppm), each one with a minimum total purity of 99.999 %.

2.2.2. Photocatalytic experimental apparatus

A schematic representation of the experimental unit used for this study is shown in Figure 2.1 and entails three main parts: feed generation (Figure 2.1a), the photoreactor (Figure 2.1b and Figure 2.3) and the photoreactor feed and exit stream analytic system (Figure 2.1c).

2.1.1.1. Feed generation

The lab-scale apparatus used for generation of air streams containing PCE and water vapour is schematically represented in Figure 2.1a

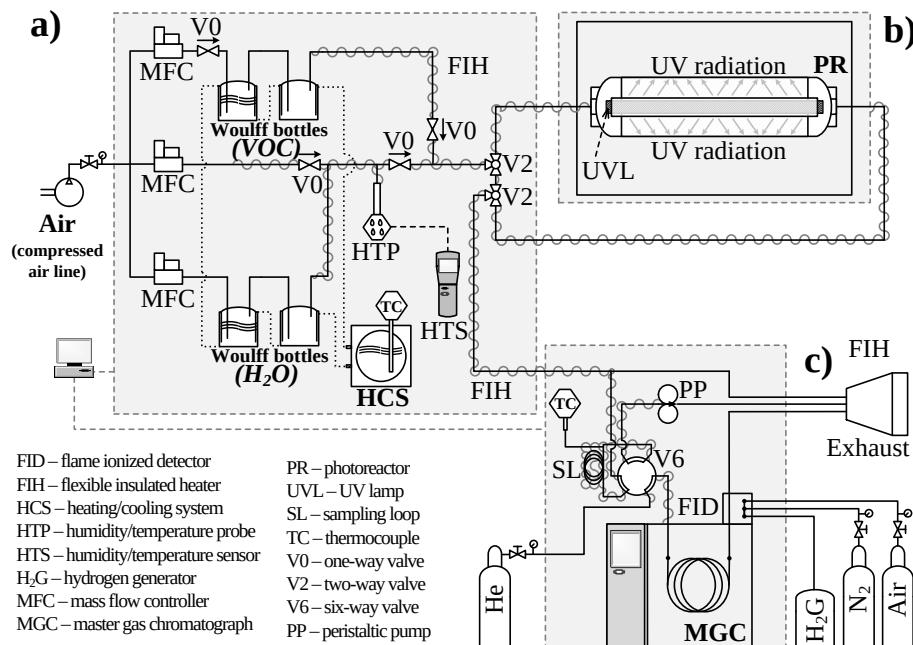


Figure 2.1. Schematic representation of the lab-scale experimental unit used for the study of decontamination of air contaminated with PCE: a) lab-scale facility used for the generation of air streams containing PCE and water vapour; b) single-pass continuous-flow annular UV-photoreactor; c) master gas chromatographic analysis system used for the analysis of the photoreactor feed and exit streams.

The lab-scale apparatus comprises three mass flow controllers (El-Flow, Bronkhorst High-Tech B.V.) that allow the generation of air contaminated with different PCE concentrations and with different relative humidities. For that, an air stream saturated with water vapour is generated by flowing air through two Wouff bottles (supplied by Normax, Lda), one after the other (the second for trapping). To control the relative humidity of this stream, a pure air stream is used to dilute it in accordance to the needs/requirements. The relative humidity and temperature of the mixed stream are read using a relative humidity/temperature probe (9735, Testo), placed in a stainless steel cylinder connected throughout the line. This probe measures air relative humidity and temperature in the ranges of 253 - 343 K (± 0.3 K) and 0 - 100 % (± 2 %), respectively (connected to a data logger: 635-2, Testo). At the end, the air stream (with the desired water vapour content) can be mixed with any pollutant (for this study, PCE) in gas phase. Thus, another air stream passes through two extra Wouff bottles, consecutively, the first filled with a pure PCE liquid solution and the second for trapping. The PCE vapour content was fixed as a result of controlling the flow rate of the air stream and its temperature. Note that, the temperature of

Woulff bottles was kept constant using a temperature controlling system (thermostatic bath GD100 R2, Grant Instruments). All tubing, fittings, connectors, adapters, and valves are made of stainless steel (Swagelok Company) to prevent unit deterioration with the highly VOCs-concentrated air streams employed in the experiments; the 1/4" stainless steel tubing and components are covered with a flexible insulated heater to avoid pollutant and water condensation.

A routine in LabVIEW environment (NI Corporation) was designed to control/monitor the mass flow controllers and thermocouples throughout the experimental time. The work environment developed for that purpose can be seen in Figure 2.2.

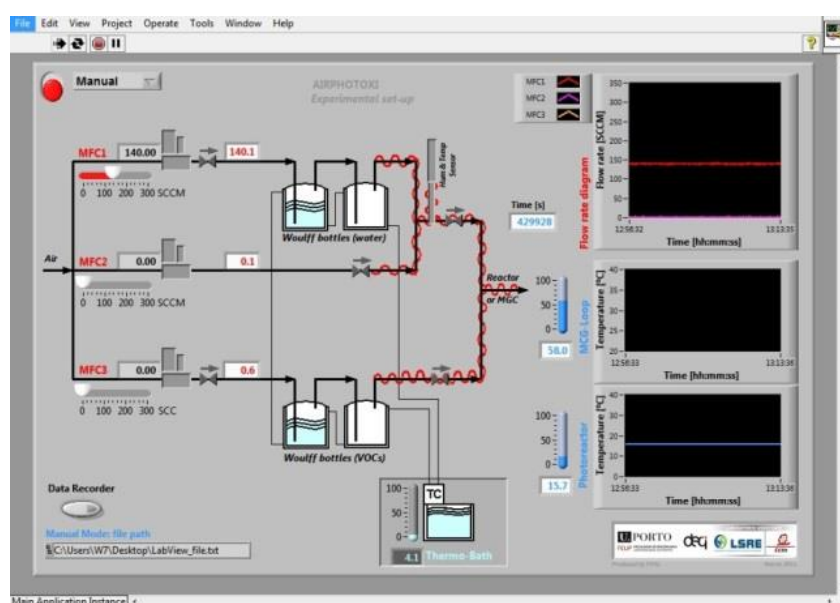


Figure 2.2. LabVIEW routine designed to control/monitor the mass flow controllers and thermocouples throughout the experimental time.

2.1.1.2. Lab-scale photoreactor

A lab-scale single-pass continuous-flow annular UV-photoreactor prototype was designed and manufactured for the study of air decontamination systems. Figure 2.1b shows the schematic representation of the UV-photoreactor. It comprises two concentric tubes with a photocatalytic bed that fills the void in-between. The outer tube is a Pyrex-glass cylinder (Duran borosilicate glass 3.3, Schott-Rorhglas GmbH) and the inner tube, centred in the axial position along the bed, can be either a glass cylinder (Soda-lime glass, Linex) or a quartz cylinder (Quarzglas-Rohr, Quarzglasstechnik, GmbH & Co KG). The catalytic bed is made of glass spheres (1401/7, Karl Hecht Assistent GmbH) packed with TiO_2 catalyst filling the voids between the spheres. To avoid the release of the small catalyst particles into the atmosphere, in both sides of the photocatalytic bed, a layer of ~15 mm of glass wool was added. A detailed representation of

the photoreactor is illustrated in Figure 2.3.

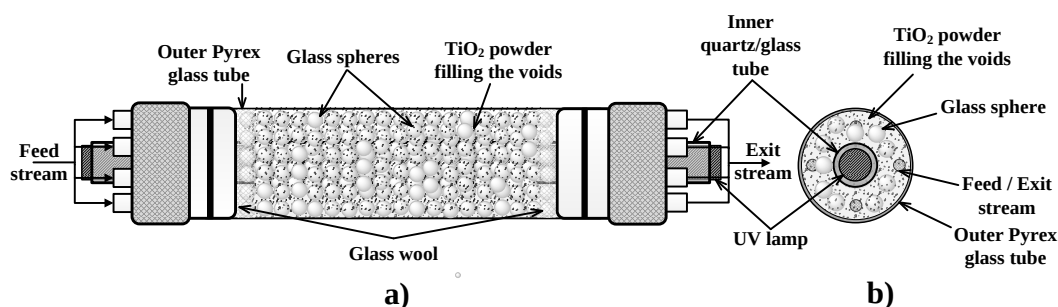


Figure 2.3. Detailed schematic representation of single-pass continuous flow packed bed annular photoreactor employed in the study of decontamination of air contaminated with PCE: a) side view; b) frontal view.

Tubes dimensions and catalytic bed characteristics are described in Table 2.1. It should be mentioned that, each cap of the photoreactor (both inlet and outlet sides) has four equidistant inlets to ensure a better distribution of the feed stream throughout the reactor.

Table 2.1. Photoreactor tubes dimensions employed in the gas-phase photooxidation of PCE under non-catalytic (UV) and catalytic (UV-TiO₂) conditions; catalytic bed characteristics used in the PCE photocatalytic reaction.

Photoreactor tubes		
Outer tube (Pyrex-glass tube)	L_{ot} [cm]	30.0
	$d_{ot,e}$ [cm]	5.00
	$d_{ot,i}$ [cm]	4.64
Inner tube (Glass or quartz tube)	L_{in} [cm]	30.0
	$d_{in,e}$ [cm]	2.00
	$d_{in,i}$ [cm]	1.64
Catalytic bed		
Photocatalytic bed	L_R [cm]	20.0
	V_R [cm ³]	275
	ε	0.406
TiO ₂ P25 (Evonik®)	m_{P25} [g]	15.3
	ρ_{P25} [g cm ⁻³]	3.8
	S_{BET} [m ² g ⁻¹]	50
	Crystal structure	80 % A/20 % R*
	Average particle size [nm]	21
Glass spheres	d_{GS} [cm]	0.71
	V_{GS} [cm ³]	124

* A stands for Anatase and R stands for Rutile

An UV lamp (TUV TL Mini 8W, Koninklijke Philips Electronics N.V.) was used as radiation source. This lamp is placed inside the inner tube; it features short-wave UV radiation with a peak centred at 253.7 nm (UVC). Prior to completely mount the reactor, the intensity of the

UV radiation was measured with a broadband UV radiometer (CUV 5, Kipp & Zonen B.V.) within a spectral range of 280 – 400 nm corresponding to the UV fraction of the solar radiation, placed on the outside of the inner tube and in contact with it; the radiometer needs to be plugged into a handheld display unit (Meteon, Kipp & Zonen B.V.) to produce readings in terms of incident irradiance (W m^{-2}). The use of this packed bed reactor configuration (*i.e.*, a annular photoreactor comprising two concentric tubes with a photocatalytic bed of glass spheres and TiO_2 P25 catalyst filling the void in-between) may cause that only a fraction of the TiO_2 P25 catalyst receives UV radiation; this “shading effect” becomes more significant as the distance to the radiation source increases (near to the photoreactor outer tube) or in the “back” of the glass spheres [13-15]. Because of the “shading effect” and also due to the radiation gradient in the radial direction of the photoreactor [16, 17], the irradiance passing through the catalytic bed was also measured.

2.1.1.3. Photoreactor feed and exit streams analysis

The feed and exit streams of the photoreactor were analysed in a master gas chromatographic (MGC) analysis system (Figure 2.1c) mainly composed by a gas chromatograph (MGC Fast GC, Dani Instruments S.p.A.). The MGC is able to analyse samples of air containing several VOCs using a fused silica capillary column (Volcol – $L_{cc} = 20$ m, $d_{i,cc} = 0.18$ mm, $d_{f,cc} = 1.00$ μm ; Supelco, Sigma-Aldrich Co. LLC.). A two-position valve mounted on the MGC allows the storage of a gas sample for further pollutant concentration analysis through a flame ionization detector (FID) installed in the MGC (see Figure 2.1c). The MGC operates with constant fluxes of helium (carrier gas), hydrogen and air (flame), and nitrogen (make-up) of 2, 30, 300, and 15 $\text{cm}^3 \text{min}^{-1}$ (at 298 K and 1 atm), respectively. For PCE analysis the oven temperature initially starts at 343 K for 1.2 min, followed by a 2 K min^{-1} heating ramp to reach 351 K (fixed for 1.8 min). All connections of this apparatus are 1/16” (Swagelok Company) to reduce dead volumes. Note that the gas exiting the photoreactor is at atmospheric pressure before reaching the MGC analysis system and the pressure decay produced by the 1/16” connections is large enough allowing sample release to the exhaust. Consequently, a peristaltic pump (313F, Watson-Marlow Pumps Group) placed at the end of the line secures that the loop of the two-position valve is completely filled with the sample. Appendix A presents a detailed description of the data treatment as well as the calibration curves for PCE.

VOCs by-products of photochemical and photocatalytic oxidation of PCE were also analysed at steady-state, sampling the photoreactor exit stream to a Tedlar bag (232-05SKC, SKC Inc.) of 5 L. Afterwards, the air sample was transferred to stainless steel tubes with Tenax TA60/80 mesh (Supelco, Sigma-Aldrich Co. LLC.), using portable air pumps (Casella

Measurement), with a flow rate range of 60 – 135 cm³ min⁻¹, provided with on line flow meters (Cole-Parmer). The sampled volume was around 1.5 L. After sampling, the Tenax tubes were analysed with a thermal desorption system (SDT 33.50, Dani Instruments S.p.A.) on line with gas chromatography (GC 6890N, Agilent Technologies, Inc.) coupled to a mass spectrometer detector (MSD 5973, Agilent Technologies, Inc.) for VOC identification and quantification (GC/MSD). The concentration of the major compounds was calculated using the response factor of toluene (according to standard ISO 16000-6 [18]), except for PCE and trichloroethylene, for which specific response factors were used (calibrations solutions prepared with pure compounds).

2.2.3. UV photochemical and UV-TiO₂ photocatalytic conversion of PCE

Initially, the continuous-flow photoreactor was mounted without catalytic bed (glass spheres and TiO₂ P25 catalyst) in order to study the PCE photochemical oxidation. Then, PCE conversion through PCO was studied at different experimental conditions of the feed stream, such as different PCE concentrations, flow rates (residence time/surface velocity), and humidity contents. This first set of experiments was performed using the lab-scale continuous-flow annular photocatalytic reactor with a glass inner tube.

All experimental conditions are reported in Table 2.2. Before all experiments, activation and degassing of the photocatalytic bed was carried out overnight using an air stream with 40 % of water vapour content and a total flow rate of 30 cm³ min⁻¹ (measured at 1 bar and 298 K). Afterwards, the catalytic bed was continuously fed with a contaminated air stream (see Table 2.2) for 3 h, to ensure a constant volatilization of the pollutant and, consequently, a constant feed composition. During each experiment, before turning on the UVC lamp, several samples of the outlet stream were stored in the loop of the two-position valve to confirm a constant feed composition; then, the same procedure was carried out for the analysis of TiO₂-UV PCO efficiency for PCE conversion. It should be mentioned that, after storing each sample, its content was analysed by the MGC FID detector (2 min in “injection mode” to ensure the analysis of all stored content). This procedure was automatically repeated for, at least, 5.5 h. The photocatalyst was repeatedly used (13 experiments) and no loss of its activity was observed. For each experiment, the PCE conversion in PCO ($C_{\text{PCE, exit}} / C_{\text{PCE, feed}}$, where $C_{\text{PCE, feed}}$ (mol m⁻³) and $C_{\text{PCE, exit}}$ (mol m⁻³) are the PCE concentrations on the feed and exit streams, respectively) was determined at steady-state conditions.

Table 2.2 Experimental conditions employed in gas-phase PCO of PCE carried out in continuous-flow annular photoreactor under non-catalytic (UV) and catalytic (UV-TiO₂) conditions.

<i>Gas-phase photooxidation of PCE under UV photolysis</i>			
Run	Q_{feed}^* [cm ³ min ⁻¹]	$C_{\text{PCE, feed}}$ [ppm]	RH^* [%]
1 ^{a,b,c}	150	1221	40
<i>Gas-phase photooxidation of PCE under UV-TiO₂ photocatalysis</i>			
Run	Q_{feed}^* [cm ³ min ⁻¹]	$C_{\text{PCE, feed}}$ [ppm]	RH^* [%]
1 ^{a,b,c}	150	1221	40
2 ^a	150	574	40
3 ^a	150	784	40
4 ^a	150	1353	40
5 ^a	150	1942	40
6 ^a	150	2442	40
7 ^b	59	1221	40
8 ^b	92	1221	40
9 ^b	220	1221	40
10 ^b	300	1221	40
11 ^c	150	1221	12
12 ^c	150	1221	20
13 ^c	150	1221	32
$T = 298 \text{ K} ; P = 1 \text{ bar} ; I = 0.5 \text{ W m}^{-2}$			

* measured at 298 K and 1 bar.

^a constant feed flow rate and humidity content.

^b constant PCE concentration and humidity content.

^c constant feed flow rate and PCE concentration.

Moreover, the glass inner tube of the annular photoreactor was replaced by an equivalent cylinder of quartz, again centred in the axial position along the bed. The photochemical oxidation of PCE was tested employing this photoreactor inner filter in order to determine the possible relevance of the higher transmittance of the quartz tube in the overall process.

2.3. Theoretical

2.3.1. Photoreactor mathematical model

A mathematical model was developed taking into consideration the following main assumptions: (a) steady-state operation; (b) isothermal and isobaric conditions; (c) ideal gas behaviour throughout the photocatalytic bed; (d) axial symmetry; (e) constant porosity along the bed (uniform packing shape and distribution); (f) axially dispersed plug flow along the bed; (g) no heat transfer resistances and no thermal and UV radiation gradients along the bed; (h) no mass, velocity, and UV radiation gradients in the radial direction. Despite being an important factor in heterogeneous PCO process design [16], the radial model distribution of the UV radiation

throughout the photocatalytic bed was neglected. Employing a packed bed reactor configuration, the diffusion of the fluid species may be dominated by the packing shape and distribution (if $Re \times Sc > 1$) or by molecules interaction (when $Re \times Sc < 1$), where Re and Sc are the Reynolds and Schmidt numbers, respectively [16]. Within this work, the range of operational conditions employed resulted in the operation of the photoreactor under kinetics controlled regimes (basically free of mass transfer limitations).

According to the assumptions stated before, the resulting mass balance equation for each component i (second order in the axial coordinate and independent on the radial coordinate), is expressed by:

$$\frac{d}{dz} \left(\varepsilon D_{ax} \frac{dC_i}{dz} \right) - \frac{d}{dz} (u_0 C_i) - v_i r = 0 \quad i = N_2, O_2, H_2O, PCE \quad 2.1$$

where ε is the photocatalytic bed porosity, D_{ax} ($m^2 s^{-1}$) is the axial dispersion coefficient, C_i ($mol m^{-3}$) is the gas phase concentration of compound i , z (m) is the partition of the photoreactor length (L_R in m), u_0 ($m s^{-1}$) is the superficial velocity, v_i is the stoichiometric coefficient of compound i in the overall reaction, and r ($mol m^{-3} s^{-1}$) is the conversion rate. The axial dispersion coefficient can be estimated by [19]:

$$D_{ax} = (0.45 + 0.55\varepsilon) D_m + 0.35 R_p \frac{u_0}{\varepsilon} \quad 2.2$$

where D_m ($m^2 s^{-1}$) is the molecular diffusivity of the feed mixture; it is assumed a particle radius (R_p in m) equal to the averaged radius of the glass spheres ($R_p = \frac{1}{2} d_{GS}$). The mixture molecular diffusivity can be approximated using the Wilke correlation (molecular diffusion coefficients) [20]. The Chapman-Enskog equation [21] is employed to determine the binary molecular diffusivity; the Lennard-Jones parameters (σ_i in Å and ε_i/k_B in K) of each feed compound i are: N_2 (3.667 Å, 99.8 K), O_2 (3.106 Å, 43.18 K), H_2O (2.641 Å, 809.0 K), and PCE (4.676 Å, 211.1 K) [21, 22].

The superficial velocity in the annular photoreactor (with two concentric tubes) is given by:

$$u_0 = Q_{feed} \left[\pi \left(\frac{d_{ot,i}}{2} \right)^2 - \pi \left(\frac{d_{in,e}}{2} \right)^2 \right]^{-1} \quad 2.3$$

where Q_{feed} ($m^3 s^{-1}$) is the total feed flow rate, and $d_{ot,i}$ (m) and $d_{in,e}$ (m) are the internal diameter of the outer tube and the external diameter of the inner tube, respectively.

Assuming that the bulk concentration of each component i is known as well as there is no concentration gradient at the photoreactor exit, the boundary conditions at the photoreactor feed ($z = 0$) and exit ($z = L_R$) are:

$$C_i|_{z=0} = C_{i, \text{feed}} \quad i = N_2, O_2, H_2O, PCE \quad 2.4$$

$$\left. \frac{dC_i}{dz} \right|_{z=L_R} = 0 \quad i = N_2, O_2, H_2O, PCE \quad 2.5$$

where $C_{i, \text{feed}}$ ($\text{m}^3 \text{s}^{-1}$) is the gas phase concentration of component i on the feed stream. To complete the mathematical model, it is necessary to describe a PCO rate expression able to cover the range of operating conditions, such as pollutant concentration, feed flow rates, relative humidity, and incident irradiance.

2.3.2. PCO rate expressions

Several models have been proposed for the simulation in the gas-phase of a single (or multiple) pollutant kinetics through PCO: empirical or based on the Langmuir-Hinshelwood (L-H) equation [4, 6, 8, 10, 15, 23-29]. Some empirical models are based on power law equations, considering that both PCE and H_2O concentrations affect the conversion rate. One of these examples suggested that the PCO rate of PCE (r_{PCE}) for gas-phase and at steady-state is described by (model M-1):

$$r_{\text{PCE}} = I \cdot k' (C_{\text{PCE}}^\alpha C_{\text{H}_2\text{O}}^\beta) \quad 2.6$$

where I is the incident irradiance, k' is the reaction rate constant (in $\text{mol m}^{-2} \text{s}^{-1} \text{W}^{-1} \text{m}^2 \text{M}^{0.76}$), C_{PCE} and $C_{\text{H}_2\text{O}}$ are the PCE and H_2O concentrations expressed in ppm, respectively, and α and β are the exponential parameters for PCE and H_2O , respectively [8, 23].

As stated before, the L-H model has been applied because it can quantitatively describe the PCO gas-solid reaction rate [8, 23, 25]. At steady-state, the L-H rate expression of PCE conversion in PCO (r_{PCE}) can be written according to the following equation (model M-2):

$$r_{\text{PCE}} = I \cdot k \left(\frac{K_{\text{PCE}} C_{\text{PCE}}}{1 + K_{\text{PCE}} C_{\text{PCE}}} \right) \quad 2.7$$

where I , and C_{PCE} are the same variables described for model M-1, k is the reaction rate constant (in this case given in $\text{mol m}^{-2} \text{s}^{-1} \text{W}^{-1} \text{m}^2$), and K_{PCE} (in M^{-1}) represents the PCE adsorption

equilibrium constant in a single site. This model only considers interactions between pollutant molecules and catalyst surface [4, 6, 8, 23-25, 28]. It is commonly called as L-H monomolecular model (M-2).

On the other hand, literature reports L-H bimolecular models that consider interactions between both pollutant and water vapour molecules; this results in a dual adsorption of both surface species on catalyst surface sites [8]. When dual adsorption occurs on the same type of site, the model is based on competitive adsorption of pollutant and water vapour molecules on equal type of sites [15, 23, 26-28]; it is generally called as L-H bimolecular competitive single site model (M-3). In this case, the L-H rate expression of PCE conversion in PCO (r_{PCE}) can be determined at steady state by:

$$r_{\text{PCE}} = I \cdot k \left(\frac{K_{\text{PCE}} K_{\text{H}_2\text{O}} C_{\text{PCE}} C_{\text{H}_2\text{O}}}{(1 + K_{\text{PCE}} K_{\text{H}_2\text{O}} C_{\text{PCE}} C_{\text{H}_2\text{O}})^2} \right) \quad 2.8$$

where I , k , K_{PCE} , and C_{PCE} are the same variables previously described for model M-2 while $K_{\text{H}_2\text{O}}$ and $C_{\text{H}_2\text{O}}$ represent the H₂O adsorption equilibrium constant in a single site (expressed in M⁻¹) and the H₂O gas phase concentration (in ppm), respectively. However, this model can be modified and rewritten as two different equations: if dual adsorption on two different types of sites of the catalyst surface is considered without (i) or with (ii) competition of PCE and H₂O molecules for the same type of site. These are the L-H bimolecular non-competitive two types of sites (M-4) and the L-H bimolecular competitive two types of sites (M-5) models, respectively. In this context, PCO rate of PCE (r_{PCE}) can be described at steady-state as follows (M-4 and M-5, respectively) [8, 10, 15, 23, 27, 29]:

$$r_{\text{PCE}} = I \cdot k \left(\frac{K_{\text{PCE}} C_{\text{PCE}}}{1 + K_{\text{PCE}} C_{\text{PCE}}} \right) \left(\frac{K_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}}}{1 + K_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}}} \right) \quad 2.9$$

$$r_{\text{PCE}} = I \cdot k \left(\frac{K_{\text{PCE},1} C_{\text{PCE}}}{1 + K_{\text{PCE},1} C_{\text{PCE}} + K_{\text{H}_2\text{O},1} C_{\text{H}_2\text{O}}} \right) \left(\frac{K_{\text{H}_2\text{O},2} C_{\text{H}_2\text{O}}}{1 + K_{\text{PCE},2} C_{\text{PCE}} + K_{\text{H}_2\text{O},2} C_{\text{H}_2\text{O}}} \right) \quad 2.10$$

where I , k , K_{PCE} , $K_{\text{H}_2\text{O}}$, C_{PCE} , and $C_{\text{H}_2\text{O}}$ are once again the variables previously described for model M-3, and in eq. 2.10, $K_{\text{PCE},1}$, $K_{\text{PCE},2}$, $K_{\text{H}_2\text{O},1}$, and $K_{\text{H}_2\text{O},2}$ are the PCE and H₂O adsorption equilibrium constants on the two types of sites (1 and 2), respectively.

A more complex model was also proposed (M-6), based on quantum efficiencies and incident photon flux to derive the rate equation of PCE conversion in PCO (r_{PCE}) [23]:

$$r_{\text{PCE}} = \left(\frac{\alpha_1 C_{\text{PCE}} C_{\text{H}_2\text{O}}}{(1 + K_{\text{PCE}} C_{\text{PCE}} + K_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}})^2} \right) \left(\sqrt{1 + I \frac{\alpha_2 \cdot \varphi (1 + K_{\text{PCE}} C_{\text{PCE}} + K_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}})}{C_{\text{H}_2\text{O}}}} - 1 \right) \quad 2.11$$

where two kinetic coefficients are considered, α_1 and α_2 (expressed $\mu\text{mol m s}^{-1} \mu\text{M}^{-1}$ and $\text{W}^{-1} \text{m}^2$, respectively), and φ is the wavelength averaged quantum efficiency.

All reported models assume that intermediates and/or reaction products do not influence PCE kinetics of conversion through PCO, considering that only PCE and H_2O are the major species; the only exception is M-2 that disregards H_2O adsorption.

The mathematical model combined with each suggested rate expression was solved numerically in gPROMS environment (Process System Enterprise, London, UK), using the orthogonal collocation on finite elements method. The number of elements used was 90 with third order polynomials (two interior collocation points); an absolute and relative tolerance of 1×10^{-5} was considered. The estimation of the unknown kinetic and equilibrium parameters resulting from the application of models M-1 to M-6, eqs. (2.6) - (2.11), in the complete mathematical model (see eqs. (2.1) - (2.5), in Theoretical Section 2.3.1) were performed through a sequential quadratic programming algorithm (gPROMS, Process System Enterprise, London, UK). This algorithm is based on the Newton method for unconstrained optimization, employing the first order derivative to determine its search direction.

2.4. Results and discussion

2.4.1. UV photolysis of PCE

Direct photolysis of PCE was evaluated in a lab-scale prototype (Figure 2.1). For the same experimental conditions, direct photolysis of PCE was studied employing the photoreactor with a quartz inner tube and without catalyst.

VOCs in contaminated air streams (in this particular case, PCE) are able to absorb light over a wide range of wavelengths; however, the absorption is often more stronger at shorter wavelengths [30]. Figure 2.4a shows the transmissivity of both photoreactor glass and quartz inner tubes in comparison to the solar spectrum (solar spectrum reported by Malato *et al.* (2002) used as reference [30]). Thus, if a glass tube is used as inner jacket of the reactor, it will absorb most of the UV radiation (see Figure 2.4a). On the other hand, the quartz tube is transparent to UV short wavelengths (high energy), as shown in Figure 2.4a. Thus, using the latter, direct photolysis of PCE with UVC leads to ionization (Figure 2.4b), resulting in removal of chlorine

radicals from PCE molecules (~98 % of conversion). When the glass inner tube is used the shorter wavelengths of the radiation are absorbed by the glass tube, and no conversion of PCE is observed (Figure 2.4b); however, the apparatus with the glass inner tube (where the amount of UVC radiation that passes through the glass tube mimics the UV sunlight radiation; see Figure 2.4a) is particularly more interesting for real case applications: an UV source significantly increases the operation cost of the process [31].

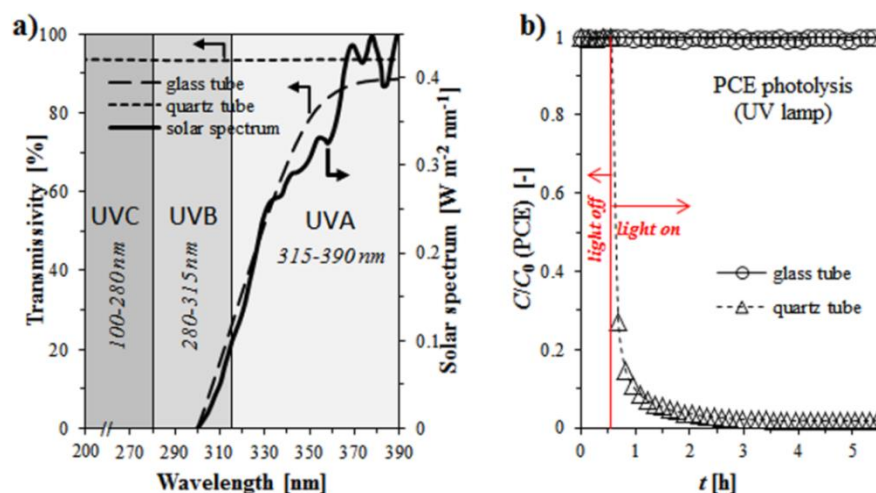


Figure 2.4. a) Transmissivity of glass (----) and quartz (—) inner tubes compared to the solar spectrum at sea level (—, [30]). b) PCE photolysis using different photoreactor inner tubes: glass (—○—) and quartz (—△—); $C_{\text{PCE, feed}} = 1221$ ppm, $Q_{\text{feed}}^* = 150$ cm³ min⁻¹, $RH = 40$ %, and $T = 298$ K; operation conditions reported in Table 2.2 * measured at 298 K and 1 bar.

2.4.2. UV-TiO₂ photocatalytic conversion of PCE

2.4.2.1. Influence of operation parameters

Besides the catalyst optical properties, PCE gas-phase photooxidation also depends on the optical properties of the materials used in the reactor construction. As mentioned before, prior to enter in the reactor, a large fraction of the UV radiation is absorbed by the glass inner tube of the photoreactor; it was measured an incident irradiance (I) of 0.8 W m^{-2} , when the radiometer was placed on the outside of the glass inner tube and in contact with it. Afterwards, part of the remaining UV radiation is absorbed by the glass spheres; the rest is absorbed by the TiO₂ P25 catalyst powder, transmitted through the voids between the catalyst particles and/or glass spheres, as well as reflected on the surface of both materials. Since an irradiance of $\sim 0.4 \text{ W m}^{-2}$ was measured outside of the photoreactor and considering both “shading effects” and the fact that a gradient in UV intensity exists in the radial direction due to a simple geometric $2 \times (d_{\text{ot},i} - d_{\text{in},e})^{-1}$ factor [13-17], an averaged irradiance of 0.5 W m^{-2} was assumed throughout the photocatalytic

bed.

UV-TiO₂ photocatalytic conversion tests of PCE were carried out in the lab-scale photoreactor previously described in section 2.1.1.2. Note that no changes in PCE level were observed in the absence of radiation throughout all experiments. PCE conversion in PCO ($C_{\text{PCE, Exit}} / C_{\text{PCE, Feed}}$) was determined under steady-state conditions as a function of three parameters: PCE concentration (574 – 2442 ppm), feed flow rate (59 - 300 cm³ min⁻¹) and humidity content (12 – 40 %), all measured at 298 K and 1 bar. Figure 2.5 discloses the effects PCE conversion through PCO for air feed streams contaminated with different concentrations of PCE (Table 2.2: runs 1 - 6), Figure 2.6 shows PCE contaminated air applying different feed flow rates (Table 2.2: runs 1, 7 - 10), and Figure 2.7 when applying different humidity contents (Table 2.2: runs 1, 11 - 13).

Figure 2.5 shows that the PCE conversion decreases with the feed concentration of PCE ($C_{\text{PCE, feed}}$).

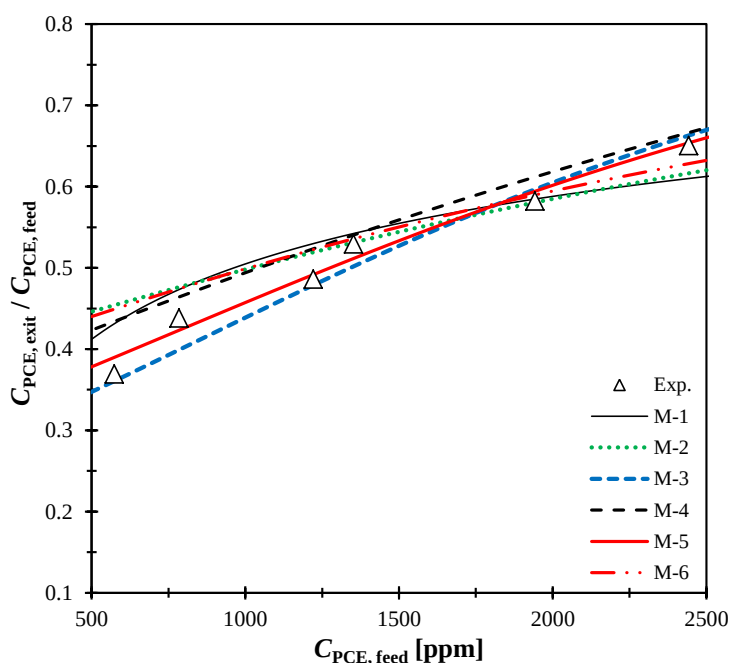


Figure 2.5. Effect on PCE conversion fraction through PCO ($C_{\text{PCE, exit}} / C_{\text{PCE, feed}}$ at steady-state conditions) for air feed streams contaminated with different concentrations of PCE [$C_{\text{PCE, feed}}$]: experimental points (Δ) and M-1 (—), M-2 (·····), M-3 (---), M-4 (- · -), M-5 (—), M-6 (- · ·); $Q_{\text{feed}}^a = 150 \text{ cm}^3 \text{ min}^{-1}$, $RH^a = 40 \%$, $T = 298 \text{ K}$, and $I = 0.8 \text{ W m}^{-2}$; operation conditions reported in Table 2.2 (runs 1-6) [^a measured at 298 K and 1 bar].

For a 4.25 fold increase in PCE concentration feed, the PCE conversion decreases about 1.8 times. This is due to the fact that more PCE molecules passes through the catalytic bed

without being decomposed, either by the hydroxyl or chlorine radicals, or by direct surface oxidation (higher amount of molecules passing through “shadowed” zones) [26]. This “shading effect” can be minimized: *e.g.*, employing transparent monoliths for supporting a thin catalytic film [13-17].

According to Figure 2.6, increasing the feed flow rate (Q_{feed}), higher surface velocities are achieved while the residence time decreases. A substantial reduction of the residence time (~ 5 fold) will appreciatively reduce the contact time between PCE molecules both with bulk hydroxyl radicals and surface electron-hole pairs, leading to poor degrees of conversion. Competitive adsorption between H₂O and PCE molecules to the available hydroxyl adsorption sites, may affect the process efficiency [10]. Therefore, the effect on PCE conversion in PCO for PCE contaminated air applying different humidity contents was also evaluated.

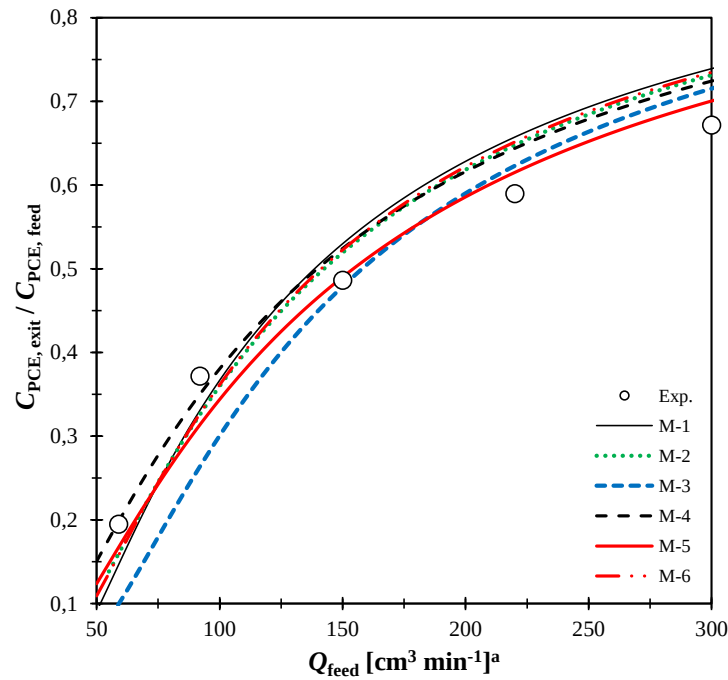


Figure 2.6. Effect on PCE conversion fraction through PCO ($C_{\text{PCE, Exit}} / C_{\text{PCE, Feed}}$, at steady-state conditions) for air contaminated with PCE applying different feed flow rates [Q_{feed}]: experimental points (○) and M-1 (—), M-2 (·····), M-3 (---), M-4 (- · - ·), M-5 (—), M-6 (- · · ·); $C_{\text{PCE, feed}} = 1221$ ppm, $RH^a = 40\%$, $T = 298$ K, and $I = 0.8$ W m⁻²; operation conditions reported in Table 2.2 (runs 1, 7-10) [^a measured at 298 K and 1 bar].

Figure 2.7 shows that reducing the relative humidity (RH), the PCE conversion merely decreased ~ 1.2 times. This observation was also reported by Yamazaki *et al.* (2001) [32], after stating that, if mole fraction of H₂O is 50 - 60 times higher than that of PCE, the conversion decreases due to PCE/H₂O competition for the same TiO₂ surface adsorption sites. In our case the

mole fraction of H_2O at 40 % of RH is approximately 7 times higher than that of PCE. Clearly, water molecules are a key factor for the formation of hydroxyl radicals but, within the RH range studied, this parameter plays a secondary role in comparison to other parameters. Furthermore, it must be pointed out that, since the PCE conversion by UV photolysis (using this apparatus scheme: reactor inner tube of glass) was negligible, the photoactivity of the TiO_2 P25 catalyst promoted the gas-phase photooxidation of PCE (see Figures 2.5 to 2.7).

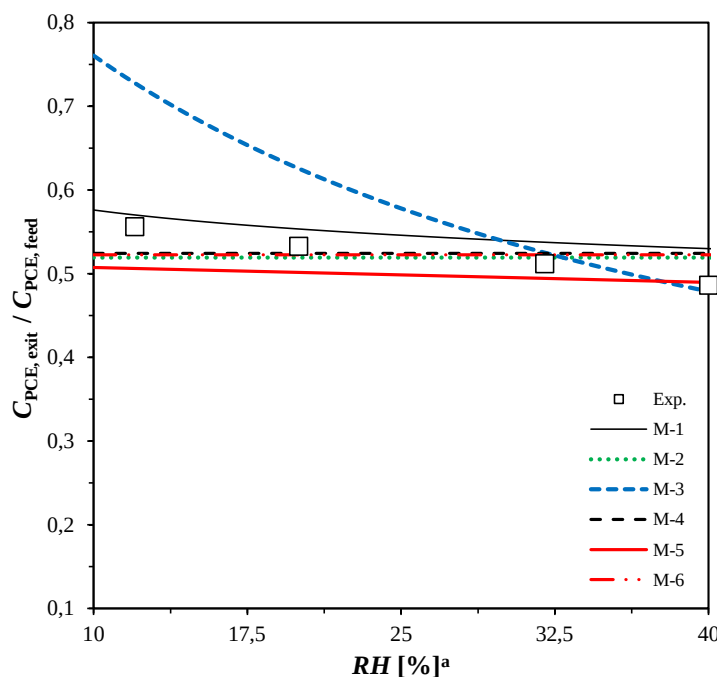


Figure 2.7. Effect on PCE conversion fraction through PCO ($C_{PCE, exit} / C_{PCE, feed}$ at steady-state conditions) for air contaminated with PCE applying different humidity contents [RH]: experimental points ($\square$) and M-1 (—), M-2 (·····), M-3 (---), M-4 (-.-), M-5 (—), M-6 (-.-.-); $C_{PCE, feed} = 1221$ ppm, $Q_{feed}^a = 150$ cm³ min⁻¹, $T = 298$ K, and $I = 0.8$ W m⁻²; operation conditions reported in Table 2.2 (runs 1, 11-13) [^a measured at 298 K and 1 bar].

2.4.2.2. Mathematical modelling

Within this work, six kinetics expressions were employed in a complete mathematical model for simulating the PCE kinetics of conversion through PCO (see eqs. (2.1)-(2.11)). Table 2.3 reports the kinetic and adsorption equilibrium parameters resulting from model fitting to experimental data in the UV- TiO_2 PCO of PCE. Our measurements on the PCE conversion, when applying feed streams of air with different pollutant concentrations, are qualitatively well fitted by all models, except M-1 and M-2 (see Figure 2.5). However, M-3 (and also M-1) fails to produce an acceptable fit when different feed flow rates are used (Figure 2.6). In addition, M-3 completely fails to fit the change in humidity (Figure 2.7). According to Table 2.3 and Figures 2.5 to 2.7,

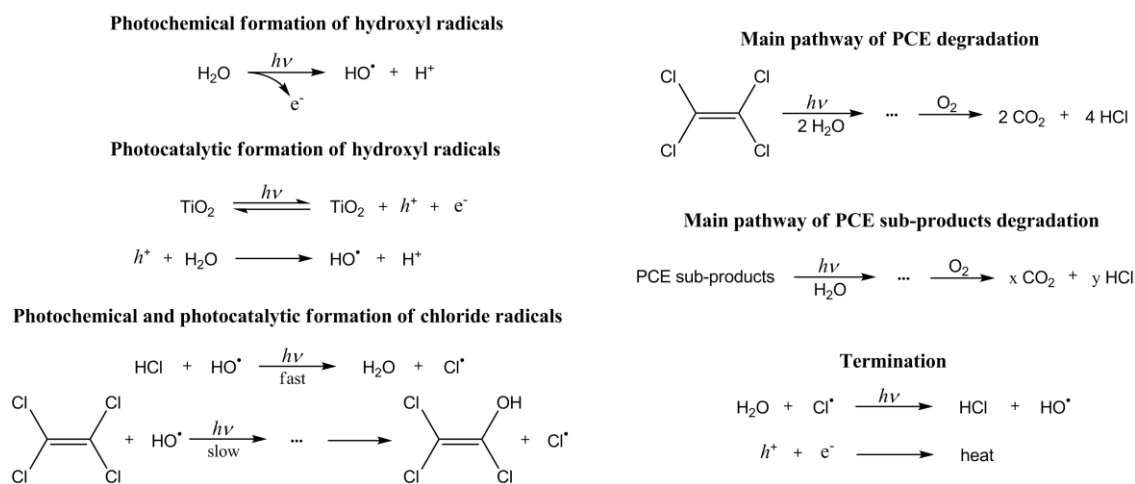
M-4, M-5 and M-6 produce the best fit results, suggesting that regardless the competition of PCE and H₂O molecules to the surface, they must be considered independent and targeting different active sites of the photocatalyst. From a purely statistical stand point, the M-5 model produces the best fit for the existing data; however, for the sake of simplicity, due to the least number of required parameters the L-H bimolecular non-competitive two types of sites model (M-4) is more appropriate to describe the experimental data.

Table 2.3. Kinetic and adsorption equilibrium parameters resulting from the application of rate expressions M-1 to M-6 in the complete mathematical model, including the statistical parameter squared correlation coefficient (R^2) and sum of squared residuals between experimental and calculated rates (S^2_R).

<i>Kinetic parameters</i>					
Model	Par.	Values	Units	R^2	$S^2_R \times 10^6$ [mol ² m ⁻⁴ s ⁻²]
M-1	k'	1.16×10^{-3}	mol m ⁻² s ⁻¹ W ⁻¹ m ² M ^{0.76}	0.978	6.06
	α	0.67	—		
	β	0.09	—		
M-2	k	1.44×10^{-3}	mol m ⁻² s ⁻¹ W ⁻¹ m ²	0.982	4.46
	K_{PCE}	12.1	M ⁻¹		
M-3	k	2.63×10^{-3}	mol m ⁻² s ⁻¹ W ⁻¹ m ²	0.938	17.0
	K_{PCE}	1.06×10^{-3}	M ⁻¹		
	K_{H_2O}	1.57×10^{-2}	M ⁻¹		
M-4	k	2.33×10^{-2}	mol m ⁻² s ⁻¹ W ⁻¹ m ²	0.988	3.34
	K_{PCE}	0.492	M ⁻¹		
	K_{H_2O}	2.49	M ⁻¹		
M-5	k	1.10×10^{-2}	mol m ⁻² s ⁻¹ W ⁻¹ m ²	0.991	3.22
	$K_{PCE,1}$	1.21	M ⁻¹		
	$K_{H_2O,1}$	1.01×10^{-7}	M ⁻¹		
	$K_{PCE,2}$	9.98×10^{-5}	M ⁻¹		
M-6	α_1	4.21	mol m s ⁻¹ M ⁻¹	0.984	4.94
	$\alpha_2 \times \varphi$	8.57×10^{-3}	W ⁻¹ m ²		
	K_{PCE}	14.0	M ⁻¹		
	K_{H_2O}	9.97×10^{-9}	M ⁻¹		

2.4.3. PCO reaction of PCE: product analysis and reaction mechanism

Several studies have demonstrated that the photochemical or photocatalytic conversion of PCE can occur through two initiation steps: hydroxyl radical (HO[•]) and chlorine radical (Cl[•]) pathways [2, 32-34]. Under UV radiation, the main pathways for the gas-phase photooxidation of PCE are: the photochemical or photocatalytic HO[•] and Cl[•] formation, the complete mineralization of PCE and its by-products, and the termination reactions (see Scheme 2.1) [2].

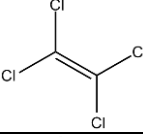
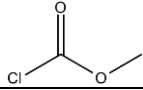
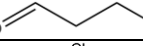
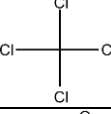
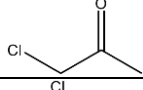
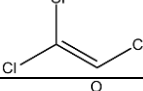
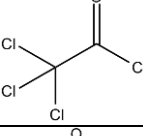
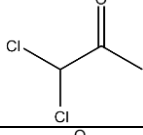
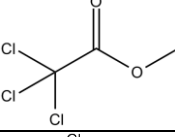
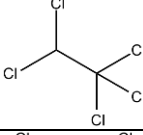


Scheme 2.1 Main pathways for the gas-phase photooxidation of PCE under UV radiation; adapted from Petit *et al.* (2007) [2].

Yamazaki *et al.* (2001, 2004) [32, 33] reported theoretical calculations which have demonstrated that $\text{HO}^\bullet$ addition to PCE is more exothermic than the addition of $\text{Cl}^\bullet$ (43.8 and 9.2 kcal mol⁻¹, respectively); the authors also stated that $\text{Cl}^\bullet$ initial reaction rarely occurs on the catalyst surface [32, 33]. On the other hand, after comparison of kinetic data published in literature [35-46], Nicovich *et al.* (1996) [47] reported that the reaction rate coefficient for $\text{Cl}^\bullet$ addition to PCE is several hundred times faster than the reaction rate coefficient for addition of $\text{HO}^\bullet$ to PCE [2, 47]; additionally, Thüner *et al.* (1999) [48] demonstrated that it is 2.35 fold faster than $\text{HO}^\bullet$ addition (at 298 K and 1 atm). Consequently, the addition of $\text{HO}^\bullet$ to PCE can be neglected.

Product analysis by GC/MSD for PCE photochemical reaction (quartz inner tube) and PCE photocatalytic reaction (glass inner tube) isolated the intermediates described in Tables 3.4 and 3.5, respectively (experimental conditions detailed in Table 2.2). Taking into consideration the identified by-products, we propose the reaction mechanism described in Scheme 2.2 for both direct and photocatalytic conversion of PCE under UV radiation. Numerous pathways (A_1 to E_4) were proposed in order to cover all by-products formed (intermediates in brackets: 1 to 9).

Table 2.4. Product analysis by GC/MSD for PCE photochemical reaction (reactor with a quartz inner tube); experimental conditions described in Table 2.2 (UV photolysis, run 1).

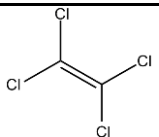
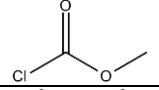
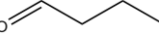
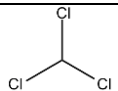
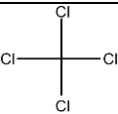
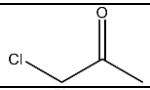
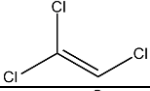
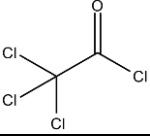
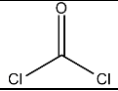
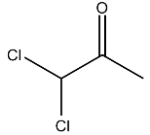
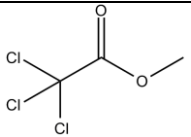
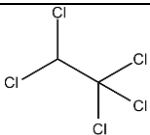
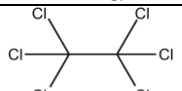
<i>Gas-phase photooxidation of PCE under UV photolysis (quartz inner tube)</i>					
Compound (i)	Molecular		CAS no.	C_i [ppm] ^a	$C_{i, C-PCE}$ [ppm] ^c
	Formula	Structure			
Perchloroethylene ^b	C ₂ Cl ₄		127-18-4	22.3	3.23
Methyl chloroformate	C ₂ H ₃ ClO ₂		79-22-1	1.31	0.33
Butanal	C ₄ H ₈ O		123-72-8	0.06	0.04
Chloroform	CHCl ₃		67-66-3	0.85	0.09
Carbon tetrachloride	CCl ₄		56-23-5	0.26	0.02
Chloroacetone	C ₃ H ₅ ClO		78-95-5	---	---
Trichloroethylene	C ₂ HCl ₃		79-01-6	0.03	0.005
Trichloroacetyl chloride	C ₂ Cl ₄ O		76-02-8	---	---
Phosgene	CCl ₂ O		75-44-5	---	---
1,1-dichloroacetone	C ₃ H ₄ Cl ₂ O		513-88-2	0.004	0.001
Methyl trichloroacetate	C ₃ H ₃ Cl ₃ O ₂		598-99-2	0.37	0.08
Pentachloroethane	C ₂ HCl ₅		76-01-7	0.002	0.0002
Hexachlorethane	C ₂ Cl ₆		67-72-1	0.02	0.002

^a VOC concentration of the major compounds was calculated using the response factor of toluene, except for PCE and trichloroethylene, for which specific response factors were used (calibrations solutions).

^b PCE concentration of the feed stream was analysed by MGC: $C_{PCE, feed} = 1221$ ppm; $C_{C-PCE, feed} = 177$ ppm, where $C_{C-PCE, feed}$ is the carbon atoms concentration of PCE on the feed stream.

^c $C_{i, C-PCE}$ stands for carbon atoms concentration of compound i formed by PCE conversion (ppm).

Table 2.5. Product analysis by GC/MSD for PCE photocatalytic reaction (reactor with a glass inner tube); experimental conditions described in Table 2.2 (UV-TiO₂ photocatalysis, run 1).

<i>Gas-phase photooxidation of PCE under UV-TiO₂ photolysis (glass inner tube)</i>					
Compound (i)	Molecular		CAS no.	C _i ^a [ppm]	C _{i, C-PCE} ^c [ppm]
	Formula	Structure			
Perchloroethylene ^b	C ₂ Cl ₄		127-18-4	594	86
Methyl chloroformate	C ₂ H ₃ ClO ₂		79-22-1	0.006	0.002
Butanal	C ₄ H ₈ O		123-72-8	0.02	0.02
Chloroform	CHCl ₃		67-66-3	0.53	0.05
Carbon tetrachloride	CCl ₄		56-23-5	1.2	0.09
Chloroacetone	C ₃ H ₅ ClO		78-95-5	---	---
Trichloroethylene	C ₂ HCl ₃		79-01-6	0.007	0.001
Trichloroacetyl chloride	C ₂ Cl ₄ O		76-02-8	---	---
Phosgene	CCl ₂ O		75-44-5	---	---
1,1-dichloroacetone	C ₃ H ₄ Cl ₂ O		513-88-2	0.03	0.008
Methyl trichloroacetate	C ₃ H ₃ Cl ₃ O ₂		598-99-2	0.006	0.001
Pentachloroethane	C ₂ HCl ₅		76-01-7	---	---
Hexachlorethane	C ₂ Cl ₆		67-72-1	0.1	0.01

^a VOC concentration of the major compounds was calculated using the response factor of toluene, except for PCE and trichloroethylene, for which specific response factors were used (calibrations solutions).

^b PCE concentration of feed and exit streams were analysed by MGC: $C_{\text{PCE, feed}} = 1221$ ppm; $C_{\text{C-PCE, feed}} = 177$ ppm where $C_{\text{C-PCE, feed}}$ is the carbon atoms concentration of PCE on the feed stream.

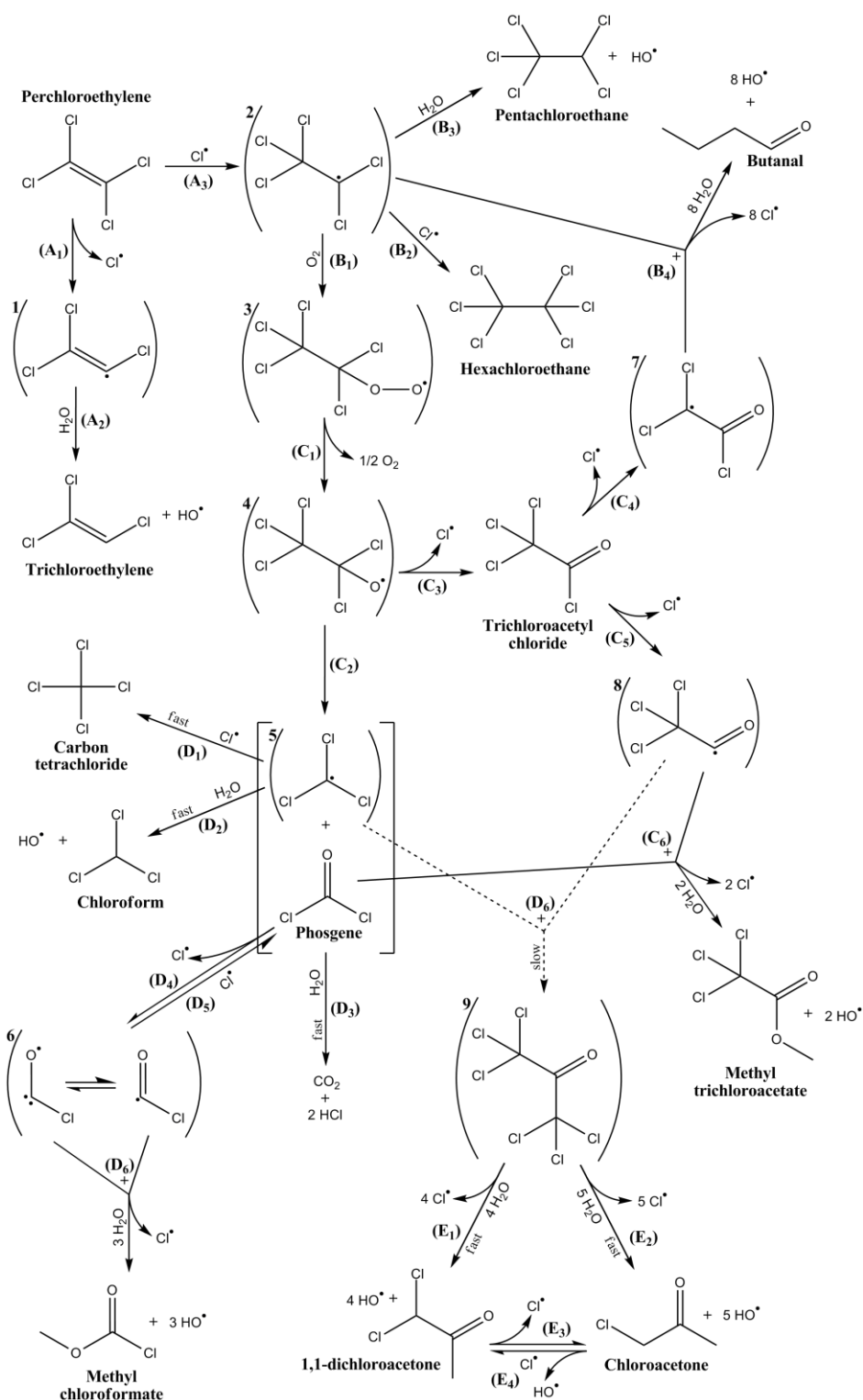
^c $C_{\text{i, C-PCE}}$ stands for carbon atoms concentration of compound i formed by PCE conversion (ppm).

According to Scheme 2.2, PCE can suffer a reductive dechlorination under UV radiation (A₁), leading to the formation of intermediate **1** (trichloroethenyl radical); its reaction with water (A₂) generates the by-product trichloroethylene (C₂HCl₃). Nevertheless, PCE can also react with Cl[•] (A₃), leading to the formation of intermediate **2** (pentachloroethyl radical); then, **2** can react with O₂ (B₁) generating **3** (pentachloroethaneperoxy radical), followed by its dimerization (C₁), decomposing into **4** (pentachloroethoxyl radical) and oxygen. The cleavage of the C–C bond of the intermediate **4** (C₂), yields to **5** (trichloromethyl radical) and phosgene (CCl₂O) formation [9, 32, 49, 50]. The trichloromethyl radicals (**5**) can react with Cl[•] (D₁) as well as with water (D₂), yielding to the by-products carbon tetrachloride (CCl₄) and chloroform (CHCl₃), respectively. As reported by Suárez *et al.* (2011) [51], the generation of highly toxic phosgene through PCO of a similar halogenated organic compound (trichloroethylene) is unclear: some authors observed the COCl₂ production [51-54], in contrast to many others that stated that humidification promotes the phosgene hydrolysis reaction [32, 50, 55-57]. In this case, phosgene could not be detected as by-product of both reactions (photochemical and photocatalytic) due to its reaction with water (D₃), forming the mineralized final products carbon dioxide and hydrochloric acid [32, 50]. According to Montgomery and Rollefson (1934) [58] and other researchers [59-61], it was also proposed a sequential decomposition mechanism (D₄) via formation of the intermediate **6** (chloroformyl radical). This thermally instable radical (**6**) is known as an intermediate in photochemical induced formation of phosgene (D₅) [62]; but, the chloroformyl radicals (**6**) can also react between each other and, in the presence of water followed by Cl[•] elimination (D₆), the by-product methyl chloroformate (C₂H₃ClO₂) and hydroxyl radicals are formed.

Regarding intermediate **2** (pentachloroethyl radical), it can also react with Cl[•] in the gas phase (B₂), leading to formation of by-product hexachlorethane (C₂Cl₆); or, if it reacts with water (B₃), it generates another identified by-product, pentachloroethane (C₂HCl₅) and HO[•] [9, 47]. Intermediate **4** (pentachloroethoxyl radical) can generate by-product trichloroacetyl chloride (C₂Cl₄O), after a chlorine radical subtraction (C₃) [49]. Another Cl[•] elimination may yields to intermediates **7** (1,1,2-trichloro-2-oxoethyl radical) or **8** (2,2,2-trichloro-1-oxoethyl radical) (C₄ and C₅, respectively). When intermediate **7** reacts with intermediate **2**, in the presence of water followed by Cl[•] elimination (B₄), the identified by-product butanal (C₄H₈O) and hydroxyl radicals are formed.

Besides, it is possible to occur in the gas phase the reaction between intermediate **8** (2,2,2-trichloro-1-oxoethyl radical) and phosgene; thus, in the presence of water followed by Cl[•] subtraction (G₆), by-product methyl trichloroacetate (C₃H₃Cl₃O₂) and hydroxyl radicals are obtained. On the other hand, if intermediate **8** (2,2,2-trichloro-1-oxoethyl radical), reacts with a trichloromethyl radical (**5**), the unstable intermediate **9** (2-propanone, hexachloro-) is generated

(D₆); subsequent multiple chlorine radicals subtraction in water media results in the formation of by-products 1,1-dichloroacetone (C₃H₃Cl₂O₂), chloroacetone (C₃H₃ClO₂), and hydroxyl radicals (E₁ to E₄).



Scheme 2.2. Reaction mechanism proposed for the gas-phase photooxidation of PCE under UV radiation; pathways: (A₁) to (E₄); intermediates in brackets: 1 to 9.

Results showed that ~ 98 % of PCE degraded (~ 97 % of PCE fed) in the non-catalytic experiment using the photoreactor with a quartz inner jacket were completely mineralized to CO₂, H₂O, and HCl. For the photocatalytic experiment, employing the glass inner tube, 99 % of PCE degraded (~ 51 % of PCE fed) were totally mineralized to final reaction products.

2.5. Conclusions

UVC photolysis has demonstrated that PCE conversion is negligible (~ 0 %) or almost complete (98 %), depending on the material of the concentric inner tube of the lab-scale single-pass continuous-flow annular photoreactor (depending on if it is made of glass or quartz, respectively). PCE conversion in PCO was evaluated upon three parameters: (1) for a 4.25 fold increase in PCE concentration feed, a reduction of ~44 % on the PCE conversion was observed; (2) increasing the feed flow rate (from 59 to 300 cm³ min⁻¹), a ~5 fold reduction of the residence time is observed, leading to poor degrees of conversion (~33 %); (3) for a 3.33 fold reduction in relative humidity, the PCO efficiency merely decreases ~1.2 times. The different kinetic rate expressions employed in the developed mathematical model for simulating the kinetics through PCO indicated that PCE and H₂O molecules may have to be considered in association with different specific active sites of the surface of the catalyst. It was also concluded that the L-H bimolecular non-competitive two types of sites model (M-4) describes better the experimental data. Under steady-state conditions, product analysis by GC/MSD for PCE pure photochemical reaction isolated the main following intermediates: methyl chloroformate; butanal; chloroform; carbon tetrachloride; methyl trichloroacetate. For the PCE photocatalytic reaction, butanal, chloroform, and carbon tetrachloride were the main isolated intermediates. The photochemical process leads to a 97 % PCE conversion with almost complete mineralization to CO₂, H₂O, and HCl. The photocatalytic approach leads to a 51 % PCE conversion with complete mineralization. Finally, a reaction mechanism was proposed for UV photolysis and UV-TiO₂ photocatalysis of PCE covering the formation of all identified intermediates and by-products.

2.6. References

- [1] D.-K. Lee, I.-C. Cho, *Microchem. J.* 68 (2001) 215-223.
- [2] N. Petit, A. Bouzaza, D. Wolbert, P. Petit, J. Dussaud, *Catal. Today* 124 (2007) 266-272.
- [3] G. Imoberdorf, H. Irazoqui, A. Cassano, O. Alfano, *Ind. Eng. Chem. Res.* 44 (2005) 6075-6085.
- [4] S.B. Kim, S.C. Hong, *Appl. Catal. B: Environ.* 35 (2002) 305-315.
- [5] S.B. Kim, H.T. Hwang, S.C. Hong, *Chemosphere* 48 (2002) 437-444.
- [6] J. Zhao, X. Yang, *Build. Environ.* 38 (2003) 645-654.
- [7] N. Fukami, M. Yosida, B.-D. Lee, K. Taku, M. Hosomi, *Chemosphere* 42 (2001) 345-350.
- [8] J. Mo, Y. Zhang, Q. Xu, J.J. Lamson, R. Zhao, *Atmos. Environ.* 43 (2009) 2229-2246.
- [9] C. Feiyan, S.O. Pehkonen, M.B. Ray, *Water Res.* 36 (2002) 4203-4214.
- [10] S. Wang, H.M. Ang, M.O. Tade, *Environ. Int.* 33 (2007) 694-705.
- [11] A.G. Kontos, A. Katsanaki, T. Maggos, V. Likodimos, A. Ghicov, D. Kim, J. Kunze, C. Vasilakos, P. Schmuki, P. Falaras, *Chem. Phys. Lett.* 490 (2010) 58-62.
- [12] P. Ávila, B. Sánchez, A.I. Cardona, M. Rebollar, R. Candal, *Catal. Today* 76 (2002) 271-278.
- [13] G.E. Imoberdorf, A.E. Cassano, H.A. Irazoqui, O.M. Alfano, *Chem. Eng. Sci.* 62 (2007) 1138-1154.
- [14] H.T. Chang, N.-M. Wu, F. Zhu, *Water Res.* 34 (2000) 407-416.
- [15] T.N. Obee, *Environ. Sci. Technol.* 30 (1996) 3578-3584.
- [16] G.B. Raupp, J.A. Nico, S. Annangi, R. Changrani, R. Annapragada, *AIChE J.* 43 (1997) 792-801.
- [17] H. Al-Ekabi, N. Serpone, E. Pelizzetti, C. Minero, M.A. Fox, R.B. Draper, *Langmuir* 5 (1989) 250-255.
- [18] ISO 16000-6. Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS or MS/FID, 2004.
- [19] D.M. Ruthven, *Principal of adsorption and adsorption processes*, John Wiley & Sons, New York, 1984.
- [20] C.R. Wilke, *Chem. Eng. Prog.* 46 (1950) 95-104.
- [21] R.B. Bird, W.E. Stewart, E.N. Lightfoot, *Transport Phenomena*, 2nd ed., Wiley International, Singapore, 2002.
- [22] J. Vrabec, J. Stoll, H. Hasse, *J. Phys. Chem. B* 105 (2001) 12126-12133.
- [23] G. Li Puma, I. Salvadó-Estivill, T.N. Obee, S.O. Hay, *Sep. Purif. Technol.* 67 (2009) 226-232.
- [24] R.M. Alberici, W.F. Jardim, *Appl. Catal. B: Environ.* 14 (1997) 55-68.
- [25] C.N. Satterfield, *Mass transfer in heterogeneous catalysis*, MIT Press, Massachusetts Institute of Technology, Cambridge, MA, USA, 1970.
- [26] K.-H. Wang, H.-H. Tsai, Y.-H. Hsieh, *Appl. Catal. B: Environ.* 17 (1998) 313-320.
- [27] T.N. Obee, R.T. Brown, *Environ. Sci. Technol.* 29 (1995) 1223-1231.
- [28] T.N. Obee, S.O. Hay, *Environ. Sci. Technol.* 31 (1997) 2034-2038.
- [29] J. Peral, X. Domènech, D.F. Ollis, *J. Chem. Technol. Biotechnol.* 70 (1997) 117-140.
- [30] S. Malato, J. Blanco, A. Vidal, C. Richter, *Appl. Catal. B: Environ.* 37 (2002) 1-15.
- [31] W.A. Jacoby, D. Blake, R.D. Noble, C.A. Koval, *J. Catal.* 157 (1995) 87-96.

- [32] S. Yamazaki, H. Tsukamoto, K. Araki, T. Tanimura, I. Tejedor-Tejedor, M.A. Anderson, *Appl. Catal. B: Environ.* 33 (2001) 109-117.
- [33] S. Yamazaki, T. Tanimura, A. Yoshida, K. Hori, *J. Phys. Chem. A* 108 (2004) 5183-5188.
- [34] S.-J. Hwang, C. Petucci, D. Raftery, *J. Am. Chem. Soc.* 120 (1998) 4388-4397.
- [35] J.S. Chang, F. Kaufman, *J. Chem. Phys.* 66 (1977) 4989-4994.
- [36] C.J. Howard, *J. Chem. Phys.* 65 (1976) 4771-4777.
- [37] K. Kirchner, D. Helf, P. Ott, S. Vogt, *Berich. Bunsen. Gesell.* 94 (1990) 77-83.
- [38] A.M. Winer, A.C. Lloyd, K.R. Darnall, J.N. Pitts, *J. Phys. Chem.* 80 (1976) 1635-1639.
- [39] P.B. Ayscough, A.J. Cocker, F.S. Dainton, S. Hirst, M. Weston, *Proc. Chem. Soc.* (1961) 244.
- [40] D.D. Davis, W. Braun, A.M. Bass, *Int. J. Chem. Kinet.* 2 (1970) 101-114.
- [41] J.A. Franklin, G. Huybrechts, C. Cillien, *Trans. Faraday Soc.* 65 (1969) 2094-2102.
- [42] P. Goldfinger, G. Huybrechts, G. Martens, *Trans. Faraday Soc.* 57 (1961) 2210-2219.
- [43] P. Goldfinger, M. Jeunehomme, G. Martens, *J. Chem. Phys.* 29 (1958) 456-458.
- [44] J. Knox, K.C. Waugh, *Trans. Faraday Soc.* 65 (1969) 1585-1594.
- [45] R. Atkinson, S.M. Aschmann, *Int. J. Chem. Kinet.* 19 (1987) 1097-1105.
- [46] F.W. Breitbarth, S. Rottmayer, *Plasma Chem. Plasma P.* 6 (1986) 381-399.
- [47] J.M. Nicovich, S. Wang, M.L. McKee, P.H. Wine, *J. Phys. Chem.* 100 (1996) 680-688.
- [48] L.P. Thüner, I. Barnes, K.H. Becker, T.J. Wallington, L.K. Christensen, J.J. Orlando, B. Ramacher, *J. Phys. Chem. A* 103 (1999) 8657-8663.
- [49] R.M. Alberici, M.A. Mendes, W.F. Jardim, M.N. Eberlin, *J. Am. Soc. Mass Spectr.* 9 (1998) 1321-1327.
- [50] S. Yamazaki-Nishida, X. Fu, M.A. Anderson, K. Hori, *J. Photochem. Photobiol. A* 97 (1996) 175-179.
- [51] S. Suárez, N. Arconada, Y. Castro, J.M. Coronado, R. Portela, A. Durán, B. Sánchez, *Appl. Catal. B: Environ.* 108-109 (2011) 14-21.
- [52] S. Suárez, J.M. Coronado, R. Portela, J.C. Martín, M. Yates, P. Avila, B. Sánchez, *Environ. Sci. Technol.* 42 (2008) 5892-5896.
- [53] M.D. Hernández-Alonso, S. García-Rodríguez, S. Suárez, R. Portela, B. Sánchez, J.M. Coronado, *Catal. Today* 206 (2013) 32-39.
- [54] W.A. Jacoby, M.R. Nimlos, D.M. Blake, R.D. Noble, C.A. Koval, *Environ. Sci. Technol.* 28 (1994) 1661-1668.
- [55] S. Yamazaki-Nishida, K.J. Nagano, L.A. Phillips, S. Cervera-March, M.A. Anderson, *J. Photochem. Photobiol. A* 70 (1993) 95-99.
- [56] W.A. Zeltner, C.G. Hill Jr, M.A. Anderson, *Chemtech* 23 (1993) 21-29.
- [57] J. Fan, J.T. Yates, *J. Am. Chem. Soc.* 118 (1996) 4686-4692.
- [58] C.W. Montgomery, G.K. Rollefson, *J. Am. Chem. Soc.* 56 (1934) 1089-1092.
- [59] Z.B. Vukmirović, S.V. Ribnikar, *J. Chem. Phys.* 66 (1977) 7-12.
- [60] T. Einfeld, A. Chichinin, C. Maul, K.-H. Gericke, *J. Chem. Phys.* 116 (2002) 2803-2810.
- [61] S.-H. Chen, L.-K. Chu, Y.-J. Chen, I.C. Chen, Y.-P. Lee, *Chem. Phys. Lett.* 333 (2001) 365-370.
- [62] T. Krossner, L. Zülicke, M. Staikova, S.D. Peyerimhoff, *Chem. Phys. Lett.* 241 (1995) 511-515.

3. Gas-phase solar photocatalysis of PCE and n-decane over different TiO₂ photocatalysts using a lab-scale fixed bed annular photoreactor

The present chapter reports studies on the photocatalytic oxidation (PCO) of n-decane and PCE using an annular photoreactor packed with a cellulose acetate monolithic structure coated with two commercially available TiO₂, namely PC500 and P25, irradiated by simulated solar light and equipped with a compound parabolic collector, CPC. The influence of the type of photocatalytic film, Q_{feed} , $C_{\text{VOC, feed}}$, RH, oxygen and I on the pollutants PCO. PC500 film showed higher conversion of VOCs in comparison to that of P25 film. Photocatalytic conversions close to 100 % were obtained for n-decane and PCE ($C_{\text{dec, feed}} = 71$ ppm and $C_{\text{PCE, feed}} = 1095$ ppm, respectively) when $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$, $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$ ($\tau = 88$ s), and $\text{RH} = 40$ %. The mineralization of PCE ($C_{\text{PCE, feed}} = 1095$ ppm) showed no differences over both photocatalytic films. Over PC500 film the complete mineralization of n-decane ($C_{\text{dec, feed}} = 71$ ppm) was observed while over P25 film only 69 % was mineralized in the following conditions $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$ ($\tau = 88$ s), $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ and $\text{RH} = 40$ %. Competitive adsorption between the VOC and water molecules on the TiO₂ film surface was observed above 20 % of RH. Low RH results suggest that $\text{Cl}^\bullet$ radicals chain propagation reactions may be involved in the PCO mechanism of PCE. Finally, the absence of oxygen drastically impairs the photoreaction.

This chapter is based on the research article “Monteiro, R.A.R., Miranda, S.M.M., Rodrigues-Silva, C., Faria, J.L., Silva, A.M.T., Boaventura, R.A.R., Vilar, V.J.P., Gas phase oxidation of n-decane and PCE by photocatalysis using an annular photoreactor packed with a monolithic catalytic bed coated with P25 and PC500, Applied Catalysis B: Environmental, in press, DOI: 10.1016/j.apcatb.2014.10.026”.

3.1. Introduction

VOCs represent a very active group of air pollutants discharged into the atmosphere by household and industrial activities, such as fuel combustion, residential cleaning agents, among several others. For example, Teixeira *et al.* [1] reported a large concentration of VOCs (including PCE and *n*-decane) in the indoor air of different stages of a wastewater treatment plant (WWTP), mainly associated with the aeration and mechanical agitation processes, as well as with the different sludge treatment stages. PCE, in particular, is widely used as model target pollutant due to its toxicity and carcinogenic potential to humans.

Since the pioneer work by Fujishima and Honda in 1972 [2], the interest on photocatalytic processes applied to environmental issues has been growing every year, not only regarding photocatalytic processes (PCO) for water/wastewater treatment applications, but also for air purification [3-5]. The degradation of air pollutants by PCO is an attractive and efficient route when compared to other conventional techniques, such as adsorption on activated carbon, since the photocatalytic semiconductors are able to mineralize the pollutants, instead of a simple and more common phase transfer.

Several semiconductors are often employed as photocatalysts [6-11] and among them, TiO₂ (also known as titania) stands out as one of the most photoactive [12] under UV radiation. A number of commercial photocatalytic TiO₂ powders are available on the market, being TiO₂ Aeroxide P25 from Evonik® the most commonly employed [13]. It is generally accepted that the high activity of P25 comes from the formation of heterojunctions between the two types of crystalline phases, anatase (80%) and rutile (20%), which may also explain the low activity of P25 under visible light in some particular cases [14]. Specifically, rutile, owing to its lower conduction band, may absorb some light in the visible range (red) and thus serve as a photosensitizer of the anatase phase. The respective positions and the difference between the higher energy levels of the conduction bands of the two phases may cause a transfer of electrons from anatase towards rutile, preventing at the same time charge recombination [15].

Although the actuating mechanism of pure anatase is well established, as regards P25 it has been over the years a matter of debate [16, 17]. In a study conducted by Hajaghazadeh *et al.* [18], PC500 (consisting of 100 % anatase) yielded a higher reaction rate than P25 in the degradation of gaseous methylethylketone under UVA light. The superior photocatalytic activity of PC500 was attributed to its higher specific surface area (SSA). Taranto *et al.* [19] also reported a slight higher photocatalytic activity of P25 over PC500 in the degradation of methanol and *n*-octane as gas-phase model pollutants. In another study conducted by Águia *et al.* [13], ten distinct commercially available photocatalysts were incorporated into a water-based exterior paint aiming

NO photoabatement. The highest yields were obtained with the catalysts consisting of 100% anatase, such as PC500.

Reactor geometry is also a key factor in gas-phase photocatalysis due to its influence on optimizing the catalyst exposure to both radiation and reactants [20]. The most common photoreactors are tubular, annular and flat plate types [20-22]. Regarding the photocatalyst structural configuration, thin-film powder layer and/or fluidized bed [21, 23], coated wall-parallel [24, 25] and honeycomb/foam monolithic reactors [26-28] are probably the most representative.

This chapter presents the results from a study on gas-phase solar photo-oxidation of two VOCs: *n*-decane and PCE. Two different commercially available TiO₂ photocatalysts (P25 from Evonik® and PC500 from Cristal®) were deposited onto the surface of a monolithic and transparent structure of cellulose acetate. Applying such structure into a annular reactor allows a high surface-area-to-volume ratio and a low pressure drop, typical of honeycomb reactors [29]. The photocatalytic efficiency of both photocatalytic films, using a continuous-flow annular photoreactor equipped with a compound parabolic collector (CPC), were compared. This configuration allows the illumination of the whole reactor perimeter and catalytic bed, enhancing therefore the photonic efficiency [30, 31]. The PCO of *n*-decane and PCE over PC500 and P25 films was studied for different operating conditions, namely the feed flow rate (Q_{feed}), feed VOC concentration ($C_{\text{dec, feed}}$ or $C_{\text{PCE, feed}}$), and incident irradiance (I). The influence of relative humidity (RH), and the presence or absence of oxygen, in the photodegradation of such compounds was also assessed using PC500 film. To the best of our knowledge, few papers have compared the efficiency of PC500 and P25 films in the gas-phase PCO of VOCs.

3.2. Experimental

3.2.1. Materials and methods

TiO₂ P25 and PC500 powders were supplied by Evonik® and Cristal®, respectively, and used as delivered, without further modification or purification. Some characteristics of PC500 and P25 powders provided by the suppliers are given in Table 3.1. Cellulose acetate monolithic structures (TIMax CA50-9/S – $L_C = 80$ mm, $d_{\text{ch}}^2 = 9$ mm $\times$ 9 mm, $e_{\text{w, ch}} = 0.1$ mm; Wacotech GmbH & Co. KG.) were used as substrate to affix the powders.

The reagents used for the generation of humidified air streams contaminated with PCE as well as the gases provided by Air Liquide are described in sub-section 2.2.1 of Chapter 2. Additionally, *n*-decane (≥ 94 %; CAS no. 124-18-5; Merck), was used without previous

purification.

Cellulose acetate monolithic structures were evenly coated using aqueous suspensions of P25 and PC500 by the dip-coating method (Dip-Coater RDC21-K, Bungard Elektronik GmbH & Co. KG.). Before coating, the honeycomb structures were soaked for 1 h with distilled water and alkaline detergent (Derquim LM 01, Panreac Química, S.A.U.), subsequently washed with Milli-Q water, and dried at 323 K. The photocatalysts aqueous suspensions (2 % wt.) were sonicated for 10 min at 50 kHz in order to better disperse the particles. Based on Lopes *et al.* [32] work, where the influence of the number of layers upon the PCE photocatalytic conversion was assessed, nine layers of P25 or PC500 powder were deposited at a withdrawal rate of 0.8 mm s⁻¹ assuring a thin and uniform film of 0.850 to 1.150 µm of thickness (data not shown) on each substrate surface. It is worth noting that samples were dried at 323 K for 30 min between each layer deposition. Finally, the coated monolithic structures were assembled into the annular photocatalytic reactor (see section 2.2) for the PCO study of *n*-decane and PCE. The catalytic bed properties are also detailed in Table 3.1.

Table 3.1. Catalysts, catalytic bed properties and dimensions of the photoreactor employed in the PCO of *n*-decane and PCE under simulated solar radiation.

TiO₂ Catalysts		
PC500 (Cristal [®])		
	PCO of <i>n</i> -decane	PCO of PCE
Crystal structure	> 99 % Anatase	
Crystal size [nm]	5-10	
Surface area [m ² g ⁻¹]	345	
<i>m</i> _{PC500} [mg]	52.3	35.3
<i>ρ</i> _{A, PC500} [mg cm ⁻²]	6.48 × 10 ⁻²	4.38 × 10 ⁻²
P25 (Evonik [®])		
	PCO of <i>n</i> -decane	PCO of PCE
Crystal structure	80 % Anatase, 20 % Rutile	
Crystal size [nm]	21	
Surface area [m ² g ⁻¹]	50	
<i>m</i> _{P25} [mg]	74.7	100.4
<i>ρ</i> _{A, P25} [mg cm ⁻²]	9.26 × 10 ⁻²	1.24 × 10 ⁻¹
Photoreactor		
Outer tube	<i>d</i> _{ot, e} [cm]	5.00
(Pyrex-glass)	<i>d</i> _{ot, i} [cm]	4.64
Inner tube	<i>d</i> _{in, e} [cm]	2.00
(quartz)	<i>d</i> _{in, i} [cm]	1.64
Photoreactor	<i>L</i> _R [cm]	16.0
	<i>V</i> _R [cm ³]	220

3.2.2. Experimental setup and photocatalytic experiments

The schematic representation of the experimental setup is shown in Figure 3.1 which is carefully described in the Chapter 2 sub-section 2.2.2. However, a few issues regarding the experimental unit were updated at this stage of the work and are highlighted (dark) in Figure 3.1:

- Additional oxygen-free experiments were performed by replacing the flowing air by nitrogen and removing dissolved oxygen in water by replacing deionized water by a $10 \text{ g L}^{-1} \text{ Na}_2\text{SO}_3$ solution in the Woulff bottle.
- The UV lamp located inside the inner tube of the photoreactor used in Chapter 2 was replaced by the following devices (Figure 3.1b): *i*) a solar light simulator (Atlas, model Suntest XLS+) with 0.110 m^2 of working area illuminated by a 1700 W air-cooled Xenon arc lamp and an infrared coated quartz glass daylight filter reproducing the solar light spectrum within $300 < \lambda < 800 \text{ nm}$; *ii*) an electropolished anodized aluminium CPC with 0.023 m^2 of irradiated area able to use both direct and diffuse radiation [30, 31].
- The CO_2 concentration of the photoreactor feed/exit stream was monitored online using an Indoor Air IAQ-Calc™ quality meter 7545 (TSI, Inc.).

Table 3.1 summarizes the tube dimensions of the photoreactor and Figure 3.1b₁ and b₂ schematically represent the side and frontal views of the lab-scale annular photoreactor, respectively.

Gas-phase PCE and *n*-decane concentration histories were monitored using the gas chromatograph (and method) described in sub-section 2.2.2 of Chapter 2. For *n*-decane analysis the oven temperature initially starts at 343 K for 1.2 min, after which raises up to 351 K using a 2 K min^{-1} heating ramp followed by a heating ramp of 30 K min^{-1} until reaching 433 K. Appendix A presents a detailed description of the data treatment as well as the calibration curves for PCE and *n*-decane.

All experiments were carried out inside the chamber of the solar light simulator (Figure 3.1b) being the incident irradiance measured by a broadband UV radiometer (CUV 5, Kipp & Zonen B.V.), placed outside the outer tube and at the same height, within a spectral range of 280 – 400 nm corresponding to the UV fraction of the solar radiation.

Before PCO studies, the photolytic oxidation of PCE and *n*-decane was assessed (i.e. photoreactor assembled with the cellulose acetate supporting substrate without TiO₂-photocatalytic film).

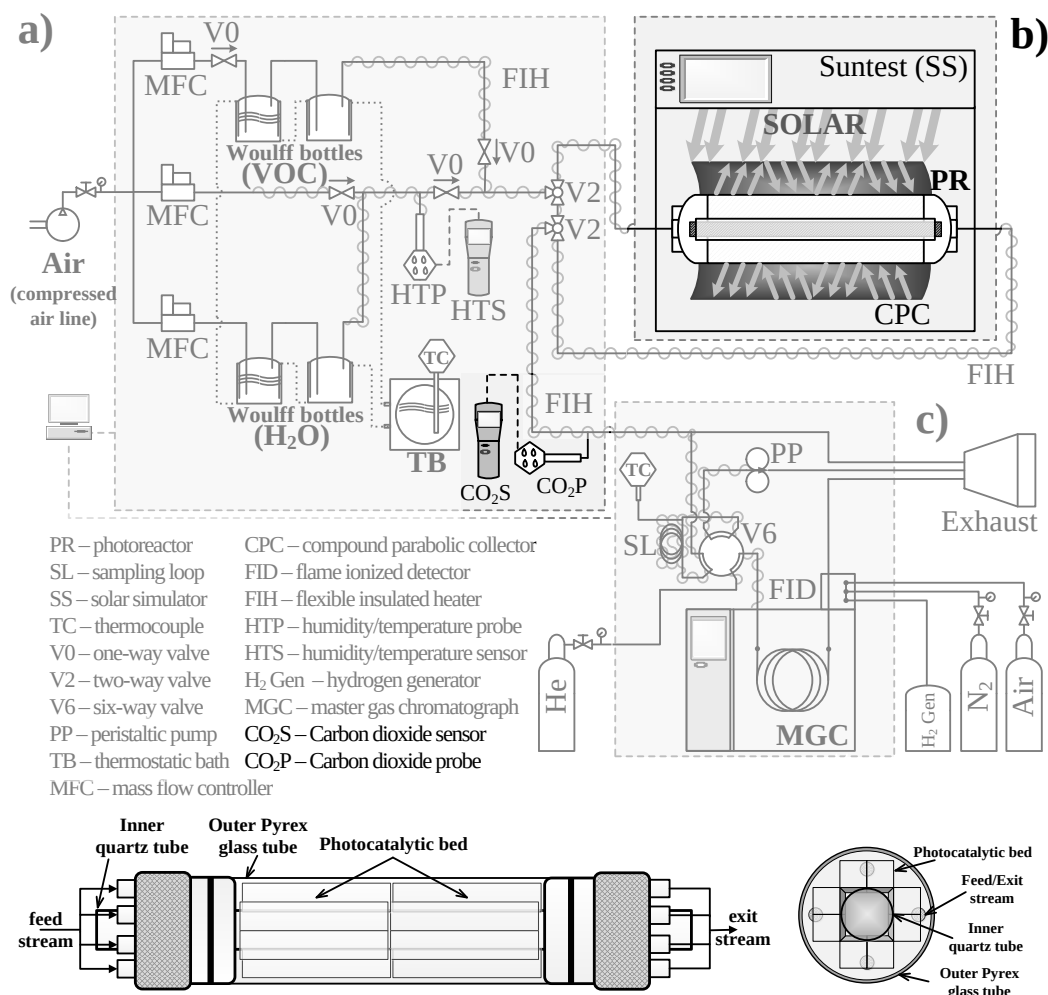


Figure 3.1. Schematic representation of the lab-scale experimental set-up and the continuous-flow photoreactor: a) generation of air streams containing *n*-decane and water vapour; b) sunlight simulator containing the photoreactor: b₁) side view and b₂) frontal view; c) master gas chromatograph analytic system used for the analysis of the photoreactor feed and exit gas streams.

The efficiencies of the process over both TiO₂ photocatalysts toward *n*-decane and PCE photocatalytic degradation were compared in similar operational conditions and calculated as described in eq. 3.1.

$$\text{Conversion (\%)} = \left(1 - \frac{C_{\text{VOC, exit}}}{C_{\text{VOC, feed}}} \right) \times 100 \quad 3.1$$

At steady-state, VOC conversion (where $C_{\text{VOC, feed}}$ and $C_{\text{VOC, exit}}$ are the pollutant

concentration in the feed and exit gas streams, respectively, expressed in ppm) were studied for different experimental conditions as described in sub-section 2.2.3 of Chapter 2; briefly: Q_{feed} ($75 - 300 \text{ cm}^3 \text{ min}^{-1}$, measured at 1 bar and 298 K), $C_{\text{VOC, feed}}$ ($C_{\text{dec, feed}} = 71 - 284 \text{ ppm}$ and $C_{\text{PCE, feed}} = 548 - 2738 \text{ ppm}$), RH of the feed gas stream in the presence and absence of oxygen (3 - 40 %, measured at 1 bar and 298 K), and I ($18.9 - 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$, measured in the spectral range 280 - 400 nm: UV fraction of the incident sunlight).

The mineralization yield of *n*-decane and PCE due to PCO was also evaluated and calculated as follows:

$$\text{Mineralization (\%)} = \left(\frac{C_{\text{CO}_2, \text{exit}}}{C_{\text{VOC, feed}}} \times \frac{1}{n} \right) \times 100 \quad 3.2$$

where n is the number of carbon atoms of each pollutant molecular structure and $C_{\text{CO}_2, \text{exit}}$ is the CO_2 exit stream concentration.

3.3. Results and discussion

3.3.1. VOCs photolysis

Blank experiments (*i.e.* photoreactor without TiO_2 -photocatalytic film) were performed under three different incident irradiances, *i.e.*, 18.9, 29.1, and $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (reference values to the sunlight UV fraction on the 280 – 400 nm range) in order to establish the effect of direct photolysis on the conversion of PCE and *n*-decane. No degradation of PCE or *n*-decane was observed for the range of irradiances tested (data not shown).

3.3.2. Catalytic film performances

3.3.2.1. Influence of the feed flow rate and VOC concentration

Figure 3.2 illustrates the effect of the feed flow rate (Q_{feed}) on the *n*-decane (Figure 3.2a) and PCE (Figure 3.2c) conversion over PC500 (blue columns) and P25 (orange columns) films. Increasing Q_{feed} , the conversion of *n*-decane and PCE reduced regardless the employed irradiance (*i.e.* 18.9, 29.1, and $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$) or the type of catalytic film. More than 99 % of the initial *n*-decane ($C_{\text{dec, feed}} = 71 \text{ ppm}$) and PCE ($C_{\text{PCE, feed}} = 1095 \text{ ppm}$) were converted over PC500 under $I = 38.4 \text{ W m}^{-2}$ when the feed flow rates of $75 \text{ cm}^3 \text{ min}^{-1}$ and $150 \text{ cm}^3 \text{ min}^{-1}$ were set; on the other hand, 93 % and 86 % of *n*-decane and 99 % of PCE conversions were attained over P25 film for the same experimental conditions. Increasing Q_{feed} to $300 \text{ cm}^3 \text{ min}^{-1}$, *n*-decane conversion

decreased to approximately 65 and 91 % while PCE conversion decreased to 67 % and 92 %, respectively over P25 and PC500 films.

In order to better understand the extent of the catalytic film activity toward the conversion of *n*-decane and PCE, the effect of Q_{feed} on the pollutant photocatalytic reaction rate, r_{VOC} , was also assessed as shown in Figure 3.2b and 3.2d, respectively. The upmost values of *n*-decane reaction rate over PC500 (blue columns) and P25 (orange columns) films – $1.64 \times 10^{-5} \text{ mol min}^{-1}$ and $1.17 \times 10^{-5} \text{ mol min}^{-1}$, respectively – were attained when using the highest Q_{feed} ($300 \text{ cm}^3 \text{ min}^{-1}$) under $I = 38.4 \text{ W m}^{-2}$. Although the highest conversion was observed at $Q_{\text{feed}} = 75 \text{ cm}^3 \text{ min}^{-1}$ and $I = 38.4 \text{ W m}^{-2}$ ($> 99 \%$), r_{dec} was the lowest ($4.43 \times 10^{-6} \text{ mol min}^{-1}$ and $4.15 \times 10^{-6} \text{ mol min}^{-1}$ respectively over PC500 and P25 films). Similarly, Figure 3.2d shows the PCE reaction rate, r_{PCE} , over PC500 and P25 films. As seen before for *n*-decane, higher Q_{feed} ($300 \text{ cm}^3 \text{ min}^{-1}$) promoted higher reaction rates of PCE ($2.20 \times 10^{-4} \text{ mol min}^{-1}$ and $1.59 \times 10^{-4} \text{ mol min}^{-1}$ respectively over PC500 and P25 films) under $I = 38.4 \text{ W m}^{-2}$. In opposition, setting the lowest Q_{feed} ($75 \text{ cm}^3 \text{ min}^{-1}$) both TiO₂ photocatalytic films promoted the highest PCE conversions (99 %) and the lowest PCE reaction rates for each employed irradiance.

In both cases, the results suggest a double antagonistic effect as the feed flow rate increases [34, 35]: i) a decrease in the residence time inside the reactor decreases the adsorption of the pollutant molecules on the photocatalytic film surface which impairs the efficiency of the PCO process; ii) higher organic load entering the photoreactor will enhance the mass transfer between the pollutant molecules and the catalytic film surface resulting in higher PCO reaction rates.

Regarding the efficiency of both catalytic films, it is worth noting that P25 film provided lower values of photocatalytic reaction rate than PC500 film in the PCO of *n*-decane and PCE: P25 film provided values of *n*-decane reaction rate 6 % up to 41 % lower than PC500 film depending on I and Q_{feed} as well as, the differences in reaction rates between both catalytic films become greater as the Q_{feed} increases and I decreases. For example, fixing Q_{feed} at $75 \text{ cm}^3 \text{ min}^{-1}$ the photocatalytic reaction rates of *n*-decane over P25 film 6, 8 and 13 % under 38.4, 29.1 and 18.9 W m^{-2} whereas for $Q_{\text{feed}} = 300 \text{ cm}^3 \text{ min}^{-1}$ the reaction rate over P25 film is 29, 34 and 41 % lower than over PC500 film under the same irradiances. The same trend can be observed for the PCO of PCE but, in this case, P25 film provides up to 34 % lower values of reaction rate of PCE than PC500 film employing the above described experimental conditions.

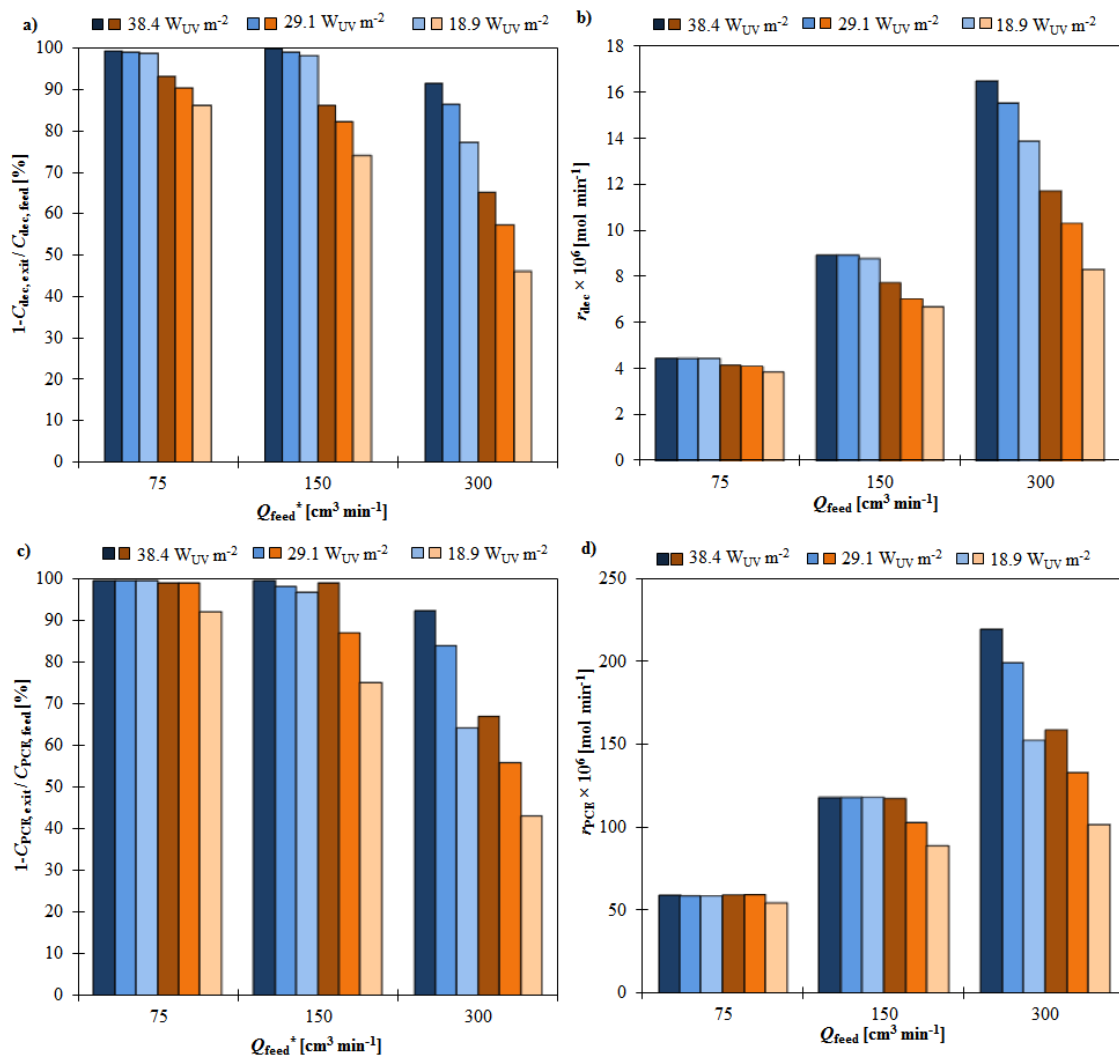


Figure 3.2. Effect of feed flow rate [Q_{feed}^*] on the conversion of *n*-decane (a) and PCE (c) and on the photocatalytic reaction rate, r_{VOC} (b) and (d), respectively). Experimental points for incident irradiances of 38.4 $\text{W}_{\text{UV}} \text{m}^{-2}$ (■, ■), 29.1 $\text{W}_{\text{UV}} \text{m}^{-2}$ (■, ■), and 18.9 $\text{W}_{\text{UV}} \text{m}^{-2}$ (■, ■), measured within the spectral range of 280 – 400 nm, at steady-state conditions; $C_{\text{dec, feed}} = 71 \text{ ppm}$, $C_{\text{PCE, feed}} = 1095 \text{ ppm}$, $RH^* = 40 \%$ and 21 % oxygen. Blue columns represent TiO₂ PC500 (■, ■, ■) and orange columns P25 (■, ■, ■). * measured at 298 K and 1 bar.

Figure 3.3 shows the influence of the feed concentration of *n*-decane ($C_{\text{dec, feed}}$) and PCE ($C_{\text{PCE, feed}}$) on the conversion and on photocatalytic reaction rate of *n*-decane and PCE. For the same residence time in the photoreactor ($\tau = 88 \text{ s}$; $Q_{\text{feed}} = 150 \text{ cm}^3 \text{min}^{-1}$) the conversion of *n*-decane (Figure 3.3a) and PCE (Figure 3.3c) decreased as the feed concentration increased, regardless the catalytic film used. Employing PC500 film more than 98 % of *n*-decane conversion was attained for the three irradiances employed (*i.e.* 18.9, 29.1, and 38.4 $\text{W}_{\text{UV}} \text{m}^{-2}$) when the initial *n*-decane concentration was 71 ppm, whereas P25 film yielded 74 up to 86 % of conversion, depending on the irradiance (Figure 3.3a). Also, increasing *n*-decane feed concentration ($C_{\text{dec, feed}} = 142 \text{ ppm}$) the conversion of *n*-decane over PC500 film decreased in the range of 5 – 25 % for an irradiance reduction from 38.4 to 18.9 $\text{W} \text{m}^{-2}$; over P25 film the

reduction was around 20 -30 % for the same irradiance reduction. It is interesting to note that, at this concentration and fixing $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$ and $RH = 40 \%$, the *n*-decane conversion over P25 film is closer to that found when the photoreactor was packed with PC500 film and fed with twice the *n*-decane feed concentration, *i.e.* 283 ppm. In particular, 50, 62 and 69 % of *n*-decane ($C_{\text{dec, feed}} = 142 \text{ ppm}$) was converted over P25 film, while 37, 51 and 62 % was converted over PC500 film ($C_{\text{dec, feed}} = 283 \text{ ppm}$) under 18.9, 29.1 and $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$.

The activity of both photocatalytic films towards PCE conversion as a function of the PCE feed concentration ($C_{\text{PCE, feed}}$) is shown in Figure 3.3c. As seen before for *n*-decane conversion over P25 and PC500 films, PCE conversion follows the same trend, *i.e.*, the efficiency of the process decreases as the PCE feed concentration increases. In the range of 549 – 2738 ppm of $C_{\text{PCE, feed}}$ a 42 % reduction in the PCE conversion (from 99 to 57 %) can be observed under $I = 18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (Figure 3.3c). It is worth noting that under higher irradiance ($38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$) no efficiency loss was observed in the same PCE concentration range. Although P25 film promoted PCE conversions of approximately 99 % ($Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$, $C_{\text{PCE, feed}} = 1095 \text{ ppm}$ and $RH = 40 \%$) under $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$, it is under lower irradiances that the differences between both catalytic film activities become greater: 87 and 75 % of PCE conversion were attained under 29.1 and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ of irradiance over P25 film, while 98 and 97 % were converted over PC500 film under the same operational conditions. Increasing the PCE feed concentration from 1095 ppm to 1643 ppm, the P25 film promoted 13, 27 and 56 % less PCE conversion than over PC500 respectively under 38.4, 29.1 and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$.

A similar approach regarding the photocatalytic reaction rate of *n*-decane can be followed as plotted in Figure 3.3b and 3.3d: in these cases, for the three incident irradiances employed ($38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$, $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$) and over PC500 and P25 films the reaction rate of *n*-decane and PCE increases as the feed concentration increases. In other words, higher $C_{\text{dec, feed}}$ and $C_{\text{PCE, feed}}$ for a same flow rate ($Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$), enhances the mass transfer between the feed gas stream and the catalyst surface, increasing the reaction rate of the pollutant.

The results show that P25 film provides lower pollutant reaction rates in comparison to PC500 film. The former provides 13 up to 32 % lower reaction rates of *n*-decane than the latter depending on $C_{\text{dec, feed}}$ and I : for example, fixing $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$, $C_{\text{dec, feed}} = 142 \text{ ppm}$ and $I = 38.4 \text{ W m}^{-2}$ the *n*-decane reaction rate over P25 and PC500 films were respectively $2.27 \times 10^{-5} \text{ mol min}^{-1}$ and $3.39 \times 10^{-5} \text{ mol min}^{-1}$. The PCO of PCE over PC500 film also revealed higher reaction rates than over P25 film as the latter promotes reaction rates up to 40 % lower than over PC500 in the range of PCE feed concentration tested (1095 ppm and 1643 ppm) and depending on the incident irradiance.

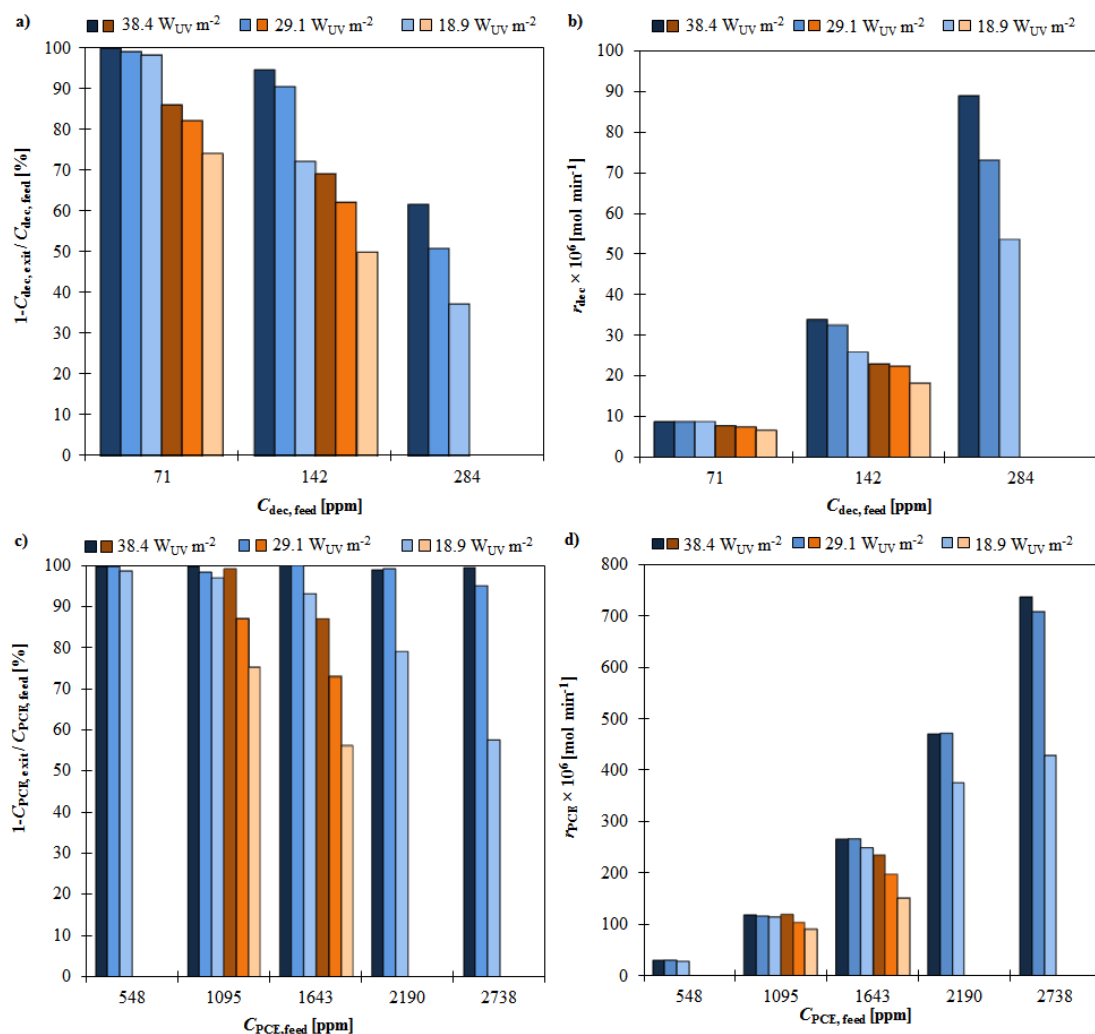


Figure 3.3. Effect of VOC feed concentration ($C_{dec, feed}$ and $C_{PCE, feed}$) on the conversion of *n*-decane (a) and PCE (c) and on the photocatalytic reaction rate, r_{VOC} ((b) and (d), respectively). Experimental points for incident irradiances of 38.4 $W_{UV} m^{-2}$ (■, ■), 29.1 $W_{UV} m^{-2}$ (■, ■), and 18.9 $W_{UV} m^{-2}$ (■, ■) measured within the spectral range of 280 - 400 nm, at steady-state conditions; $Q_{feed}^* = 150\ cm^3\ min^{-1}$, $RH^* = 40\ %$ and 21 % oxygen. Blue columns represent the activity of PC500 (■, ■, ■) and orange columns P25 (■, ■, ■) films. * measured at 298 K and 1 bar.

For a given pollutant feed concentration and/or feed flow rate, the photocatalytic reaction rate depends on the number of oxidant species formed at the surface of the catalytic film. Likewise, the number of oxidant species depends on the photon flux. Hereupon, an increase in the irradiance is followed by an increase in the number of generated photons which will form an equivalent number of electro-hole pairs (and oxidant species) ultimately resulting in VOCs conversion gains. From Figure 3.2 and Figure 3.3 it is possible to see that the photocatalytic reaction rate of *n*-decane (Figure 3.2b and Figure 3.3b) and PCE (Figure 3.2d and Figure 3.3d) over PC500 and P25 films becomes more dependent on the incident irradiation as the organic load increases (higher Q_{feed} or $C_{VOC, feed}$): while for low organic loads the incident irradiance has almost no effect on the reaction rate of the VOC, for higher organic loads the reaction rate is nearly

proportional to the irradiance employed, within the range $18.9 - 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$. This phenomenon is related to number of organic molecules entering the reactor and the number of photons available: at low organic loads the photons are in excess under the three irradiances, converting all or almost all available pollutant molecules; in opposition, at high organic loads the number of pollutant molecules to be converted is higher and the photons are no longer in excess requiring higher number of photons to achieve similar conversion values. This means that, higher organic loads make a better use of the photons regardless the efficiency loss of the PCO process.

The mineralization of *n*-decane and PCE over PC500 and P25 photocatalytic films is represented in Figure 3.4. Although the mineralization of PCE over both photocatalytic films provided similar values for each irradiance (*ca.* 39, 31 and 24 % under 38.4 , 29.1 and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$, respectively) the results show that PC500 film was able to yield higher mineralization of *n*-decane: 100 % of *n*-decane ($C_{\text{dec, feed}} = 71 \text{ ppm}$) was mineralized into CO_2 and water whereas over P25 film only 69 % of *n*-decane was mineralized under $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$. As expected, decreasing the irradiance so did the *n*-decane mineralization: under 29.1 and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$, PC500 film was able to mineralize 83 and 73 % while P25 film only mineralized 54 and 40 %, respectively.

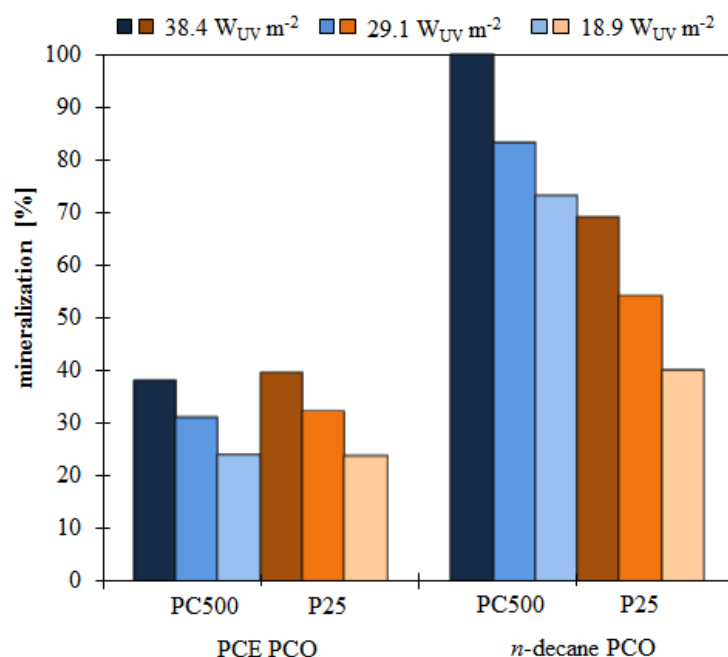


Figure 3.4. Mineralization yields of PCE and *n*-decane over PC500 and P25 films. Experimental points for incident irradiances of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■, ■), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■, ■), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■, ■) measured within the spectral range of 280 - 400 nm, at steady-state conditions; $C_{\text{PCE, feed}}^* = 1095 \text{ ppm}$, $C_{\text{dec, feed}}^* = 71 \text{ ppm}$ $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$, $RH^* = 40 \text{ \%}$ and 21 % oxygen; Blue columns represent the activity of PC500 (■, ■, ■) and orange columns P25 (■, ■, ■) films. * measured at 298 K and 1 bar.

It should be pointed out that after more than 50 h under simulated solar radiation and continuous feed (humid air contaminated with *n*-decane or PCE), similar *n*-decane and PCE conversions (less than 1 % of variation) were obtained under the same operating conditions and for both photocatalytic films (data not shown). Considering the results and our previous works where cellulose acetate monolithic structures were used as substrates [32, 36, 37] it is suggested that deterioration of the support and/or the photocatalytic film was negligible.

From this study, seems clear that PC500 film promotes higher conversions and higher reaction rates of *n*-decane and PCE than P25 film, under solar radiation, even considering that the produced PC500 film has lower mass of PC500 photocatalyst which may be an economic advantage. However, it is a challenging task to explain why PC500 film promoted higher photocatalytic conversions than P25 film in gas-phase experiments. For the last decades, several research works have been focused on the structure of P25 craving to understand the generally accepted superior activity of P25 over other commercially available photocatalysts mainly in liquid-phase studies [14, 15, 38-40]. Bickley *et al.* [15] attributed high photocatalytic activity of P25 to the presence of rutile and anatase phases. Admitting that each photocatalyst particle consists of an anatase core and a thin rutile cover layer, photogenerated holes of the anatase core would be effectively transferred to the rutile layer. However, Ohno *et al.* [38] stated that P25 powder consists, in fact, of relatively large rutile particles and very small anatase particles, which independently form agglomerates before mixing. They also stated that the superior activity of P25 was due to the proper band bending in rutile particles, which are in contact to anatase particles. Hurum *et al.* [14] concluded that the higher activity of mixed-phase TiO₂ was due to a more stable charge separation by electron transfer from rutile to lower energy anatase lattice trapping sites.

On the other hand, Sun *et al.* [39] proposed that, in aqueous phase, the contact between anatase and rutile phases and a subsequently band bending between the two phases promotes a good charge-carrier separation. But such synergistic effect of anatase and rutile in aqueous phase is not exclusive to P25. Ohno *et al.* [40] reported the enhanced efficiency for mixed anatase and rutile at different ratios as well as thermally treated anatase yielding the two phases. It is worth noting that rutile phase can be formed in anatase samples by heat treatment [41] changing the crystallinity and the size of TiO₂ particles which can affect the photocatalytic activity [14, 42].

In gas-phase photocatalytic reactions, the contact between the two P25 phases may not be so effective and, thus, the synergistic effect may not be observed. An insufficient band bending will impair the contact between the two phases resulting in poor charge-carrier separation and, subsequently, in a loss of photocatalytic efficiency of mixed-phases TiO₂. In the absence of any synergistic effect between the anatase and rutile mixed TiO₂ phases, it is accepted that anatase is much more active than rutile in the PCO of organic compounds in water and air [43]. Even

considering that the smaller crystal size of PC500 (Table 1) may foresee higher density in surface defects [19] reducing the electron-hole recombination time, which ultimately results in lower photocatalytic efficiencies, the larger surface area of PC500 in comparison to P25 may justify the superior activity of PC500 [34, 43, 44].

3.3.2.2. Effect of the RH on PCO of n-decane and PCE over PC500 films

The effect of the water content on the conversion of *n*-decane (Figure 3.5a) and PCE (Figure 3.5b) over PC500 film was evaluated for three *RH* conditions (3, 20, and 40 %). Figure 3.5a presents the conversion of *n*-decane attained under each *RH* condition for three given $C_{\text{dec, feed}}$. Fixing $C_{\text{dec, feed}}$ at 71 ppm ($2.87 \times 10^{-3} \text{ mol m}^{-3}$), a negligible decrease of 1.4 % was observed as the water content decreases from 40 to 3 % ($3.61 \times 10^{-1} \text{ mol m}^{-3}$ to $2.71 \times 10^{-2} \text{ mol m}^{-3}$ of water; water/*n*-decane molar ratio of 125.8 and 9.4, respectively). The effect of *RH* on the *n*-decane conversion became clearer as the initial concentration of *n*-decane increases. Setting the *n*-decane feed concentration four times higher ($C_{\text{dec, feed}} = 284 \text{ ppm}$ or $1.15 \times 10^{-2} \text{ mol m}^{-3}$), it was observed that when *RH* was reduced from 20 % ($1.81 \times 10^{-1} \text{ mol m}^{-3}$ of water) to 3 % the *n*-decane conversion also decreased (from 69 to 54 %). The water/*n*-decane molar ratio is approximately 2.4 and 15.7 for *RH* of 3% to 20%. This indicates that water/*n*-decane molar ratios higher than 2.4 and lower than 9.4 are required to produce the necessary number of hydroxyl radicals for the pollutant degradation. On the other hand, at higher *RH* (40 %) no improvement in the *n*-decane conversion was observed most likely due to competitive adsorption of *n*-decane and water molecules on the photocatalytic film surface. The same behaviour was observed for a $C_{\text{dec, feed}} = 142 \text{ ppm}$, but in this case, the differences are less evident, probably due to the high conversions of *n*-decane hiding the real effect of the water content variation.

Figure 3.5b shows the effect of *RH* on the conversion of PCE over PC500 film, but instead of varying the feed concentration of the pollutant, two feed flow rates were tested ($150 \text{ cm}^3 \text{ min}^{-1}$ and $300 \text{ cm}^3 \text{ min}^{-1}$) for the same $C_{\text{PCE, feed}}$ (1095 ppm). For $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$, no effect owed to the variation of *RH* was observed on the PCE conversion. However, doubling the total flow rate to $300 \text{ cm}^3 \text{ min}^{-1}$, it becomes clear that *RH* has the same impact on the PCE conversion, in comparison with that described before for *n*-decane (Figure 3.5a). The conversion of PCE reached its highest value (98 %) when *RH* was set to 20 %, while 92 % and 89 % of the initial PCE were converted at 40 % and 3 % of *RH*, respectively. It is important to note that at *RH* = 3 % the concentration of water is lower than that of PCE ($C_{\text{H}_2\text{O, feed}} = 2.71 \times 10^{-2} \text{ mol m}^{-3}$ and $C_{\text{PCE, feed}} = 4.43 \times 10^{-2} \text{ mol m}^{-3}$) which would foresee a drastic reduction of PCE conversion regardless the Q_{feed} . However such reduction was not observed which may indicate further

mechanisms in the photodegradation of PCE besides the classical attack of hydroxyl radicals. Chlorine radical chain propagation reactions have been a matter of discussion by several research groups in an attempt to explain the PCO mechanism of chlorinated compounds [45-47].

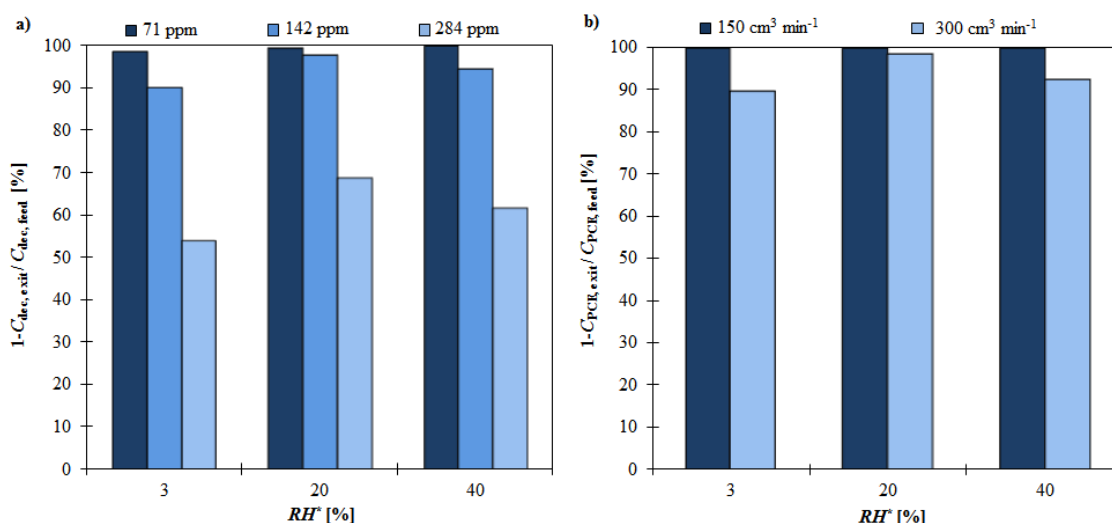


Figure 3.5. Effect of water content [RH^*] on the conversion over PC500 film, at steady-state conditions, of: (a) *n*-decane for $C_{dec, feed} = 71$ ppm (■), $C_{dec, feed} = 142$ ppm (■) and $C_{dec, feed} = 284$ ppm (■); (b) PCE ($C_{PCE, feed} = 1095$ ppm) for $Q_{feed}^* = 150$ cm³ min⁻¹ (■) and $Q_{feed}^* = 300$ cm³ min⁻¹ (■); $I = 38.4$ W_{UV} m⁻², measured within the spectral range of 280 - 400 nm. * measured at 298 K and 1 bar.

The opposing effect of the water content has already been discussed in several research works and even so it still is a matter of debate [35, 48-51]. Several authors reported that the absence of water vapour will seriously retard the conversion of several chemicals and their mineralization to CO₂ may become incomplete, but excessive water vapour may inhibit the degradation by competitive adsorption on the photocatalyst surface [48, 52]. For instance, Obee and Brown [49] demonstrated that the oxidation rates of formaldehyde, toluene, and 1,3-butadiene (sub-ppm_v concentrations) increase as the humidity decreases (for water content above *ca.* 1000 ppm). They suggested that the influence of humidity and trace contaminant concentrations on the oxidation rates on TiO₂ surface is due to the competitive adsorption on the available hydroxyl adsorption sites and to changes in hydroxyl radical population levels. The effect of water content on PCO of 1-butene (1.12×10^{-4} mol m⁻³) over TiO₂ and SnO₂ was also investigated by Cao *et al.* [50]. These authors observed high photoactivity of SnO₂ at low water vapour contents (< 1000 ppm or 4.09×10^{-2} mol m⁻³) and a drastic reduction of photoactivity after increasing the water content above 2000 ppm (8.18×10^{-2} mol m⁻³). TiO₂ films showed stable performance for water concentrations between 0 and 3000 ppm (1.12×10^{-1} mol m⁻³). Pengyi *et al.* [50] showed that the photocatalytic conversion of trace toluene concentrations (4.09×10^{-5} – 8.18×10^{-4} mol m⁻³) by O₃/UV, TiO₂/UV and O₃/TiO₂/UV processes was slightly affected by the relative humidity in the range 20 - 55 % (2.04×10^{-1} – 7.77×10^{-1} mol m⁻³) being the optimal

humidity around 35 % ($4.82 \times 10^{-1} \text{ mol m}^{-3}$). In a similar study, Zhang and Liu [53] reported that the relative humidity played a significant role in reducing trace hexane concentrations (5.73×10^{-5} - $3.12 \times 10^{-4} \text{ mol m}^{-3}$) by TiO₂/UV and O₃/TiO₂/UV processes. The authors found that little humidity improved the decomposition of hexane whereas relative humidity above 45 % ($1.96 \times 10^{-1} \text{ mol m}^{-3}$) would depress the decomposition. Jo and Park [51] revealed that photo-oxidation of benzene, ethyl benzene, and *o*-, *m*-, *p*-xylenes, trichloroethylene, and perchloroethylene in trace levels was independent of humidity in the range 10 – 100 % (0.10 – 1.03 mol m^{-3}).

3.3.2.3. Effect of oxygen on *n*-decane and PCE PCO over PC500 film

The effect of the gas-phase molecular oxygen absence on the pollutants conversion over PC500 film under different water content conditions is depicted in Figure 3.6 (orange columns). Figure 3.6a shows a drastic reduction on the *n*-decane conversion after removing the oxygen feed gas stream from the reaction: only 16 % of *n*-decane was converted at *RH* = 40 % against more than 99 % conversion when 21 % of oxygen was present, under the highest irradiance used in this study ($I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$). Reducing *RH* from 40 to 3 % the conversion of *n*-decane decreased by 36 %, *i.e.* from 16 % to 10 % under the same irradiance. Reducing the irradiance to $I = 29 \text{ W}_{\text{UV}} \text{ m}^{-2}$ so does the *n*-decane conversion. For instance, 14 % of *n*-decane was converted at *RH* = 40 %, while only 1 % of *n*-decane was converted at *RH* = 3 %. For the lowest irradiance applied ($I = 18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$), no *n*-decane conversion was observed for both *RH* conditions in the absence of oxygen. A similar trend may be perceived from Figure 3.6b, which represents PCE photocatalytic conversion experiments. Under 40 % of *RH* the initial PCE was converted 15 % and 6 % for $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ and $I = 29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$, respectively, whereas under 3 % of *RH* no PCE conversion was detected. In addition, no PCE conversion was observed under $I = 18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ irrespective of the *RH* value in the gas stream.

The presence of oxygen has been reported as essential for the photoreaction and increasing the oxygen concentration so does the pollutant decomposition rate [30, 54-57]. Yet, the mechanism of action is not clear. Larson *et al.* [30] found that the complete oxidation of 2-propanol by UV/TiO₂ was dependent on the presence of oxygen: the conversion of acetone increased from 20 to 70 % after 6 min of UV radiation as the oxygen content increased from 0 % to 5 % (v/v). They also observed that in the absence of gas-phase oxygen the photo-oxidation of propanol could still take place through TiO₂ lattice oxygen atoms and that oxygen was needed only to replenish the produced oxygen vacancies on the TiO₂ lattice. Muggli *et al.* [54-56] reported the photo-oxidation of acetic and formic acids over TiO₂ lattice oxygen and found that gas-phase oxygen replenishes the lattice oxygen vacancies even in the dark. On the other hand,

they observed that when gas-phase oxygen was present the oxidation rate of formic acid was greatly improved, suggesting the important role of adsorbed oxygen. Likewise, El-Maazawi *et al.* [57] proposed that the photocatalytic reaction could take place in the absence of oxygen due to the TiO_2 lattice oxygen. The oxygen from TiO_2 lattice is depleted during the conversion of gaseous acetone being replenished by the oxygen from the feed gas stream.

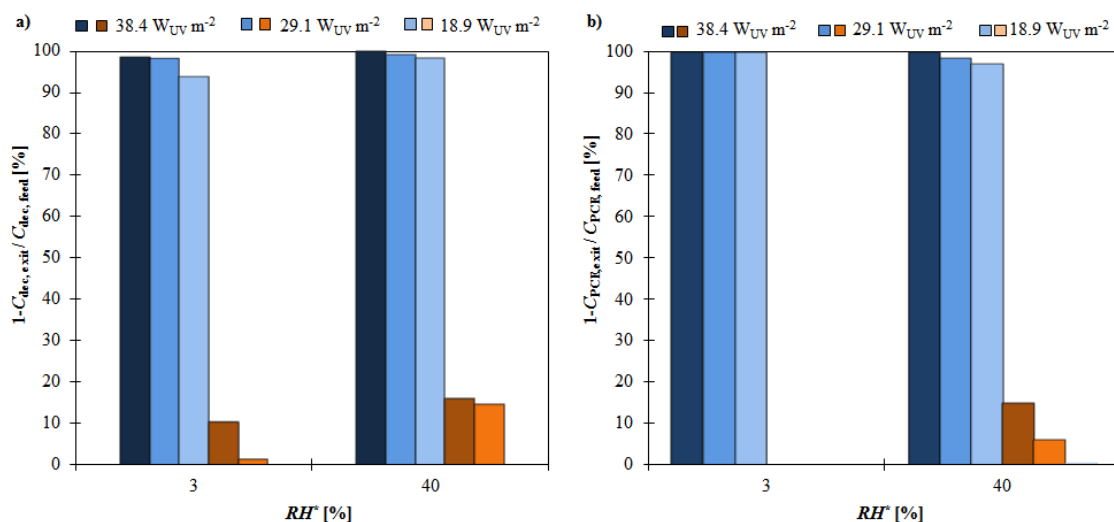


Figure 3.6. Effect of water content [RH^*] on: (a) n -decane conversion at steady-state conditions for $C_{\text{dec, feed}} = 71$ ppm and $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$; (b) PCE conversion at steady-state conditions for $C_{\text{PCE, feed}} = 1095$ ppm and $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$. Blue columns (■, ■, ■) and orange columns (■, ■, ■) represent, respectively, the presence and absence of oxygen; Incident irradiances of 38.4 $\text{W}_{\text{UV}} \text{m}^{-2}$ (■, ■), 29.1 $\text{W}_{\text{UV}} \text{m}^{-2}$ (■, ■), and 18.9 $\text{W}_{\text{UV}} \text{m}^{-2}$ (■, ■) were measured within the spectral range of 280 – 400 nm. * measured at 298 K and 1 bar.

Considering that the conversion of the two pollutants (n -decane and PCE) was drastically hindered after removing the gas-phase molecular oxygen from the gas stream, two oxygen-related mechanisms may be involved in the photocatalytic conversion [30, 54-57]. The first is based on the photodissociation of gas-phase molecular oxygen from the feed stream at the TiO_2 surface into $\text{O}^\bullet$, which spontaneously reacts with O_2 forming $\text{O}_3^\bullet$. These species may greatly contribute to the conversion of pollutants being at the same time the limiting step of the photocatalytic reaction. The second mechanism, where no gas-phase oxygen is present, may be related to the oxygen existing in the TiO_2 lattice. Assuming the limited availability of surface lattice oxygen, it would be expected that the photocatalytic process would be considerably impaired, as it was, in fact, observed (see Figure 3.6). Regardless of the presence or absence of gas-phase molecular oxygen and the surface density of TiO_2 on the substrate, it is possible to observe in both Figures 3.5 and 3.6 that increasing the RH the conversion of the pollutant also increases as it was already previously discussed. The contribution of the classic photocatalytic mechanism where $\text{HO}^\bullet$ radicals initiate the photocatalytic process certainly explain such behaviour. Another hypothesis

for the role of HO[•] radicals is based on the ability of such species to act as effective traps for the holes preventing electron-hole recombination [58, 59]. In this way the reduced titanium centres (produced by reductive reaction between $e_{CB}^{-}(\text{TiO}_2)$ and Ti^{4+} centre of the TiO_2) will enhance the space charge layer resulting in a longer lifetime, which ultimately promotes the oxidation of more gas-phase molecular oxygen [58, 59].

Several authors have followed another meaningful approach to clarify the mechanism of PCE degradation by PCO [45-48, 60-62]. However, agreement is yet to be found. On one hand, different authors [45-47] claimed that Cl[•] radical addition to PCE occurs several times faster than HO[•] radical addition, neglecting therefore the role of HO[•] radical. Such conclusion was further substantiated by Lu *et al.* [61] and Fan and Yates [62] after finding that the surface hydroxyl groups were inactive in the oxidation of methylchloride and trichloroethylene. On the other hand, Yamazaki *et al.* [48, 60], for example, stated that the PCO of PCE could occur via HO[•] radical or Cl[•] radical, but they concluded that Cl[•] radical initial reaction rarely occurs on the catalyst surface since the reaction with HO[•] radical is thermodynamically favourable.

3.4. Conclusions

Different photocatalytic oxidation (PCO) reactions under simulated solar radiation showed that films using the commercial TiO₂ photocatalyst PC500 provide higher conversions of PCE and *n*-decane than those obtained with P25. It was also found that PC500 film provides higher mineralization of *n*-decane than P25 film. Although the smaller crystallite size suggests the possibility of higher density in surface defects impairing the charge carriers and, therefore the photocatalytic efficiency, the higher surface area of PC500 catalyst particles may justify the superior performance of the film towards the conversion of *n*-decane and PCE in comparison to that of P25 under steady state conditions.

Regarding PC500 film, it was evidenced the effect of the relative humidity (*RH*) on the photocatalytic conversion of both pollutants. The results suggest that for *RH* in the range 3 - 20 % the competitive adsorption between water and pollutant molecules is unlikely to occur since the pollutants conversion increases with *RH*. On the other hand, at 40 % of *RH* the pollutant conversion over of PC500 film decreases, which means competitive adsorption between the above-mentioned molecules. The conversion of *n*-decane and PCE by PCO was drastically impaired or even not observable in the absence of gas-phase molecular oxygen indicating the key role of oxygen in photocatalysis. Three major mechanisms may be implicit in the effect of the oxygen content. One is the formation of reactive species from the adsorbed gas-phase molecular oxygen, which will oxidize the pollutants. The second involves the action of the oxygen from the

lattice of TiO_2 . The third mechanism involves the classical hydroxyl radical formation on the TiO_2 surface. Acting directly over the pollutant molecules or as a trap for holes delaying the charge recombination and therefore promoting the formation of other oxidant species, $\text{HO}^\bullet$ radicals cannot be excluded from the reaction. Chlorine radicals, $\text{Cl}^\bullet$, chain propagation reactions may also be involved in the PCO reaction mechanism of chlorinated compounds such as PCE.

3.5. References

- [1] J.V. Teixeira, S.M. Miranda, R.A.R. Monteiro, F.V.S. Lopes, J. Madureira, G.V. Silva, N. Pestana, E. Pinto, V.J.P. Vilar, R.A.R. Boaventura, *Environ. Monit. Assess.* 185 (2013) 59-72.
- [2] A. Fujishima, K. Honda, *Nature* 238 (1972) 37-38.
- [3] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69-96.
- [4] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, *J. Chem. Technol. Biotechnol.* 77 (2002) 102-116.
- [5] J.-M. Herrmann, *Top. Catal.* 34 (2005) 49-65.
- [6] M. Anpo, *Pure Appl. Chem.* 72 (2000) 1787-1792.
- [7] C.F. Lin, C.H. Wu, Z.N. Onn, *J. Hazard. Mater.* 154 (2008) 1033-1039.
- [8] T. Ohno, T. Mitsui, M. Matsumura, *Chem. Lett.* 32 (2003) 364-365.
- [9] Q. Xiao, L. Ouyang, *J. Phys. Chem. Solids* 72 (2011) 39-44.
- [10] J.C. Colmenares, A. Magdziarz, D. Łomot, O. Chernyayeva, D. Lisovytskiy, *Appl. Catal. B: Environ.* 147 (2014) 624-632.
- [11] C. Li, X. Yang, R. Chen, J. Pan, H. Tian, H. Zhu, X. Wang, A. Hagfeldt, L. Sun, *Sol. Energ. Mat. Sol. C.* 91 (2007) 1863-1871.
- [12] R.L. Pozzo, M.A. Baltanás, A.E. Cassano, *Catal. Today* 39 (1997) 219-231.
- [13] C. Águia, J. Ângelo, L.M. Madeira, A. Mendes, *J. Environ. Manage.* 92 (2011) 1724-1732.
- [14] D.C. Hurum, A.G. Agrios, K.A. Gray, T. Rajh, M.C. Thurnauer, *J. Phys. Chem. B* 107 (2003) 4545-4549.
- [15] R.I. Bickley, T. Gonzalez-Carreno, J.S. Lees, L. Palmisano, R.J.D. Tilley, *J. Solid State Chem.* 92 (1991) 178-190. [16] J. Moon, C.Y. Yun, K.-W. Chung, M.-S. Kang, J. Yi, *Catal. Today* 87 (2003) 77-86.
- [1] J.V. Teixeira, S.M. Miranda, R.A.R. Monteiro, F.V.S. Lopes, J. Madureira, G.V. Silva, N. Pestana, E. Pinto, V.J.P. Vilar, R.A.R. Boaventura, *Environ. Monit. Assess.* 185 (2013) 59-72.
- [2] A. Fujishima, K. Honda, *Nature* 238 (1972) 37-38.
- [3] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69-96.
- [4] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, *J. Chem. Technol. Biotechnol.* 77 (2002) 102-116.
- [5] J.-M. Herrmann, *Top. Catal.* 34 (2005) 49-65.
- [6] M. Anpo, *Pure Appl. Chem.* 72 (2000) 1787-1792.
- [7] C.F. Lin, C.H. Wu, Z.N. Onn, *J. Hazard. Mater.* 154 (2008) 1033-1039.
- [8] T. Ohno, T. Mitsui, M. Matsumura, *Chem. Lett.* 32 (2003) 364-365.
- [9] Q. Xiao, L. Ouyang, *J. Phys. Chem. Solids* 72 (2011) 39-44.
- [10] J.C. Colmenares, A. Magdziarz, D. Łomot, O. Chernyayeva, D. Lisovytskiy, *Appl. Catal. B: Environ.* 147 (2014) 624-632.
- [11] C. Li, X. Yang, R. Chen, J. Pan, H. Tian, H. Zhu, X. Wang, A. Hagfeldt, L. Sun, *Sol. Energ. Mat. Sol. C.* 91 (2007) 1863-1871.
- [12] R.L. Pozzo, M.A. Baltanás, A.E. Cassano, *Catal. Today* 39 (1997) 219-231.

- [13] C. Águia, J. Ângelo, L.M. Madeira, A. Mendes, *J. Environ. Manage.* 92 (2011) 1724-1732.
- [14] D.C. Hurum, A.G. Agrios, K.A. Gray, T. Rajh, M.C. Thurnauer, *J. Phys. Chem. B* 107 (2003) 4545-4549.
- [15] R.I. Bickley, T. Gonzalez-Carreno, J.S. Lees, L. Palmisano, R.J.D. Tilley, *J. Solid State Chem.* 92 (1991) 178-190.
- [16] A.G. Agrios, K.A. Gray, E. Weitz, *Langmuir* 20 (2004) 5911-5917.
- [17] D.C. Hurum, K.A. Gray, T. Rajh, M.C. Thurnauer, *J. Phys. Chem. B* 108 (2004) 16483-16487.
- [18] M. Hajaghazadeh, V. Vaiano, D. Sannino, H. Kakooei, R. Sotudeh-Gharebagh, P. Ciambelli, *Catal. Today* 230 (2014) 79-84.
- [19] J. Taranto, D. Frochot, P. Pichat, *Ind. Eng. Chem. Res.* 48 (2009) 6229-6236.
- [20] Y. Paz, in: I.d.L. Hugo, R. Benito Serrano (Eds.), *Advances in Chemical Engineering Photocatalytic Technologies*, Academic Press, 2009, pp. 289-336.
- [21] M. Lewandowski, D.F. Ollis, *Appl. Catal. B: Environ.* 43 (2003) 309-327.
- [22] C. Águia, J. Ângelo, L.M. Madeira, A. Mendes, *Catal. Today* 151 (2010) 77-83.
- [23] L.A. Dibble, G.B. Raupp, *Environ. Sci. Technol.* 26 (1992) 492-495.
- [24] J. Araña, A. Peña Alonso, J.M. Doña Rodríguez, J.A. Herrera Melián, O. González Díaz, J. Pérez Peña, *Appl. Catal. B: Environ.* 78 (2008) 355-363.
- [25] Y. Yamin, N. Keller, V. Keller, *J. Photochem. Photobiol. A* 245 (2012) 43-57.
- [26] R. Portela, S. Suárez, R.F. Tessinari, M.D. Hernández-Alonso, M.C. Canela, B. Sánchez, *Appl. Catal. B: Environ.* 105 (2011) 95-102.
- [27] G.B. Raupp, A. Alexiadis, M.M. Hossain, R. Changrani, *Catal. Today* 69 (2001) 41-49.
- [28] A.N. Kouamé, R. Masson, D. Robert, N. Keller, V. Keller, *Catal. Today* 209 (2013) 13-20.
- [29] R.E. Hayes, S.T. Kolaczowski, W.J. Thomas, *Comput. Chem. Eng.* 16 (1992) 645-657.
- [30] S.A. Larson, J.A. Widegren, J.L. Falconer, *J. Catal.* 157 (1995) 611-625.
- [31] T.H.K. Lim, S. D. , *Chemosphere* 54 (2004) 305-312.
- [32] F.V.S. Lopes, S.M. Miranda, R.A.R. Monteiro, S.D.S. Martins, A.M.T. Silva, J.L. Faria, R.A.R. Boaventura, V.J.P. Vilar, *Appl. Catal. B: Environ.* 140-141 (2013) 444-456.
- [33] F.V.S. Lopes, R.A.R. Monteiro, A.M.T. Silva, G.V. Silva, J.L. Faria, A.M. Mendes, V.J.P. Vilar, R.A.R. Boaventura, *Chem. Eng. J.* 204-206 (2012) 244-257.
- [34] M. Hussain, N. Russo, G. Saracco, *Chem. Eng. J.* 166 (2011) 138-149.
- [35] Z. Pengyi, L. Fuyan, Y. Gang, C. Qing, Z. Wanpeng, *J. Photochem. Photobiol. A* 156 (2003) 189-194.
- [36] S.M. Miranda, F.V.S. Lopes, C. Rodrigues-Silva, S.D.S. Martins, A.M.T. Silva, J.L. Faria, R.A.R. Boaventura, V.J.P. Vilar, *Environ. Sci. Pollut. Res.* (2014) 1-13.
- [37] R.A.R. Monteiro, F.V.S. Lopes, A.M.T. Silva, J. Ângelo, G.V. Silva, A.M. Mendes, R.A.R. Boaventura, V.J.P. Vilar, *Appl. Catal. B: Environ.* 147 (2014) 988-999.
- [38] T. Ohno, K. Sarukawa, K. Tokieda, M. Matsumura, *J. Catal.* 203 (2001) 82-86.
- [39] B. Sun, A.V. Vorontsov, P.G. Smirniotis, *Langmuir* 19 (2003) 3151-3156.
- [40] T. Ohno, K. Tokieda, S. Higashida, M. Matsumura, *Appl. Catal. A: Gen.* 244 (2003) 383-391.
- [41] S. Sankar, K.G. Gopchandran, P. Kuppusami, S. Murugesan, *Ceram. Int.* 37 (2011) 3307-3315.

- [42] X. Wang, L. Sørensen, R. Su, S. Wendt, P. Hald, A. Mamakhel, C. Yang, Y. Huang, B.B. Iversen, F. Besenbacher, *J. Catal.* 310 (2014) 100-108.
- [43] V. Puddu, H. Choi, D.D. Dionysiou, G.L. Puma, *Appl. Catal. B: Environ.* 94 (2010) 211-218.
- [44] M. Hussain, R. Ceccarelli, D.L. Marchisio, D. Fino, N. Russo, F. Geobaldo, *Chem. Eng. J.* 157 (2010) 45-51.
- [45] J.M. Nicovich, S. Wang, M.L. McKee, P.H. Wine, *J. Phys. Chem.* 100 (1996) 680-688.
- [46] N. Petit, A. Bouzaza, D. Wolbert, P. Petit, J. Dussaud, *Catal. Today* 124 (2007) 266-272.
- [47] L.P. Thüner, I. Barnes, K.H. Becker, T.J. Wallington, L.K. Christensen, J.J. Orlando, B. Ramacher, *J. Phys. Chem. A* 103 (1999) 8657-8663.
- [48] S. Yamazaki, H. Tsukamoto, K. Araki, T. Tanimura, I. Tejedor-Tejedor, M.A. Anderson, *Appl. Catal. B: Environ.* 33 (2001) 109-117.
- [49] T.N. Obee, R.T. Brown, *Environ. Sci. Technol.* 29 (1995) 1223-1231.
- [50] L. Cao, A. Huang, F.-J. Spiess, S.L. Suib, *J. Catal.* 188 (1999) 48-57.
- [51] W.K. Jo, K.H. Park, *Chemosphere* 57 (2004) 555-565.
- [52] J. Zhao, X. Yang, *Build. Environ.* 38 (2003) 645-654.
- [53] P. Zhang, J. Liu, *J. Photochem. Photobiol. A* 167 (2004) 87-94.
- [54] D.S. Muggli, J.L. Falconer, *J. Catal.* 191 (2000) 318-325.
- [55] D.S. Muggli, J.L. Falconer, *J. Catal.* 187 (1999) 230-237.
- [56] D.S. Muggli, S.A. Keyser, J.L. Falconer, *Catal. Lett.* 55 (1998) 129-135.
- [57] M. El-Maazawi, A.N. Finken, A.B. Nair, V.H. Grassian, *J. Catal.* 191 (2000) 138-146.
- [58] T. Ohno, K. Sarukawa, M. Matsumura, *J. Phys. Chem. B* 105 (2001) 2417-2420.
- [59] A. Hagfeldt, M. Graetzel, *Chem. Rev.* 95 (1995) 49-68.
- [60] S. Yamazaki, T. Tanimura, A. Yoshida, K. Hori, *J. Phys. Chem. A* 108 (2004) 5183-5188.
- [61] G. Lu, A. Linsebigler, J.T. Yates, *J. Phys. Chem.* 99 (1995) 7626-7631.
- [62] J. Fan, J.T. Yates, *J. Am. Chem. Soc.* 118 (1996) 4686-4692.
- [63] J. Ângelo, L. Andrade, A. Mendes, Manuscript submitted for publication (2014).
- [64] R.A.R. Monteiro, S.M. Miranda, V.J.P. Vilar, L.M. Pastrana-Martínez, P.B. Tavares, R.A.R. Boaventura, J.L. Faria, E. Pinto, A.M.T. Silva, *Appl. Catal. B: Environ.* 162 (2015) 66-74.

Part III

Chapter 4. Gas-phase solar photocatalytic oxidation of PCE over TiO₂ based paint

Chapter 5. Gas-phase solar photocatalytic oxidation of n-decane over TiO₂ based paint

4. Gas-phase solar photocatalytic oxidation of PCE over TiO₂ based paint

This chapter presents a study of the photooxidation of PCE in an annular photoreactor under simulated solar radiation employing two different configurations of a monolithic structure of cellulose acetate coated with an active TiO₂-based paint. The influence of the configuration and different experimental conditions, namely feed flow rate (Q_{feed}), initial concentration ($C_{\text{PCE, feed}}$), relative humidity (RH) in the system, absence of oxygen and incident irradiance on the PCE conversion was evaluated. Under the best experimental conditions (i.e. $C_{\text{PCE, feed}} = 1100$ ppm, $Q_{\text{feed}} = 75 \text{ cm}^3 \text{ min}^{-1}$ ($\tau = 176 \text{ s}$), $\text{RH} = 40 \%$ and $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ in the presence of oxygen). 60 % of the initial PCE concentration was converted photocatalytically. The results showed that depending on the configuration of the structure, photocatalytic degradation of PCE can be enhanced by approximately 58 %. It was also possible to observe that chlorine radicals play an important role in the degradation of PCE whereas hydroxyl radicals cannot be excluded from the photocatalytic mechanism and in the absence of oxygen the photoreaction can still take place.

This chapter is based on the research article “Monteiro, R.A.R., Silva, A.M.T., Ângelo, J.R.M., Silva, G.V., Mendes, A.M., Boaventura, R.A.R., Vilar, V.J.P., *Photocatalytic Oxidation of Gaseous Perchloroethylene over TiO₂ Based Paint*, submitted for publication, 2014”.

4.1. Introduction

Heterogeneous photocatalytic processes have been considered a good option for air and water decontamination [1-8], since they can operate at room temperature [9], uses atmospheric air as oxidant source [10], and solar radiation for the photonic activation of the photocatalyst (usually TiO₂ [11-13]), and are able to degrade/mineralize a wide range of recalcitrant organic pollutants into harmless or easily neutralized final products (CO₂, H₂O and mineral acids) [14]. In particular, a great deal of attention has been paid to the immobilization of UV-Vis active novel nanomaterials onto inert supports, avoiding the subsequent removal of the catalyst particles, make them resistant to mechanical abrasion and to environmental ageing without impairing their performance, and to the way of their packing into the photocatalytic reactor. In this sense, a substrate for the deposition of active nanomaterials for gas-phase photocatalysis should have the following requirements [15, 16]: *i*) promote good photocatalyst adherence; *ii*) be chemically inert; photo, chemical and mechanical-resistant; *iii*) transparent to UV radiation; *iv*) promote good flow rate distribution avoiding the formation of the dead volumes and the limitations of the mass transfer processes; *v*) high surface area; *vi*) good adsorption capability for the organic compounds to be degraded; *vii*) light weight and easy handling; *viii*) low cost.

TiO₂ has been incorporated into construction materials such as cement mortar [17-19], tiles [17, 20-22], paving blocks [23-25], glass [26-28], composite sheets [29, 30], wall papers [29, 31, 32] and paints [33-40], towards the improvement of air quality, self-cleaning and self-disinfecting agents. Among all construction materials, paints are especially attractive as support for photocatalytic active TiO₂ materials mainly due to the fact that almost all surfaces can be coated with a thick and opaque film without impairing its photoactivity and obviously to aesthetic applications. Bygott *et al.* [33] conducted a field trial painting 300 m² of walls with a silicate-based paint incorporating 7.5 wt.% of photocatalytic TiO₂. The authors reported a daily NO_x abatement of *ca.* 4.5 g in about 10 000 m³ of air around school children playground [33]. Maggos *et al.* [39] stated a NO and NO₂ reduction of 19 % and 20 % respectively, using a white acrylic TiO₂-containing paint coated on the ceiling surface of a car – NO_x depollution tests were conducted in an artificially closed parking area polluted by a car exhaust during the testing period. Salthammer and Fuhrmannh [38] tested two different types of commercially available wall paints in a 1 m³ test chamber with and without air exchange using artificial sunlight. The results showed that formaldehyde was photooxidised under static conditions, while for typical VOCs, under dynamic conditions, no significant photocatalytic activity was observed. In another real-outdoor conditions study, Ângelo *et al.* [41] determined the NO photoabatement efficiency of photocatalytic paints when irradiated by sunlight. The paints were applied in a fibre cement board with 70 × 20 cm² and a stable NO feed stream was fed to the photoreactor ($C_{\text{NO}} = 100 \pm 20$ ppbv).

The best performing paint tested was formulated with PC500 and calcium carbonate yielding *ca.* 95 % of NO conversion.

Several recent studies have shown that paint components can impair the photoactivity of paint films [37-39, 42-47]. Allen *et al.* [43] demonstrated that the porosity, which is related to the particulated paint components (pigments and extenders) concentration, has a positive effect on photoactivity. However, a high content in CaCO₃ as well as a high porosity makes paints prone to self-degradation. Mendes and co-workers [36, 48, 49] developed a vinyl exterior paint modified with several TiO₂ photocatalysts: P25 (Evonik/Degussa), PC50 (Millennium), PC105 (Millennium), PC500 (Millennium), ANX type PA (Kemira), UV100 (Sachtleben), AMT100 (Tayca), UVLP7500 (Kronos), VLP7000 (Kronos), and VLP7101 (Kronos); according to the authors the pigmentary TiO₂ is the most critical component affecting the photocatalytic activity for NO_x abatement due to its competitive absorption of the UV radiation; yet, the highest yields towards NO_x photocatalytic oxidation were obtained for paint formulations incorporating PC500 (Cristal[®]), PC105 (Cristal[®]), and UV100 (Sachtleben) photocatalysts [36, 48, 49].

The formation of undesirable products from incomplete deep oxidation reactions at the surface of the paints can be harmful as several studies have already demonstrated [42, 50-52]. Uhde and Salthammer [51] reported that some by-products such as formaldehyde, acetaldehyde, ethylacrolein, pentanal, 1-hydroxy-butanone, and hexanal are typically generated when such paints are under UV radiation. This observation was also made by Kolarik and Toftum [50]. Auvinen and Wirtanen [42] and Geiss *et al.* [52] found that relatively large amounts of organic compounds, such as aldehydes and ketones, are formed from the decomposition of binders and additives.

Photocatalytic paints have also been used for disinfection of air [44, 47, 53]. Hochmannova and Vytrasova [44] stated that UV emitted from typical domestic fluorescent lamps is capable to ensure the photocatalytic and antimicrobial effects of paints incorporating nanoparticles of zinc oxide. Sousa *et al.* [47] reported photoinactivation of microorganisms by using a photocatalytic paint irradiated with UVA.

Although the promising results and potential application concerning photodegradation of air pollutants and the photoinactivation of microorganisms using TiO₂-based paints, a lot has still to be done to fully understand the phenomena behind their photoactivity and subsequently to improve the paints performances.

This chapter presents a study on gas-phase photooxidation of perchloroethylene (PCE) over a TiO₂-based paint, using a lab-scale continuous-flow annular photoreactor with a compound

parabolic collector – CPC. Two configurations based on a monolithic structure of cellulose acetate were employed as catalytic bed. Applying such structure in an annular reactor it is possible to take advantage of the low pressure drop and high surface-area-to-volume ratio typical of monolithic reactors [54], as well as to profit from the fact that the whole reactor and the catalytic bed can be illuminated, enhancing the photonic efficiency through the CPC [55, 56]. Besides, the presence of an internal cylinder allows the use of a UVA or solar light lamp which enables photocatalysis even at low natural solar irradiance conditions [57, 58]. To the best of our knowledge, this is the first time that the performance of TiO₂-based paints and their applicability on gas-phase photooxidation processes for PCE abatement is evaluated. The photocatalytic oxidation (PCO) of PCE was studied for different operating conditions, such as feed flow rate, PCE concentration, relative humidity, absence of oxygen and incident irradiance. In addition, based on the previous studies and on the experimental results obtained in the present work regarding the intermediate compounds detected by GC-MS, a reaction mechanism was formulated.

4.2. Experimental

4.2.1. Materials and chemicals

TiO₂ photocatalyst PC500 (Cristal[®]) was selected to modify a vinyl paint. This choice was based on Águia *et al.* [36, 48, 49] works where is shown that it is possible to obtain higher NO conversions when this paint is prepared with PC500 than when using several other commercially available photocatalysts. PC500 photocatalyst properties are detailed in Table 4.1.

Table 4.1. TiO₂ PC500 and paint properties and photoreactor dimensions employed in the gas-phase PCO of PCE under simulated solar radiation.

Catalyst and Paint [48, 49]		
TiO ₂ PC500	Manufacturer	PC500 (Cristal [®])
	Crystal structure	>99% anatase
	Crystal size [nm]	5-10
	Shape	Agglomerates
	Surface area [m ² g ⁻¹]	345
	Agglomerate size [μm]	1.2-1.7
	Shape	Agglomerates
Exterior water-based vinyl paint (wet basis)	Pigmentary TiO ₂	18 wt. %
	Water	30 wt. %
	Extenders (CaCO ₃ and silicates)	18 wt. %
	Polymer extender slurry	8 wt. %
	Binder slurry	20 wt. %
	Additives (in slurry)	6 wt. %

Cellulose acetate monolithic structures (TIMax CA50-9/S – $L_C = 80$ mm, $d_{ch}^2 = 9$ mm $\times$ 9 mm, $e_{w, ch} = 0.1$ mm; Wacotech GmbH & Co. KG.) were used to immobilize the photocatalytic paint.

The reagents used for the generation of humidified air streams contaminated with PCE as well as the gases provided by Air Liquide are described in sub-section 2.2.1 of Chapter 2.

4.2.2. Photocatalytic paint films preparation and characterization

The TiO_2 PC500 catalyst and exterior water-based vinyl paint properties are summarized in Table 4.1 [49]. From the original exterior water-based vinyl paint, half of the pigmentary TiO_2 (9 wt.% in wet base) was removed; the photocatalytic paint (henceforth named as P) was, subsequently, formulated by adding 9 wt.% of TiO_2 PC500 (ca. 50 cm³ of paint without 50 % of pigmentary TiO_2 and mixing for 30 min at 300 rpm in a 100 cm³ stainless steel vessel), as reported by Águia *et al.* [36]. The final TiO_2 PC500 and pigmentary TiO_2 content was 9 wt.% in wet basis (ca. 18 wt.% in dry basis) (see Table 4.1).

Cellulose acetate monolithic structures were coated with a thin film of the photocatalytic paint using the dip-coating method (Dip-Coater RDC21-K, Bungard Elektronik GmbH & Co. KG.). The experimental procedure for dip-coating these monolithic structures is described in sub-section 3.2.1 of Chapter 3.

The photocatalytic paint immobilized (P) on different sets of cellulose acetate monolithic structures (C) was labelled as xPCy, where x refers to the number of layers coated and y is 1 for configuration 1 and 2 for configuration 2. A schematic representation of both configurations employed in this study can be found in Figure 4.1b.

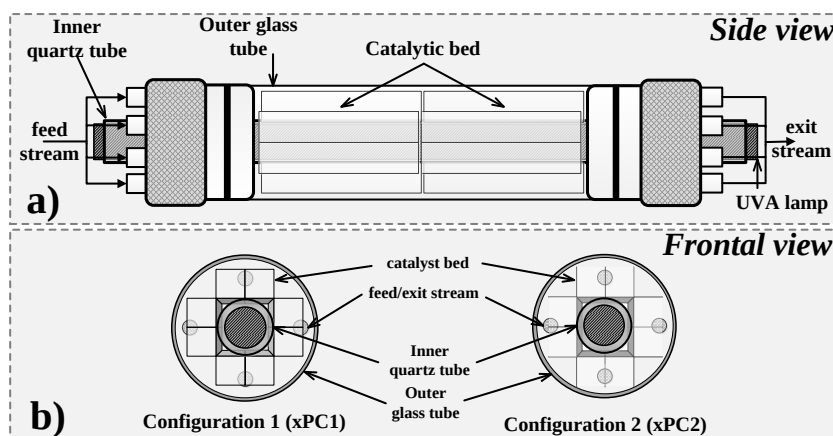


Figure 4.1. Annular photoreactor schematic representation: a) side view; b) frontal view of the two configurations used (xPC1 and xPC2).

Sets of xPC1 were prepared in order to evaluate the influence of the coat thickness upon the photocatalytic activity (configuration 1; see Figure 4.1b). It must be pointed out that monolithic structures are prone to shading effects owing not only to the structure itself but also to the coat thickness; in this way, a second configuration was tested by removing the outer wall of the above-mentioned structure (configuration 2; see Figure 4.1b). After assessing the optimum coat thickness, a set of xPC2 coated with the same photocatalytic paint having a comparable paint surface density, ρ_A , was prepared in order to clarify the influence of the configuration on the photocatalytic activity. The study of PCE degradation through PCO was carried out using the same set of xPC2. Table 4.2 summarizes the catalytic bed properties of all xPCy used in this study.

Table 4.2. Catalytic bed characteristics and configurations employed in the gas-phase PCO of PCE under simulated solar radiation.

Catalytic bed (xPCy)												
Catalyst (P)		Pigmentary	9 wt.% (wet basis)									
		PC500	9 wt.% (wet basis)									
Substrate (C)	ρ_{Cx} [mg cm ⁻³]		1.30									
	d_{ch} [cm]		0.9									
	Porosity (ϵ)		0.991									
		A_{PC1} [cm ²]	806.4									
Config. 1 (xPC1)	n_{layers} [x]		1	3	4	7	9	10	12			
	m_P [mg]		103.2	340.7	442.2	708.1	943.9	1022.8	1237.4			
	m_{C1} [mg]		3.1609	3.2698	3.1939	3.1963	3.1739	3.3170	3.2418			
	$\rho_{A, PC1}$ [mg cm ⁻²]		0.1280	0.4225	0.5484	0.8781	1.171	1.268	1.534			
			A_{PC2} [cm ²]	576.0								
Config. 2 (xPC2)	n_{layers} [x]		5									
	m_P [mg]		503.6									
	m_{C1} [mg]		2.0657									
	$\rho_{A, PC2}$ [mg cm ⁻²]		0.8743									

The surface morphology of PC500 powder was previously characterized through scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) by Águia *et al.* [48] and Monteiro *et al.* [59]. According to the authors, the estimated TiO₂ PC500 particle size is around 0.6 - 1.5 µm which ranges from half size up to the values provided by the manufacturer (Table 4.1). From EDX analysis, PC500 powder is composed by agglomerates and individual particles which are only made of TiO₂.

The surface morphology and chemical composition of xPCy samples were also determined by SEM and EDS in our previous work [59] where it was shown that photocatalytic paint was homogeneously coated on the substrate forming a film thickness of 5-10 µm. The results disclosed that after several hours under harsh operating conditions the film structure was not significantly affected.

4.2.3. Experimental setup and photocatalytic experiments

A full description of the experimental setup was already given in sub-sections 2.2.2 and 3.2.2 of Chapters 2 and 3, respectively. The photoreactor tube dimensions are listed in section 3.2.1 of Chapter 3.

All experiments were conducted inside the chamber of the solar simulator and using the CPC both described in sub-section 3.2.2 of Chapter 3.

The photolytic oxidation of PCE was already evaluated within the study described in Chapter 3. A set of xPC1 was prepared to evaluate the influence of the coat thickness on the photocatalytic activity. A new set of xPC2 was prepared by dipping a pre-establish number of layers considering the results attained with xPC1. The influence of the substrate structure configuration was assessed by comparing the results for xPC1 and xPC2. The efficiency of the process, using the set of xPC2, was expressed as described in sub-section 3.2.2 of Chapter 3.

The experimental conditions employed in this study for the PCO of PCE are similar to those detailed in sub-section 2.2.3 of Chapter 2 and listed in Table 4.3. Prior to the experiments, the catalytic bed was degassed and the photocatalytic paint coat activated under UVA radiation and by flowing 30 cm³ min⁻¹ (measured at 1 bar and 298 K) of synthetic air with 40 % of relative humidity for 24 h, as described elsewhere [36].

Table 4.3. Experimental conditions employed in the study of PCE photodegradation.

Run	Q_{feed}^* [cm ³ min ⁻¹]	$C_{\text{PCE, feed}}$ [ppm]	RH^* [%]	$I^{\#}$ [W _{UV} m ⁻²]
1 ^a , 2 ^a , 3 ^a	75	1100	40	38.4, 29.1, 18.9
4 ^b , 5, 6	150	1100	40	38.4, 29.1, 18.9
7, 8, 9	300	1100	40	38.4, 29.1, 18.9
10, 11, 12	150	600	40	38.4, 29.1, 18.9
13, 14, 15	150	2200	40	38.4, 29.1, 18.9
16, 17, 18	150	1100	20	38.4, 29.1, 18.9
19, 20, 21	150	1100	3	38.4, 29.1, 18.9
22 ^c , 23 ^c , 24 ^c	150	1100	40	38.4, 29.1, 18.9
25 ^c , 26 ^c , 27 ^c	150	1100	20	38.4, 29.1, 18.9
28 ^c , 29 ^c , 30 ^c	150	1100	3	38.4, 29.1, 18.9

* Measured at 298 K and 1 bar.

Measured within 280 – 400 nm (sunlight UV fraction).

^a) Experimental conditions employed in the experiments for evaluation of the effect of number of layers and structure configuration on photocatalytic conversion.^b) Experimental conditions used for photolysis experiment and for collecting the outlet gas stream at steady state after PCE degradation.^c) Experimental conditions employed for oxygen free experiments.

4.3. Results and discussion

4.3.1. Photocatalytic oxidation of PCE

4.3.1.1. Influence of the number of photocatalytic paint coating layers and substrate configuration

Sets of xPC1 with 1, 3, 4, 7, 9, 10 and 12 layers were prepared by dip-coating resulting in an increasing weight of photocatalytic paint P: 103.2 mg, 340.7 mg, 442.2 mg, 708.1 mg, 943.9 mg, 1022.8 mg, and 1237.4 mg, respectively (see Table 4.2).

Figure 4.2a shows that conversion increases as the number of coating layers (n_{layers}) increases up to seven layers, decreasing afterwards, when coated on the cellulose acetate structure (*ca.* 38 % for an incident irradiance of 38.4 W_{UV} m⁻², measured within 280 – 400 nm: solar UV fraction). As foreseen, increasing the amount of TiO₂ more electron-hole pairs are photogenerated and, consequently, more molecules of PCE can be oxidized. By contrast, above seven layers (9, 10 and 12 layers) the photocatalytic activity gradually decreases as the number of layers increases. This contradictory effect was already described in earlier works [60–62] and explained by the blockage of the radiation through the photocatalytic bed. For this structural configuration (Figure 4.1b₁) thicker coating may create “shadowed” [63] areas where no electron-hole pairs are generated and, consequently, no pollutant molecules are oxidized. As summarized in Table 4.2,

the available area for coating in the PC1 configuration is 806.4 cm^2 whilst, for PC2 configuration is 576.0 cm^2 since less walls are available in configuration 2 – Figure 4.1b₂. To have a comparable surface density, ρ_A , on both configurations, 5 layers of photocatalytic paint were dip-coated on xPC2. Following the same procedure described in section 5.2.2 (see Table 4.2) a set of 5PC2 was prepared.

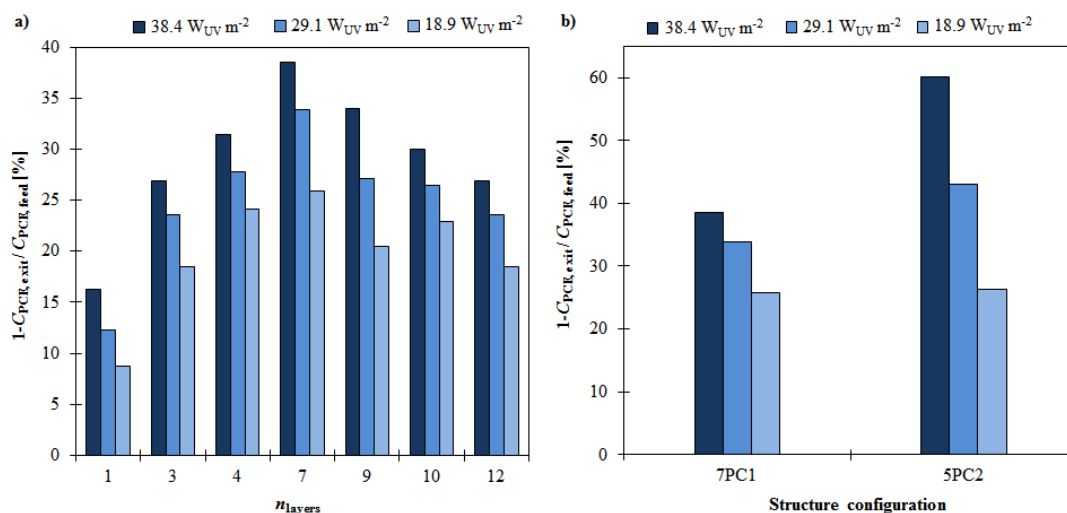


Figure 4.2. Influence on photocatalytic conversion, at steady-state conditions, of the (a) number of layers under xPC1 configuration and (b) structure configuration; I of $38.4 \text{ W}_{UV} \text{ m}^{-2}$ (■), $29.1 \text{ W}_{UV} \text{ m}^{-2}$ (■) and $18.9 \text{ W}_{UV} \text{ m}^{-2}$ (□), measured within 280 - 400 nm; $C_{PCE, feed} = 1100 \text{ ppm}$, $Q_{feed}^* = 75 \text{ cm}^3 \text{ min}^{-1}$, and $RH^* = 40 \%$; experimental conditions reported in Table 4.3. * measured at 298 K and 1 bar.

Figure 4.2b illustrates the difference in terms of PCE conversion between configuration 1 where the monolithic structure channels are closed and configuration 2 where the channels are open. For the highest irradiance used in this study ($38.4 \text{ W}_{UV} \text{ m}^{-2}$) 5PC2 originated a conversion of *ca.* 60 % of PCE against *ca.* 38 % obtained using 7PC1. Decreasing the irradiance from $38.4 \text{ W}_{UV} \text{ m}^{-2}$ to $29.1 \text{ W}_{UV} \text{ m}^{-2}$ the conversion obtained using 5PC2 and 7PC1 configurations diminished 36 % and 21 % respectively, and when the irradiance was decreased to $18.9 \text{ W}_{UV} \text{ m}^{-2}$ the PCE conversion decreased only 2 %. These preliminary results show that for lower irradiances the configuration of the monolithic structure would not affect the photocatalytic activity; instead, using PC2, the higher irradiance employed leads to higher conversions. PC1 has higher surface area available for coating than PC2 but it is worth to note that PC2 has less “shadowed zones”, *i.e.* PC2 has up to 460.8 cm^2 of surface area free of “shadows” against only 230.4 cm^2 of PC1. It should be noted the uncoated configurations 1 and 2, are transparent to radiation in the range $300 < \lambda < 800 \text{ nm}$ while the corresponding coated configurations, respectively 7PC1 and 5PC2, showed a drastic reduction in the transparency; 7PC1 is almost opaque to radiation (less than 5% of transmittance) and 5PC2 transmits up to 40 % of the incident radiation in the same wavelength

range (data not shown). The exposed area and opacity of the structure configurations may explain the differences in the photocatalytic conversion attained by both configurations.

4.3.1.2. Operating parameters affecting PCE photodegradation

PCE conversion was obtained at steady-state conditions, for five different experimental conditions (Figs. 5.3 – 5.5) using 5PC2 set: (1) feed flow rates of 75, 150, and 300 cm³ min⁻¹, measured at 298 K and 1 bar (Figure 4.3; Table 4.3: runs 1-9); (2) PCE concentrations between 600 and 2200 ppm (Figs. 4; Table 4.3: runs 4–6 and 10-15); (3) relative humidity of 3, 20 and 40 %, measured at 298 K and 1 bar (Fig. 5; Table 3: runs 4-6 and 16-21); (4) relative humidity of 3, 20 and 40 %, measured at 298 K and 1 bar in the absence of oxygen (Fig. 5; Table 4.3: runs 22-30); (5) incident UV irradiances of 38.4 W_{UV} m⁻² (Figs. 3-5; Table 4.3: runs 1, 4, 7, 10, 13, 16, 19, 22, 25, and 28), 29.1 W_{UV} m⁻² (Figs. 3-5; Table 3: runs 2, 5, 8, 11, 14, 17, 20, 23, 26, and 29), and 18.9 W_{UV} m⁻² (Figs. 3-5; Table 4.3: runs 3, 6, 9, 12, 15, 18, 21, 24, 27, 30).

Effect of the feed flow rate

Lower values of Q_{feed} mean higher residence times and lower loads of PCE per unit of time, resulting in a higher contact period between the PCE molecules and the catalyst surface, which is, at the same time, more available to convert the PCE molecules respectively. As shown in Figure 4.3a, reducing the Q_{feed} , the photocatalytic conversion of PCE increases 3.7, 3.4, and 2.7 times, respectively, for incident irradiances of 38.4 W_{UV} m⁻², 29.1 W_{UV} m⁻² and 18.9 W_{UV} m⁻² (Table 3: runs 7 and 1, runs 8 and 2, and runs 9 and 3, respectively). Notwithstanding the increasing PCE conversion with the Q_{feed} it is interesting to note that, under the highest incident irradiance (38.4 W_{UV} m⁻²), the PCE photocatalytic rate, r_{PCE} , is also maximized (5.13×10^{-5} mol min⁻¹) when using $Q_{\text{feed}} = 150$ cm³ min⁻¹ followed by 3.82×10^{-5} mol min⁻¹ for $Q_{\text{feed}} = 300$ cm³ min⁻¹). Although the highest conversion was attained for $Q_{\text{feed}} = 75$ cm³ min⁻¹ (conversion of ca. 60 %), the reaction rate is the lowest (3.58×10^{-5} mol min⁻¹). As shown in Figure 4.3b a similar behaviour is observed for all the irradiances employed. The results suggest that increasing the Q_{feed} from 75 cm³ min⁻¹ to 150 cm³ min⁻¹ the mass transfer between the PCE molecules and the catalyst surface is favoured due to a higher PCE load increasing therefore the number of converted molecules per unit of time; although $Q_{\text{feed}} = 300$ cm³ min⁻¹ implies higher PCE load per unit of time inside the reactor improving the mass transfer phenomenon, the residence time may be not enough to increase the number of converted molecules in comparison to the one obtain for 150 cm³ min⁻¹. From Figure 4.3a and 4.3b is possible to observe that for lower feed flow rates (75 cm³ min⁻¹ and 150 cm³ min⁻¹) the UV irradiance becomes more relevant on both PCE conversions and reaction rates: for 75 cm³ min⁻¹, the r_{PCE} increased from

$1.57 \times 10^{-5} \text{ mol min}^{-1}$ to $3.58 \times 10^{-5} \text{ mol min}^{-1}$ corresponding to an enhancement in terms of PCO conversion from 26 % to 60 % as the irradiance increased from $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ to $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$; for $150 \text{ cm}^3 \text{ min}^{-1}$ the r_{PCE} increased from $3.06 \times 10^{-5} \text{ mol min}^{-1}$ to $5.13 \times 10^{-5} \text{ mol min}^{-1}$ corresponding to 26 % to 43 % of enhancement in terms of PCO conversion under the same irradiance increase; in opposition for $300 \text{ cm}^3 \text{ min}^{-1}$ PCO of PCE was enhanced from 10 % ($2.36 \times 10^{-5} \text{ mol min}^{-1}$) only to 16 % ($3.82 \times 10^{-5} \text{ mol min}^{-1}$) for the same range of irradiances.

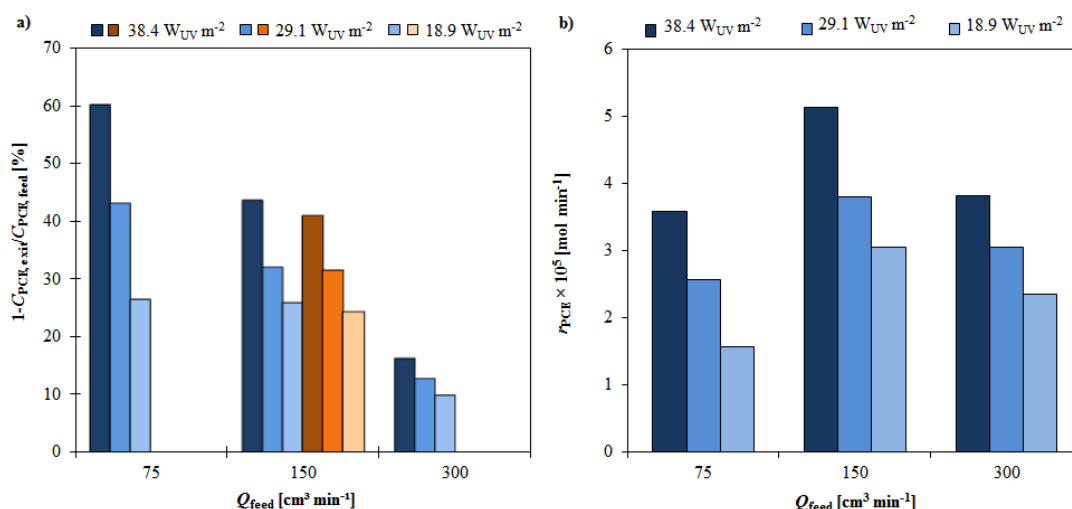


Figure 4.3. Effect of feed flow rate [Q_{feed}^*] on PCE conversion (a) and on the reaction rate, r_{PCE} (b) at steady-state conditions: experimental points for I of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■, ■), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■, ■), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■, ■), measured within 280 - 400 nm; $C_{\text{PCE, feed}} = 1100 \text{ ppm}$, $RH^* = 40 \%$; experimental conditions reported in Table 4.3. Blue columns represent 5PC2 first use (■, ■, ■) and orange columns represent 50 h under simulated solar radiation and continuous feeding (■, ■, ■).
* measured at 298 K and 1 bar.

Figure 4.3a also presents the PCE photocatalytic conversion over 5PC2 set after more than 50 h (orange columns) in experiments under simulated solar radiation and continuous feeding (humid air contaminated with PCE). Results show a slight decrease on conversion ($< 5 \%$) after 50 h, suggesting that the system is rather stable regardless the harsh experimental conditions employed.

Effect of the PCE feed concentration

In Figure 4.4a is illustrated the effect of PCE feed concentrations on photocatalytic conversion. Decreasing the PCE input molar flow rate to the reactor, more radicals such as hydroxyl ($\text{HO}^\bullet$) and chlorine ($^\bullet\text{Cl}$) become available to oxidize the PCE molecules. In fact, for $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$, decreasing the PCE feed concentration from 2200 ppm to 600 ppm, 1.8, 1.7, and 2.0 times higher PCE conversions were observed for incident irradiances of

38.4 W_{UV} m⁻², 29.1 W_{UV} m⁻² and 18.9 W_{UV} m⁻², respectively (Table 4.3: runs 13 and 10, runs 14 and 11, and runs 15 and 12, respectively).

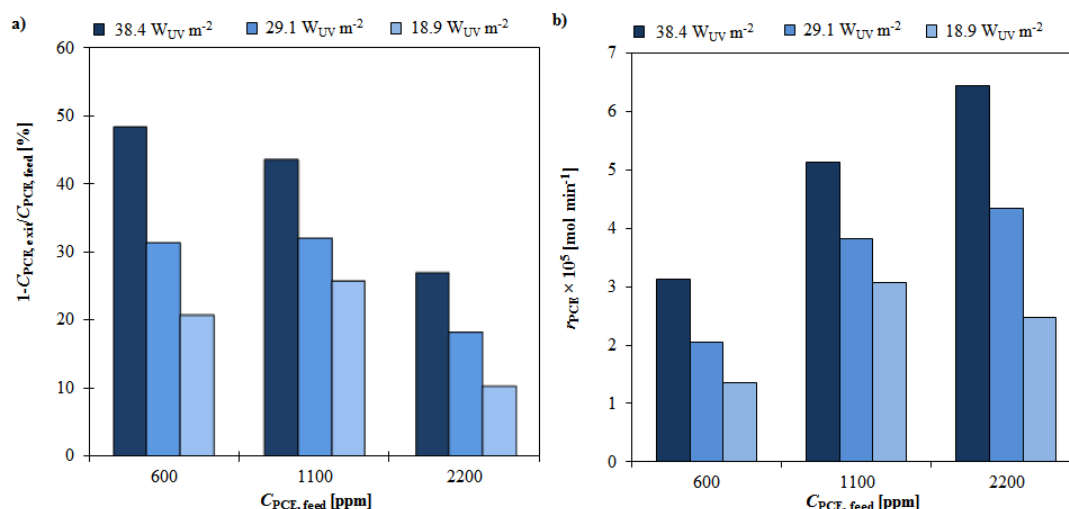


Figure 4.4. Effect of different concentrations of PCE [$C_{\text{PCE, feed}}$] on PCE conversion and on the reaction rate, r_{PCE} , at steady-state conditions: experimental points for incident irradiances of 38.4 W_{UV} m⁻² (■), 29.1 W_{UV} m⁻² (▒), and 18.9 W_{UV} m⁻² (░), measured within 280 - 400 nm; $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$ and $RH^* = 40 \%$; experimental conditions reported in Table 4.3. * measured at 298 K and 1 bar.

A similar approach regarding the photocatalytic reaction rate of PCE can be followed as plotted in Figure 4.4b: in this case, for the highest incident irradiance employed ($I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$) the r_{PCE} increases as the PCE feed concentration increases in an almost linear mode. In other words, higher $C_{\text{PCE, feed}}$ for the same flow rate ($Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$) enhances the mass transfer between the inlet gas stream and the catalyst surface increasing therefore the conversion of PCE. Decreasing the incident irradiance for $I = 29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ it is observed that the r_{PCE} as a function of $C_{\text{PCE, feed}}$ does not follow the same trend; the difference between the reaction rates obtained at 1100 ppm and 2200 ppm is progressively smaller. Under $I = 18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ the r_{PCE} for 2200 ppm of feed concentration is, in fact, lower than that of 1100 ppm. This phenomenon may be justified by the insufficient number of photons at $I = 18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ which, in their turn, will convert a less number of PCE molecules. In this case lower PCE concentration in the feed stream implies a more efficient use of the photons.

Effect of the water content

Different effects of water content on the performance of TiO₂ based catalysts have been widely reported and are still under debate [64-73]. In the absence of water vapour, the PCO of several chemicals is seriously retarded and their mineralization to CO₂ becomes incomplete; however, excessive water vapour inhibits the degradation by competitive adsorption to the

photocatalyst surface [64, 65, 73]. Obee *et al.* [66, 67] reported that the influence of humidity and contaminant concentrations (formaldehyde, toluene, and 1,3-butadiene) on the oxidation rates on titania surface is due to the competitive adsorption on available hydroxyl adsorption sites and to changes in hydroxyl radical population levels. In addition, the same authors demonstrated that the oxidation rate increases as the humidity decreases (for water content above *ca.* 1000 ppm or $4.09 \times 10^{-2} \text{ mol m}^{-3}$).

The effect of humidity on photocatalytic activity was also investigated by Cao *et al.* [74] using TiO_2 and SnO_2 for photooxidise 1-butene ($1.12 \times 10^{-4} \text{ mol m}^{-3}$). They concluded that the oxidation rate on SnO_2 drastically decreased when humidity in the feed steam increased. High photoactivity of SnO_2 is observed at low water vapour content ($< 1000 \text{ ppm}$ or $4.09 \times 10^{-2} \text{ mol m}^{-3}$), while low photoactivity was observed after increasing the water content above 2000 ppm ($8.18 \times 10^{-2} \text{ mol m}^{-3}$). Yet, TiO_2 films showed stable performance for water concentrations between 0 and 3000 ppm ($1.12 \times 10^{-1} \text{ mol m}^{-3}$). Pengyi *et al.* [69] also showed that the PCO of trace toluene ($4.09 \times 10^{-5} - 8.18 \times 10^{-4} \text{ mol m}^{-3}$) in TiO_2/UV and $\text{O}_3/\text{TiO}_2/\text{UV}$ conditions were slightly affected by the relative humidity in the range of 20 % - 55 % ($2.04 \times 10^{-1} - 7.77 \times 10^{-1} \text{ mol m}^{-3}$) being the optimal humidity around 35 % ($4.82 \times 10^{-1} \text{ mol m}^{-3}$). In different works, Jo and Park [70] revealed that photo-oxidation of benzene, ethyl benzene, and *o*-, *m*-, *p*-xylenes, trichloroethylene, and perchloroethylene in trace levels was independent of humidity in the range 10 – 100 % ($0.10 - 1.03 \text{ mol m}^{-3}$).

Figure 4.5 shows a significant reduction of 31 % (from run 4 to run 19) on the PCE conversion under $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ as the water content decreases: 43 % of the initial PCE concentration ($C_{\text{PCE, feed}} = 1100 \text{ ppm}$ or $4.46 \times 10^{-2} \text{ mol m}^{-3}$) was converted against 30 % as the relative humidity decreases from 40 % to 3 % ($3.61 \times 10^{-1} \text{ mol m}^{-3}$ to $2.71 \times 10^{-2} \text{ mol m}^{-3}$ of water). Under the lowest irradiance, $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$, a similar reduction of PCE conversion is observed: from 26 % to 18 % of converted PCE corresponding to a reduction of 29 % for the same relative humidity reduction (from run 6 to run 21). Similar to what was described in the previous chapter at $RH = 3 \%$ the concentration of water is lower than that of PCE ($C_{\text{H}_2\text{O, feed}} = 2.71 \times 10^{-2} \text{ mol m}^{-3}$ and $C_{\text{PCE, feed}} = 4.46 \times 10^{-2} \text{ mol m}^{-3}$) which would foresee a drastic reduction of PCE conversion regardless the Q_{feed} . However that reduction was not observed which indicating further mechanisms in the PCO of PCE besides the classical attack of hydroxyl radicals. Chlorine radical chain propagation reactions have been a matter of discussion by several research groups in an attempt to explain the PCO mechanism of chlorinated compounds [75-78]. A discussion on the topic will be given in the 4.3.2 sub-section.

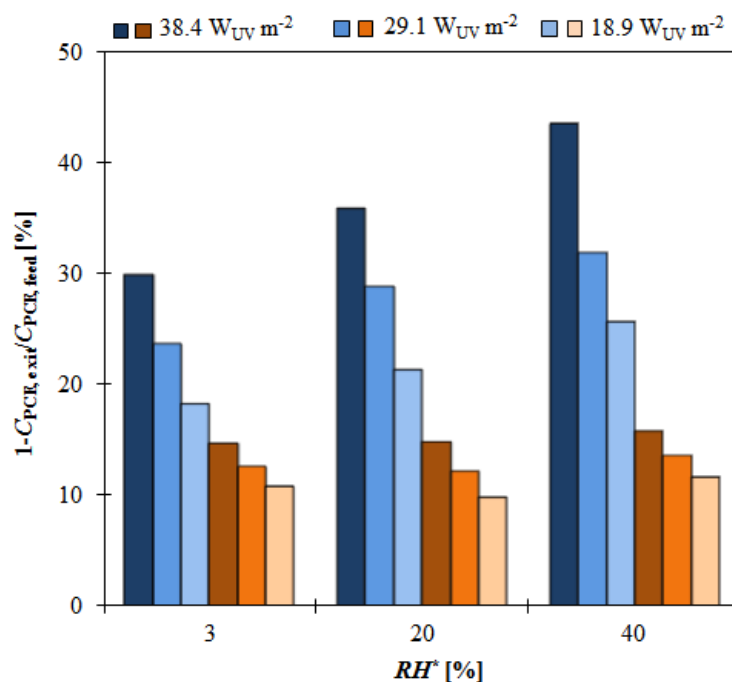


Figure 4.5. Effect of water content [RH^*] on PCE conversion at steady-state conditions in the presence of oxygen (blue columns) and in the absence of oxygen (orange columns): experimental points for incident irradiances of $38.4 \text{ W}_{\text{UV}} \text{m}^{-2}$ (■, ■), $29.1 \text{ W}_{\text{UV}} \text{m}^{-2}$ (■, ■), and $18.9 \text{ W}_{\text{UV}} \text{m}^{-2}$ (■, ■), measured within 280 - 400 nm; $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{min}^{-1}$ and $C_{\text{PCE, feed}} = 1100 \text{ ppm}$; experimental conditions reported in Table 3. * measured at 298 K and 1 bar.

Under the RH conditions employed in this study no recognizable effects related to competitive adsorption of water and PCE molecules on the catalyst surface. Obee and Brown [66] have already pointed out PCO process efficiency is a result of the combination of pollutant and RH feed concentrations and depends on the relative adsorption affinity of the photocatalyst for the pollutant and water molecules and on the mechanism of the hydroxyl radical attack (depending on the type of pollutant). Thus, the difference in the dependence of the PCE conversion on the RH between the present study and the previous studies described in Chapter 3 may be, exclusively, related to type of photocatalytic material used although further research is needed to confirm this.

Effect of oxygen

According to several authors [55, 79-81] the presence of O_2 is essential for the photoreaction and increasing the oxygen concentration the pollutant decomposition rate increases. Chang *et al.* [79] demonstrated that the photocatalytic oxidation rate of acetone increases with the oxygen content; yet, without the presence of molecular oxygen the reaction could still take place. El-Maazawi *et al.* [80] proposed that in the absence of oxygen the photocatalytic reaction could

take place due to the TiO_2 lattice oxygen. The oxygen from TiO_2 lattice is depleted during the conversion of gaseous acetone and the role of O_2 from the feed is to replenish the oxygen-deficient surface. However, in an oxygen-free reactor and considering the limited availability of surface lattice oxygen it is expectable that the pollutant conversion would be rather low compared to that found when oxygen is present in the feed stream. It is also expected that depleting oxygen from the TiO_2 lattice would deactivate the catalyst.

The dependence of the photoactivity on the gas-phase molecular oxygen absence under different water content conditions is depicted in Figure 4.5 (orange columns). The PCE conversion reached similar values for the three water content conditions (3 %, 20 % and 40 %): approximately 15 %, 13 % and, 10 % for $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$, $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$, $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$, respectively. Comparing the above values to those obtained for air-flowing experiments, it is observed a reduction in terms of PCE conversion from 54 % to 61 % as the water content reduces from 40 % to 20 %; for 3 % of relative humidity the PCE conversion reduced in the range of 40 % to 51 % depending on the employed irradiance.

These results suggest a strong contribution of the gas-phase molecular oxygen in the PCO of PCE whereas it is not clear the contribution of the oxygen from the TiO_2 lattice. Considering that in the absence of oxygen no influence in the PCE conversion was observed with the increase of the water content suggesting that hydroxyl radicals, $\text{HO}^\bullet$, may be essential to initiate of the reaction but negligible to maintain the photocatalytic process. Also, in the present of oxygen, decreasing the water concentration to levels below the concentration of PCE, its conversion was not drastically affected as it would be expected. This fact suggest that other oxidant species than hydroxyl radicals, $\text{HO}^\bullet$, may have a major role in the PCO of PCE. Chlorine radicals, $\text{Cl}^\bullet$, and the chain propagation reactions induced by them have been under debate in order to explain the PCO mechanism of chlorinated compounds such as PCE [75-78]. An approach on the PCE PCO mechanism will be given in the following sub-section.

4.3.2. PCE PCO reaction intermediated and pathway

Simultaneously with the study of PCE PCO, a 5 L sampling Tedlar bag was used to collect the outlet gas stream of the reactor, at steady state, during the PCE conversion experiment (run 4 in Table 4.3). Table 4.4 summarizes the major intermediate compounds identified and their concentrations were calculated using the response factor of toluene (according to ISO 16000-6 [82]) except for PCE, for which a specific response factor was adopted. The intermediate compounds are not present in the feed gas stream indicating their formation as PCE is converted.

Table 4.4. Reaction intermediates identified and quantified in the gas-phase photodegradation of PCE (experimental conditions reported in Table 4.3: run 4).

Compound (i)	CAS Number	Molecular formula	C_i [ppm] ^{a)}	$C_{i, \text{C-PCE}}$ [ppm]
Perchloroethylene ^{b)}	127-18-4	C ₂ Cl ₄	6.2×10^2	9.0×10^1
2-chloroacetaldehyde	107-20-0	C ₂ H ₃ ClO	3.8×10^{-2}	1.2×10^{-2}
Chloroform	67-66-3	CHCl ₃	2.0×10^{-1}	2.0×10^{-2}
Carbon tetrachloride	56-23-5	CCl ₄	1.5×10^{-1}	1.2×10^{-2}
Ethyl, trichloroacetate	515-84-4	C ₄ H ₅ Cl ₃ O ₂	3.4×10^{-1}	8.5×10^{-2}
Methyl, trichloroacetate	515-84-4	C ₄ H ₅ Cl ₃ O ₂	3.4×10^{-1}	8.5×10^{-2}
Pentachloroethane	76-01-7	C ₂ HCl ₅	7.3×10^{-3}	9.0×10^{-3}
Perchloroethane	67-72-1	C ₂ Cl ₆	4.3×10^{-2}	4.4×10^{-2}

^{a)} concentration calculated using the response factor of toluene, except for PCE for which specific response factor was used.

^{b)} PCE concentration of the feed and exit streams were analysed by MGC: $C_{\text{PCE, feed}} = 1100$ ppm; $C_{\text{C-PCE, feed}} = 159$ ppm where $C_{\text{C-PCE, feed}}$ is the carbon atoms concentration of PCE on the feed stream.

The solar PCO of PCE is initiated with the formation of electron-hole pairs, $e_{\text{cb}}^-(\text{TiO}_2)$ and $h_{\text{vb}}^+(\text{TiO}_2)$ respectively, at the catalyst surface when photons of energy $h\nu$ matching or exceeding the TiO₂ band-gap energy are absorbed (eq. 4.1).



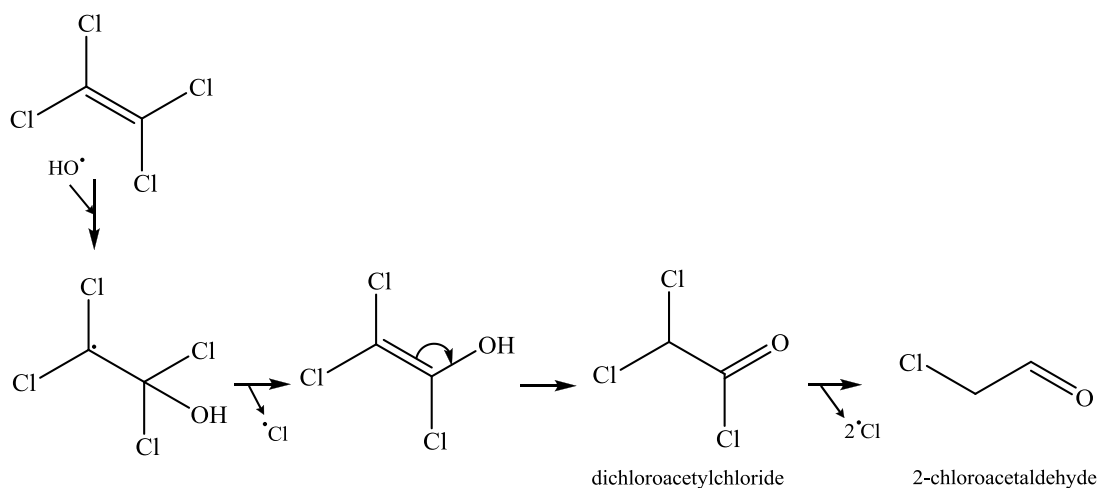
Then, the electrons and the holes may react directly with PCE molecules (eq. 4.2) [83, 84] or with water and oxygen leading to the formation of oxidizing species such as hydroxyl and reducing species such as superoxide radicals [3, 72, 85-87]. (see eqs. 4.2 – 4.5).



Several mechanisms of PCE degradation and intermediates have been described in the literature [64, 75-78, 88-90] and there is still no full agreement. Yamazaki *et al.* [64], Yamazaki *et al.* [88] stated that the photocatalytic elimination of PCE could occur via HO[•] radical or Cl[•] radical, however the reaction with HO[•] radical is thermodynamically favourable; furthermore, these authors concluded that Cl[•] radical initial reaction rarely occurs on the catalyst surface. In opposition, other authors [75-77] claimed that Cl[•] radical addition to PCE occurs several times faster than HO[•] radical addition; therefore, the HO[•] radical role in PCO of PCE could be neglected. This conclusion was further substantiated by Lu *et al.* [89] and Fan and Yates [90] after finding that the surface HO[•] groups were inactive in the oxidation of methyl chloride and

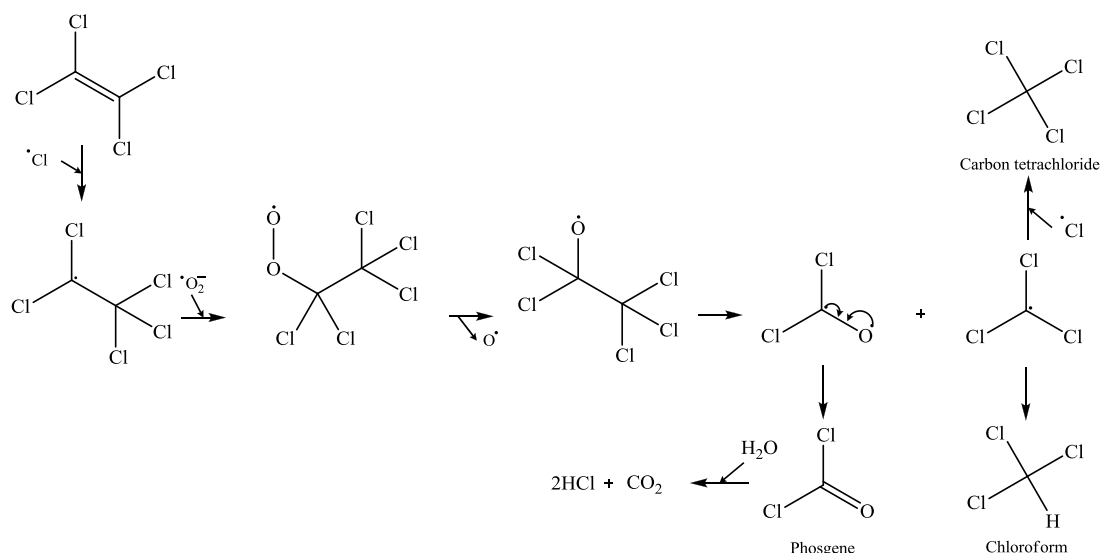
trichloroethylene.

The mechanism proposed in the following schemes relies on the assumption that PCE degradation reaction initiates with the addition of $\text{HO}^\bullet$ radicals leading to dechlorination reaction where $\text{Cl}^\bullet$ radicals are formed. Afterwards, further addition of $\text{HO}^\bullet$ and/or $\text{O}_2^{\bullet-}$ radicals will oxidize PCE into 2-chloroacetaldehyde or, alternatively, the addition of $\text{Cl}^\bullet$ radicals may produce chloroalkanes which can be involved in a chain reaction until complete mineralization. Scheme 4.1 represents the attack of a $\text{HO}^\bullet$ radical to PCE followed by a $\text{Cl}^\bullet$ radical liberation yielding trichloroethenol. The enol could tautomerize to a carbonyl compound such as dichloroacetylchloride (DCAC) and finally producing 2-chloroacetaldehyde and $\text{Cl}^\bullet$ radical. Although DCAC could not be detected in this study, several authors [91-93] have detected the presence of DCAC in the degradation of trichloroethylene and perchloroethylene.



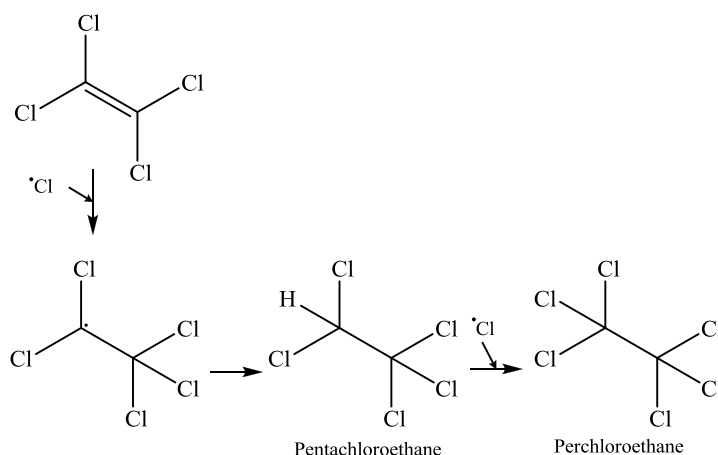
Scheme 4.1. $\text{HO}^\bullet$ radical addition to PCE followed by $\text{Cl}^\bullet$ radical generation.

The addition of $\text{Cl}^\bullet$ radicals to PCE (Scheme 4.2) results in the formation of a very unstable chloroalkyl radical promptly oxidized by superoxide radicals producing a peroxy radical. This radical can be converted into chloroethoxy radical reacting with a second peroxy radical [94] which undergoes a C-C bond scission forming CCl_2O and CCl_3 radicals. The latter converts into chloroform or carbon tetrachloride by reacting with H^+ or $\text{Cl}^\bullet$ radical, respectively, while the former produces phosgene that may be hydrolysed into CO_2 and HCl [64, 95, 96]. Phosgene was not detected in our study but it has been identified by several authors [91, 92, 97] as an intermediate of trichloroethylene reaction of degradation.



Scheme 4.2. $\text{Cl}^\bullet$ radical addition to PCE followed by $\text{O}_2^{\bullet-}$ radical addition forming chloroalkanes and phosgene.

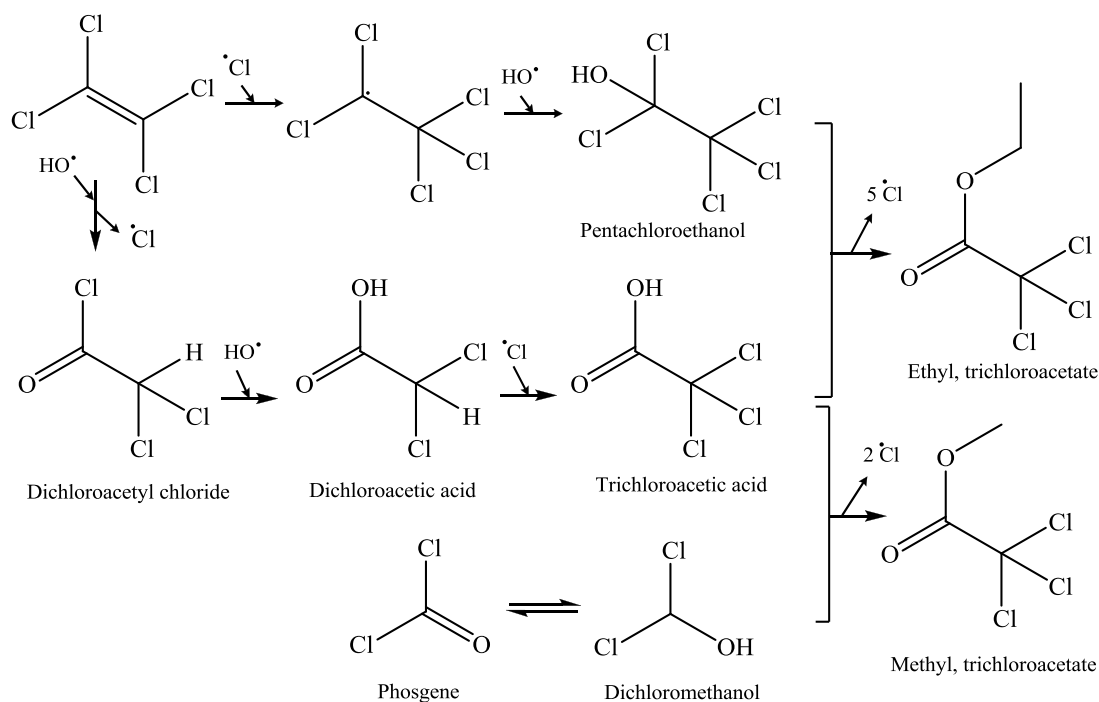
Scheme 4.3 represents the chlorination of PCE producing chloroalkanes. In this case, PCE undergoes the $\text{Cl}^\bullet$ radical attack producing chloroalkyl radical that can be hydrogenated or chlorinated producing pentachloroethane or perchloroethane, respectively.



Scheme 4.3. Chlorination of PCE by addition of $\text{Cl}^\bullet$ radicals producing chloroalkanes.

Esters derive from the reaction between carboxylic acids and alcohols. Although both kind of compounds were not detected it is possible to schematize a reaction mechanism based on our previous results [98, 99] and on organic chemistry literature [100]. In Scheme 4.4 is represented the mechanism of formation of trichloroethyl acetate and trichloromethyl acetate. Both pentachloroethanol and dichloroacetic acid may be formed from the addition of $\text{HO}^\bullet$ radical to chloroalkyl radical and dichloroacetyl chloride, respectively. The latter may be chlorinated to form trichloroacetic acid. Dichloromethanol can be easily hydrogenated at the surface of the

catalyst. Then, from the reactions between trichloroacetic acid and pentachloroethanol or dichloromethanol, ethyl, trichloroacetate and methyl, trichloroacetate may be produced.



Scheme 4.4. Esterification of ethyl, trichloroacetate and methyl, trichloroacetate.

The proposed reaction mechanisms are consistent regarding the literature, our previous results and the experimental results obtained in this study but further well-planned experiments are required to fully understand the role of HO $\cdot$ and Cl $\cdot$ radicals in the degradation of PCE.

Considering that $C_{i, \text{C-PCE}}$ refers to the carbon atoms concentration of compound i formed from the PCE photodegradation (all unreacted PCE and its major intermediates detected), it can be defined as:

$$C_{i,C-PCE} = \frac{C_i}{M_i} \cdot n(C) \cdot M(C) \quad 4.6$$

where C_i [ppm] and M_i [g mol⁻¹] are the gas phase concentration and molecular weight of compound i , respectively, $n(C)$ is the number of carbon atoms of each component i molecule, and $M(C)$ [g mol⁻¹] is the molecular weight of a carbon atom. The mineralization efficiency ($\eta_{\min}$ in %) can be determined as following:

$$\eta_{\min}[\%] = \left[1 - \frac{\Sigma_i(C_{i, \text{C-PCE}})_{\text{exit}}}{\Sigma_i(C_{i, \text{C-PCE}})_{\text{feed}}} \right] \times 100 \quad 4.7$$

Although approximately 56 % of PCE remained unreacted, from eq. 4.7 is possible to conclude that almost complete mineralization into CO₂, H₂O and HCl of the converted PCE was attained, considering the degradation intermediates detected.

4.4. Conclusions

The lab-scale continuous-flow annular photocatalytic reactor employed in this study for the degradation of PCE over a TiO₂-based paint showed good effectiveness under simulated solar light radiation. Using monolithic structures as substrate for the photocatalytic paint in an annular photoreactor, the operating advantages of a monolithic reactor (simple geometry, much better radiation distribution, low pressure drop and high catalytic surface area per unit of reactor volume) were gathered. The comparison between the two tested substrate configurations (one structure with closed channels and another with open channels) provided interesting results: by removing the outer walls of the substrate (configuration 2), ergo increasing the exposed surface area to radiation, the PCE conversion by PCO enhanced up to 58 % depending on the incident irradiance. Using such configuration, it was observed that PCE conversion is greatly affected by the flow rate of the inlet gas stream and initial PCE concentration: increasing four times the feed flow rate (from 75 to 300 cm³ min⁻¹), PCE conversion decreased from 60 % to 16 % under 38.4 W_{UV} m⁻² of irradiance corresponding to a 73 % reduction; in terms of photocatalytic reaction rate it was observed that the highest value was attained for $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$; for a 3.7-fold increase in PCE feed concentration under 38.4 W_{UV} m⁻² the PCE reaction rate also increased although the PCE conversion showed a reduction of 43 % (from 48 % of converted PCE for 600 ppm of PCE feed concentration to 27 % of converted PCE for 2200 ppm of PCE feed concentration). PCE conversion decreased substantially with the decrease of water content in the feed stream, *i.e.* at 3 % of relative humidity the PCE conversion decreased 30 % when compared to the result found at 40 % of relative humidity. Removing oxygen from the feed, only approximately 15 % of PCE was converted corresponding to an up to 56 % reduction in the PCO efficiency depending on the incident irradiance. Therefore, the action of hydroxyl radicals may be related to the initiation of the PCO process while O₂[•] and Cl[•] radicals (through Cl[•] chain propagation reactions) may be essential to maintain the process. Notwithstanding the important role of the gas-phase molecular oxygen in the PCO of PCE it is not clear the contribution of oxygen from the TiO₂ lattice.

4.5. References

- [1] C. Srinivasan, N. Somasundaram, *Curr. Sci.* 85 (2003) 1431-1438.
- [2] D.Y. Goswami, *J. Sol. Energy Eng.* 119 (1997) 101-107.
- [3] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69-96.
- [4] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, *J. Chem. Technol. Biotechnol.* 77 (2002) 102-116.
- [5] C. McCullagh, J. Robertson, D. Bahnemann, P. Robertson, *Res. Chem. Intermed.* 33 (2007) 359-375.
- [6] D. Bahnemann, *Sol. Energy* 77 (2004) 445-459.
- [7] R.W. Matthews, *J. Chem. Soc. Faraday Trans. 1* 80 (1984) 457-471.
- [8] J.-M. Herrmann, *Top. Catal.* 34 (2005) 49-65.
- [9] A.L. Linsebigler, G. Lu, J.T. Yates, *Chem. Rev.* 95 (1995) 735-758.
- [10] M. Hernandez-Alonso, I. Tejedor-Tejedor, J. Coronado, J. Soria, M. Anderson, *Thin Solid Films* 502 (2006) 125-131.
- [11] C.O. Robichaud, A.E. Uyar, M.R. Darby, L.G. Zucker, M.R. Wiesner, *Environ. Sci. Technol.* 43 (2009) 4227-4233.
- [12] E.M. Rossi, L. Pylkkänen, A.J. Koivisto, M. Vippola, K.A. Jensen, M. Miettinen, K. Sirola, H. Nykäsenoja, P. Karisola, T. Stjernvall, E. Vanhala, M. Kiilunen, P. Pasanen, M. Mäkinen, K. Hämeri, J. Joutsensaari, T. Tuomi, J. Jokiniemi, H. Wolff, K. Savolainen, S. Matikainen, H. Alenius, *Toxicol. Sci.* 113 (2010) 422-433.
- [13] R. Zhang, Y. Bai, B. Zhang, L. Chen, B. Yan, *J. Hazard. Mater.* 211–212 (2012) 404-413.
- [14] C. Guillard, J. Disdier, C. Monnet, J. Dussaud, S. Malato, J. Blanco, M.I. Maldonado, J.-M. Herrmann, *Appl. Catal. B: Environ.* 46 (2003) 319-332.
- [15] M. Kaneko, I. Okura, *Photocatalysis: Science and Technology*, Springer, 2002.
- [16] R.L. Pozzo, M.A. Baltanás, A.E. Cassano, *Catal. Today* 39 (1997) 219-231.
- [17] K. Demeestere, J. Dewulf, B. De Witte, A. Beeldens, H. Van Langenhove, *Build. Environ.* 43 (2008) 406-414.
- [18] A. Strini, S. Cassese, L. Schiavi, *Appl. Catal. B: Environ.* 61 (2005) 90-97.
- [19] A.M. Ramirez, K. Demeestere, N. De Belie, T. Mäntylä, E. Levänen, *Build. Environ.* 45 (2010) 832-838.
- [20] K. Murugan, R. Subasri, T.N. Rao, A.S. Gandhi, B.S. Murty, *Prog. Org. Coat.* 76 (2013) 1756-1760.
- [21] P.S. Marcos, J. Marto, T. Trindade, J.A. Labrincha, *J. Photochem. Photobiol. A* 197 (2008) 125-131.
- [22] M.P. Seabra, R.R. Pires, J.A. Labrincha, *Chem. Eng. J.* 171 (2011) 692-702.
- [23] C.S. Poon, E. Cheung, *Constr. Build. Mater.* 21 (2007) 1746-1753.
- [24] C.S. Poon, E. Cheung, Performance of photo-catalytic paving blocks made from waste, *Proceedings of the ICE - Waste and Resource Management*, 2006, pp. 165-171.
- [25] A. Beeldens, Air purification by pavement blocks: final results of the research at the BRRC, *Transport Research Arena Europe*, Ljubljana, 2008.

- [26] J.M. Langridge, R.J. Gustafsson, P.T. Griffiths, R.A. Cox, R.M. Lambert, R.L. Jones, *Atmos. Environ.* 43 (2009) 5128-5131.
- [27] D. Byun, Y. Jin, B. Kim, J. Kee Lee, D. Park, *J. Hazard. Mater.* 73 (2000) 199-206.
- [28] Y. Paz, Z. Luo, L. Rabenberg, A. Heller, *J. Mater. Res.* 10 (1995) 2842-2848.
- [29] H. Ichiura, T. Kitaoka, H. Tanaka, *Chemosphere* 50 (2003) 79-83.
- [30] H. Ichiura, T. Kitaoka, H. Tanaka, *J. Mater. Sci.* 37 (2002) 2937-2941.
- [31] J. Zhang, W. Liu, P. Wang, K. Qian, *J. Environ. Chem. Eng.* 1 (2013) 175-182.
- [32] H. Taoda, M. Fukaya, E. Watanabe, K. Tanaka, *Mater. Sci. Forum* 510-511 (2006) 22-25.
- [33] C.E. Bygott, J.E. Maltby, J.L. Stratton, R. McIntyre, Photocatalytic coatings for the construction industry International RILEM Symposium on Photocatalysis, Environment and Construction Materials, 8-9 October, Florence, Italy, 2007, pp. 251-258.
- [34] O. d'Hennezel, P. Pichat, D.F. Ollis, *J. Photochem. Photobiol. A* 118 (1998) 197-204.
- [35] A. Bouzaza, A. Laplanche, *J. Photochem. Photobiol. A* 150 (2002) 207-212.
- [36] C. Águia, J. Ângelo, L.M. Madeira, A. Mendes, *Catal. Today* 151 (2010) 77-83.
- [37] J. Chen, C.-s. Poon, *Build. Environ.* 44 (2009) 1899-1906.
- [38] T. Salthammer, F. Fuhrmann, *Environ. Sci. Technol.* 41 (2007) 6573-6578.
- [39] T. Maggos, J.G. Bartzis, M. Liakou, C. Gobin, *J. Hazard. Mater.* 146 (2007) 668-673.
- [40] A. Fujishima, K. Hashimoto, T. Watanabe, *TiO₂ Photocatalysis: Fundamentals and Applications*, Bkc, Incorporated, Tokyo, 1999.
- [41] J. Ângelo, L. Andrade, A. Mendes, Manuscript submitted for publication (2014).
- [42] J. Auvinen, L. Wirtanen, *Atmos. Environ.* 42 (2008) 4101-4112.
- [43] N.S. Allen, M. Edge, G. Sandoval, J. Verran, J. Stratton, J. Maltby, *Photochem. Photobiol.* 81 (2005) 279-290.
- [44] L. Hochmannova, J. Vytrasova, *Prog. Org. Coat.* 67 (2010) 1-5.
- [45] S. Laufs, G. Burgeth, W. Duttlinger, R. Kurtenbach, M. Maban, C. Thomas, P. Wiesen, J. Kleffmann, *Atmos. Environ.* 44 (2010) 2341-2349.
- [46] A. Costa, G.L. Chiarello, E. Selli, M. Guarino, *J. Environ. Manage.* 96 (2012) 86-90.
- [47] V.M. Sousa, C.M. Manaia, A. Mendes, O.C. Nunes, *J. Photochem. Photobiol. A* 251 (2013) 148-153.
- [48] C. Águia, J. Ângelo, L.M. Madeira, A. Mendes, *J. Environ. Manage.* 92 (2011) 1724-1732.
- [49] C. Águia, J. Ângelo, L.M. Madeira, A. Mendes, *Polym. Degrad. Stabil.* 96 (2011) 898-906.
- [50] J. Kolarik, J. Toftum, *Build. Environ.* 57 (2012) 396-402.
- [51] E. Uhde, T. Salthammer, *Atmos. Environ.* 41 (2007) 3111-3128.
- [52] O. Geiss, C. Cacho, J. Barrero-Moreno, D. Kotzias, *Build. Environ.* 48 (2012) 107-112.
- [53] C. Chawengkijwanich, Y. Hayata, *Int. J. Food Microbiol.* 123 (2008) 288-292.
- [54] R.E. Hayes, S.T. Kolaczowski, W.J. Thomas, *Comput. Chem. Eng.* 16 (1992) 645-657.
- [55] S.A. Larson, J.A. Widegren, J.L. Falconer, *J. Catal.* 157 (1995) 611-625.
- [56] T.H.K. Lim, S. D. , *Chemosphere* 54 (2004) 305-312.
- [57] A.V. Vorontsov, E.N. Savinov, G.B. Barannik, V.N. Troitsky, V.N. Parmon, *Catal. Today* 39 (1997) 207-218.

- [58] W.A. Jacoby, D. Blake, R.D. Noble, C.A. Koval, *J. Catal.* 157 (1995) 87-96.
- [59] R.A.R. Monteiro, F.V.S. Lopes, A.M.T. Silva, J. Ângelo, G.V. Silva, A.M. Mendes, R.A.R. Boaventura, V.J.P. Vilar, *Appl. Catal. B: Environ.* 147 (2014) 988-999.
- [60] T.N. Obee, *Environ. Sci. Technol.* 30 (1996) 3578-3584.
- [61] G.E. Imoberdorf, A.E. Cassano, H.A. Irazoqui, O.M. Alfano, *Chem. Eng. Sci.* 62 (2007) 1138-1154.
- [62] H.T. Chang, N.-M. Wu, F. Zhu, *Water Res.* 34 (2000) 407-416.
- [63] K.-H. Wang, H.-H. Tsai, Y.-H. Hsieh, *Appl. Catal. B: Environ.* 17 (1998) 313-320.
- [64] S. Yamazaki, H. Tsukamoto, K. Araki, T. Tanimura, I. Tejedor-Tejedor, M.A. Anderson, *Appl. Catal. B: Environ.* 33 (2001) 109-117.
- [65] J. Zhao, X. Yang, *Build. Environ.* 38 (2003) 645-654.
- [66] T.N. Obee, R.T. Brown, *Environ. Sci. Technol.* 29 (1995) 1223-1231.
- [67] T.N. Obee, S.O. Hay, *Environ. Sci. Technol.* 31 (1997) 2034-2038.
- [68] L. Cao, Z. Gao, S.L. Suib, T.N. Obee, S.O. Hay, J.D. Freihaut, *J. Catal.* 196 (2000) 253-261.
- [69] Z. Pengyi, L. Fuyan, Y. Gang, C. Qing, Z. Wanpeng, *J. Photochem. Photobiol. A* 156 (2003) 189-194.
- [70] W.K. Jo, K.H. Park, *Chemosphere* 57 (2004) 555-565.
- [71] W.-K. Jo, J.-H. Park, H.-D. Chun, *J. Photochem. Photobiol. A* 148 (2002) 109-119.
- [72] V. Augugliaro, S. Coluccia, V. Loddo, L. Marchese, G. Martra, L. Palmisano, M. Schiavello, *Appl. Catal. B: Environ.* 20 (1999) 15-27.
- [73] S. Wang, H.M. Ang, M.O. Tade, *Environ. Int.* 33 (2007) 694-705.
- [74] L. Cao, A. Huang, F.-J. Spiess, S.L. Suib, *J. Catal.* 188 (1999) 48-57.
- [75] J.M. Nicovich, S. Wang, M.L. McKee, P.H. Wine, *J. Phys. Chem.* 100 (1996) 680-688.
- [76] N. Petit, A. Bouzaza, D. Wolbert, P. Petit, J. Dussaud, *Catal. Today* 124 (2007) 266-272.
- [77] L.P. Thüner, I. Barnes, K.H. Becker, T.J. Wallington, L.K. Christensen, J.J. Orlando, B. Ramacher, *J. Phys. Chem. A* 103 (1999) 8657-8663.
- [78] M. Hegedűs, A. Dombi, *Appl. Catal. B: Environ.* 53 (2004) 141-151.
- [79] C.-P. Chang, J.-N. Chen, M.-C. Lu, *J. Environ. Sci. Heal. A* 38 (2003) 1131-1143.
- [80] M. El-Maazawi, A.N. Finken, A.B. Nair, V.H. Grassian, *J. Catal.* 191 (2000) 138-146.
- [81] D.S. Muggli, J.L. Falconer, *J. Catal.* 191 (2000) 318-325.
- [82] ISO 16000-6. Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS or MS/FID, 2004.
- [83] F. Benoit-Marquié, U. Wilkenhöner, V. Simon, A.M. Braun, E. Oliveros, M.-T. Maurette, *J. Photochem. Photobiol. A* 132 (2000) 225-232.
- [84] L. Cermenati, P. Pichat, C. Guillard, A. Albini, *J. Phys. Chem. B* 101 (1997) 2650-2658.
- [85] J. Peral, D.F. Ollis, *J. Catal.* 136 (1992) 554-565.
- [86] E. Pelizzetti, C. Minero, *Electrochim. Acta* 38 (1993) 47-55.
- [87] Y.V. Kolen'ko, K.A. Kovnir, A.I. Gavrilov, A.V. Garshev, P.E. Meskin, B.R. Churagulov, M. Bouchard, C. Colbeau-Justin, O.I. Lebedev, G. Van Tendeloo, M. Yoshimura, *J. Phys. Chem. B* 109 (2005) 20303-20309.

- [88] S. Yamazaki, T. Tanimura, A. Yoshida, K. Hori, *J. Phys. Chem. A* 108 (2004) 5183-5188.
- [89] G. Lu, A. Linsebigler, J.T. Yates, *J. Phys. Chem.* 99 (1995) 7626-7631.
- [90] J. Fan, J.T. Yates, *J. Am. Chem. Soc.* 118 (1996) 4686-4692.
- [91] M.R. Nimlos, W.A. Jacoby, D.M. Blake, T.A. Milne, *Environ. Sci. Technol.* 27 (1993) 732-740.
- [92] W.A. Jacoby, M.R. Nimlos, D.M. Blake, R.D. Noble, C.A. Koval, *Environ. Sci. Technol.* 28 (1994) 1661-1668.
- [93] N. Fukami, M. Yosida, B.-D. Lee, K. Taku, M. Hosomi, *Chemosphere* 42 (2001) 345-350.
- [94] A.S. Hasson, I.W.M. Smith, *J. Phys. Chem. A* 103 (1999) 2031-2043.
- [95] S. Yamazaki-Nishida, X. Fu, M.A. Anderson, K. Hori, *J. Photochem. Photobiol. A* 97 (1996) 175-179.
- [96] P.B. Amama, K. Itoh, M. Murabayashi, *J. Mol. Catal. A-Chem.* 176 (2001) 165-172.
- [97] S. Suárez, N. Arconada, Y. Castro, J.M. Coronado, R. Portela, A. Durán, B. Sánchez, *Appl. Catal. B: Environ.* 108–109 (2011) 14-21.
- [98] F.V.S. Lopes, S.M. Miranda, R.A.R. Monteiro, S.D.S. Martins, A.M.T. Silva, J.L. Faria, R.A.R. Boaventura, V.J.P. Vilar, *Appl. Catal. B: Environ.* 140-141 (2013) 444-456.
- [99] F.V.S. Lopes, R.A.R. Monteiro, A.M.T. Silva, G.V. Silva, J.L. Faria, A.M. Mendes, V.J.P. Vilar, R.A.R. Boaventura, *Chem. Eng. J.* 204–206 (2012) 244-257.
- [100] K.P.C. Vollhardt, N.E. Schore, *Organic chemistry: structure and function*, 3rd Edition ed., W. H. Freeman and company, New York, 1999.

5. Gas-phase solar photocatalytic oxidation of n-decane over TiO₂ based paint

The present chapter reports n-decane photocatalytic oxidation studies carried out in an annular photoreactor under simulated solar radiation and employing a catalytic bed made of cellulose acetate monoliths coated with a photocatalytic paint. The influence of the feed flow rate, n-decane concentration, relative humidity, and incident irradiance on the n-decane conversion kinetics was assessed. Within this work, n-decane conversions higher than 90 % were achieved, depending on the experimental conditions. Additionally, a phenomenological reaction rate model of the n-decane photocatalytic oxidation was proposed and assessed. The proposed model assumes that n-decane and water molecules compete for different active sites on the catalyst surface. Finally, despite the high n-decane conversion achieved, reaction by-products were identified and, based on these compounds, a reaction mechanism was formulated.

This chapter is based on the research article “Monteiro, R.A.R., Lopes, F.V.S., Silva, A.M.T., Ângelo, J.R.M., Silva, G.V., Mendes, A.M., Boaventura, R.A.R., Vilar, V.J.P., *Are TiO₂-based exterior paints useful catalysts for gas-phase photooxidation processes? A case study on n-decane abatement for air detoxification*, Applied Catalysis B: Environmental, 147 (2014) 988-999, DOI: 10.1016/j.apcatb.2013.09.031”.

5.1. Introduction

For a long time, society has been debating indoor air pollution and its effect on human health whether in urban or industrial areas [1-4]. Today, 70 – 90 % of our lifetime is spent at indoor environments [5, 6]. Incoming air filters or air cleaners based on ultraviolet germicidal radiation, activated carbon, ionization, or ozone generation are the most used methods for air decontamination [3, 7]. Nevertheless, photocatalysis is now seen as a valuable option for depolluting purposes [8-15], mainly because it: i) can be operated at room temperature [16]; ii) air (through water vapour and molecular oxygen) can be used as the source of oxidant [17], iii) degrades/mineralizes a wide range of organic pollutants into harmless or easily neutralized final products (CO₂, H₂O and mineral acids) [18]; iv) can take advantage of solar radiation for performing the charge separation at the semiconductor [19]. Furthermore, semiconductor titanium dioxide (TiO₂) is commonly employed as photocatalyst in photocatalytic oxidation (PCO) processes due to its inexpensiveness, resistance to photocorrosion, high oxidative power, and relatively low toxicity [20-22].

TiO₂ powders have been incorporated as white pigment in different applications from ancient times [23]. As early as 1929, Kiedel [24] stated that titanium white pigment, under sunlight radiation, was responsible for paint chalking related to photoconversion of organic binder. In 1938, Goodeve *et al.* [25] reported that UV absorption produces active oxygen species on the TiO₂ surface that cause dyes to photobleach.

Although, it was during the 1960s that, for the first time, TiO₂ photochemical effect was used to induce chemical reactions [26, 27], Mashio and co-workers [28] in 1956 conducted several studies regarding oxidation induced by TiO₂ under illumination. These works concluded that anatase is more photoactive than rutile. However, the first contribution for understanding the heterogeneous photocatalytic effect was in 1972 with the pioneer work by Fujishima and Honda [29]. These authors investigated the electrochemical photolysis of water using a single TiO₂-rutile crystal (*n*-type) as photoanode and a Pt counter electrode. This work opened the frontiers for the use of titania for photocatalysis and other applications.

Construction materials can be used to support photocatalytic TiO₂ nanoparticles and used as depolluting agents [23, 30-36]. Paint coatings, among all construction materials, are especially attractive as support for photocatalytic TiO₂ since almost all surfaces in urban areas can be painted. Bygott *et al.* [30], for instance, report a field trial in London, close to a school children playground, where an area of 300 m² of walls was painted with a silicate-based paint incorporating 7.5 wt.% of photocatalytic TiO₂. The results showed a daily NO_x abatement of ca. 4.5 g in about 10000 m³ of air around the school children playground [30]. Maggos *et al.* [36]

report NO_x depollution tests in an artificially closed parking area, which was polluted by a car exhaust during the testing period; they observed a reduction of 19 % and 20 % for NO and NO₂, respectively. Salthammer and Fuhrmann [35] studied the photocatalytic efficiency of two different types of commercially available wall paints in a 1 m³ test chamber with and without air exchange using artificial daylight. The results showed that formaldehyde was photooxidised under static conditions. In contrast, for typical VOCs, under dynamic conditions, no significant photocatalytic effect was observed.

Although the potential of photocatalytic paints to detoxify air is very promising, several studies demonstrate the formation of by-products that may be harmful for humans [37-40]. For example, Uhde and Salthammer [38] reported that UV-irradiated paints produce undesired and highly toxic by-products such as formaldehyde, acetaldehyde, ethylacrolein, pentanal, 1-hydroxybutanone, and hexanal. This observation was further emphasized by Kolarik and Toftum [37]. Auvinen *et al.* [39] and Geiss *et al.* [40] found that relatively high amounts of organic compounds, such as aldehydes and ketones, are formed from the decomposition of binders and additives. Auvinen *et al.* [39] also stated that photocatalytic surface aging and the use of different substrates (glass, gypsum or polymeric plaster) do not have a noteworthy influence on the paint photocatalytic activity.

Photocatalytic paints have been showing very promising results concerning the photoconversion of air pollutants and the photoinactivation of microorganisms. However, it is necessary to keep improving their performance, as well as understand the phenomena behind their photoactivity. This chapter presents a study on gas-phase solar photooxidation of *n*-decane over a TiO₂-containing paint, using a lab-scale continuous-flow annular photoreactor with a compound parabolic collector. To the best of our knowledge, this is the first time that the performance of TiO₂-based exterior paints and their applicability on gas-phase photooxidation processes for *n*-decane abatement is evaluated. The photocatalytic oxidation of *n*-decane was studied for different operating conditions, such as feed flow rate, *n*-decane concentration, feed relative humidity and incident irradiance. The *n*-decane conversion reaction behaviour in the continuous system was modelled considering different Langmuir-Hinshelwood kinetic-based reaction rate equations. It considers that PCO of *n*-decane is not influenced by reaction intermediates and/or products and *n*-decane and water are the major species. In addition, a reaction mechanism was proposed for *n*-decane PCO considering the conversion by-products identified by GC/MSD.

5.2. Experimental

5.2.1. Materials and chemicals

All chemicals and materials used in this chapter were already detailed in the sub-section 4.2.1. of Chapter 4.

5.2.2. Photocatalytic films preparation and characterization

The photocatalytic paint and photocatalyst properties were already described in sub-section 4.2.1. of the Chapter 4. The films preparation was also described in sub-section 4.2.2. of Chapter 4.

In this study, four layers of photocatalytic paint P were deposited on each support surface, and the resulting PC samples were packed into the annular photocatalytic reactor (described in section 5.2.3 of the present Chapter). The catalytic bed properties are detailed in Table 5.1.

Table 5.1. Catalytic bed characteristics employed in the gas-phase PCO of *n*-decane under simulated solar radiation.

Catalytic bed (PC)		
Catalyst (P)	m_p [mg]	1052
	m_C [mg]	2006
	ρ_C [g cm ⁻³]	1.30
Support (C)	d_{ch} [cm]	0.9
	A_C [cm ²]	576.0
	ρ_A [mg cm ⁻²]	1.83
	ε	0.991

Scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) analysis was performed in a FEI Quanta 400 FEG ESEM / EDAX Genesis X4M apparatus equipped with a Schottky field emission gun (for optimal spatial resolution) for the characterization of the surface morphology of PC500 powder, fresh PC, and used PC samples (after more than 50 h of PCO experiments) as well as their chemical composition. Each sample was mounted on a double-sided adhesive tape made of carbon for its surface observation at different magnifications; the cross-section of the fresh PC sample was also measured by this technique. These SEM/EDX analyses were made at CEMUP (Centro de Materiais da Universidade do Porto).

5.2.3. Experimental setup and photocatalytic experiments

A full description of the experimental setup was already given in sub-sections 2.2.2. and 3.2.2. of Chapters 2 and 3, respectively. The photoreactor tube dimensions are listed in section 3.2.1. of Chapter 3. Figures 5.1a and 5.1b schematically represent the side and frontal views of the annular photoreactor, respectively.

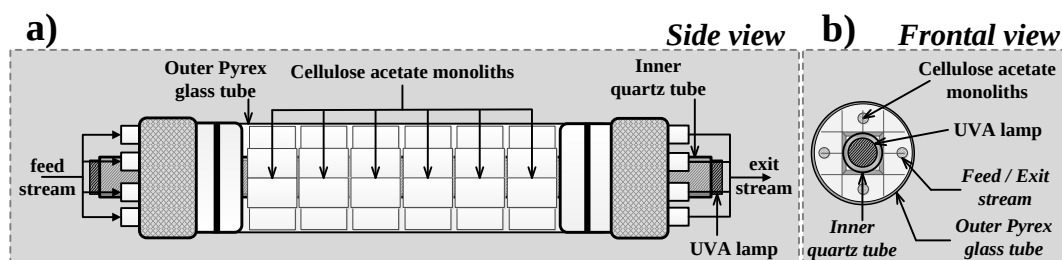


Figure 5.1. Schematic representation of the continuous-flow photoreactor: a) from a side point of view and b) from a frontal point of view.

All experiments were conducted inside the chamber of the solar simulator and using the CPC, both described in sub-section 3.2.2. of Chapter 3.

The photolytic oxidation of *n*-decane was already evaluated within the study described in Chapter 3.

The experimental conditions employed in this study aiming the study of PCO of *n*-decane are similar to those detailed in sub-section 2.2.3. of Chapter 2 and are listed in Table 5.2. of the present Chapter.

Table 5.2. Experimental conditions employed in the study of *n*-decane conversion.

Run	Q_{feed}^* [cm ³ min ⁻¹]	$C_{\text{dec, feed}}$ [ppm]	RH^* [%]	$I^\#$ [W _{UV} m ⁻²]
1, 2, 3	150	73	40	38.4, 29.1, 18.9
4, 5, 6	75	73	40	38.4, 29.1, 18.9
7, 8, 9	300	73	40	38.4, 29.1, 18.9
10, 11, 12	150	40	40	38.4, 29.1, 18.9
13, 14, 15	150	138	40	38.4, 29.1, 18.9
16, 17, 18	150	73	3	38.4, 29.1, 18.9

* Measured at 298 K and 1 bar.

Measured within 280 - 400 nm (sunlight UV fraction).

5.3. Results and discussion

5.3.1. Photocatalytic oxidation of *n*-decane

5.3.1.1. Surface characterization of photo-TiO₂ powder and PC samples

The surface morphology of PC500 powder sample and its chemical composition were determined by SEM/EDX. The SEM micrograph (Figure 5.2a) shows an estimated size of the photo-TiO₂ agglomerates of ca. 600 – 1500 nm. According to this image, the dimension of the agglomerates range from half size up to the values provided by the manufacturer (see Table 5.1); similar sizes are displayed in SEM pictures of photocatalytic paint films loaded with the same photocatalyst and reported by Águia *et al.* [41]. As previously mentioned by the same authors [41], EDX analysis of PC500 powder (Figure 5.2b) indicates that both agglomerates and individual particles are only made of TiO₂.

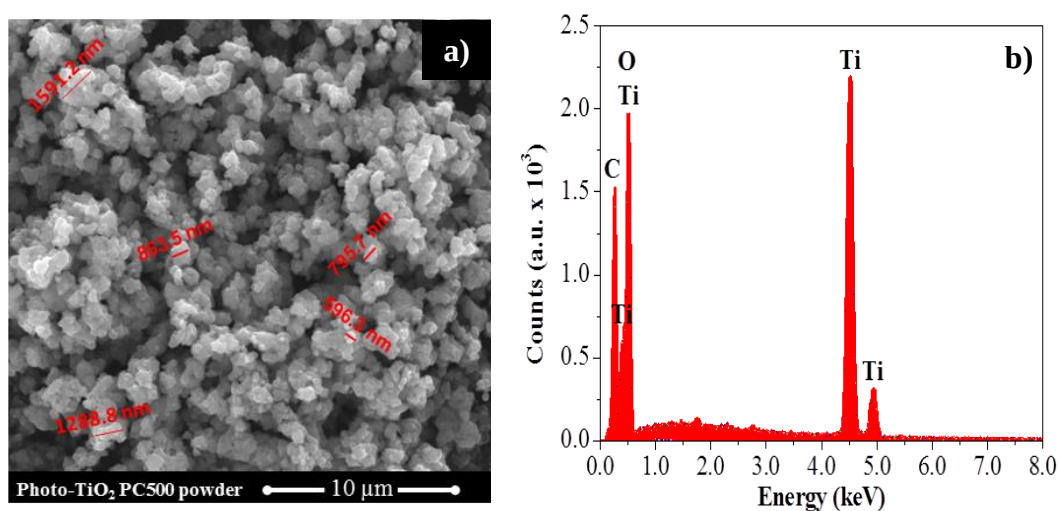


Figure 5.2. SEM micrograph (a) and EDX spectrum (b) of photo-TiO₂ PC500 powder.

The surface morphology and chemical composition of PC samples was also determined by SEM/EDX. SEM micrographs of fresh PC and used PC samples (with 50 h+ of use in PCO of *n*-decane) at three different magnifications are shown in Figures 5.3a to 5.3d. The fresh PC images (Figures 5.3a and 5.3c) show that the photocatalytic paint was homogeneously coated on the cellulose acetate monolith. After its use on the PCO experiments (Figures 5.3b and 5.3d), SEM micrographs suggest that the film structure was not significantly affected despite the harsh operating conditions employed. This conclusion was also supported by EDX analysis of both fresh and used samples (shown in Figures 5.3e and 5.3f, respectively). According to the EDX spectra, the proportion of each element remained approximately the same after the photocatalytic experiments.

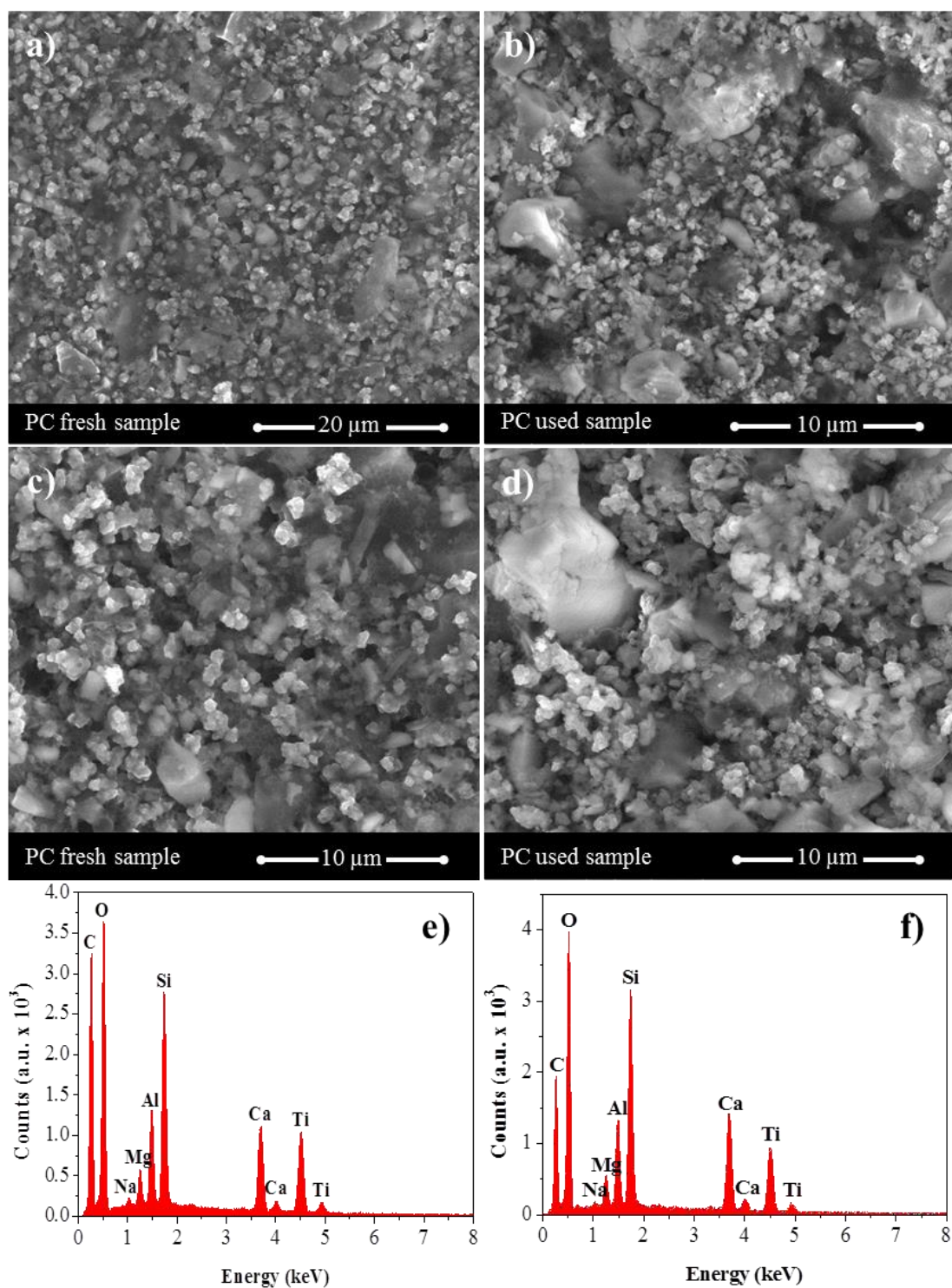


Figure 5.3. SEM micrographs (a-d) and EDX spectra (e, f) of PC before (left-side images) and after 50 h+ of use (right-side images) in PCO of *n*-decane.

From SEM images (Figure 5.4) it was also possible to estimate the paint film thickness (ca. 5 – 10 μm) and the cellulose acetate monolith thickness (ca. 50 μm). Contrarily to what have been observed by Lopes *et al.* [42] when using TiO_2 sol-gel films supported on cellulose acetate monoliths, paint films are approximately 25-fold thicker (and more resistant) than TiO_2 sol-gel

films. These properties significantly prevent film fissures, delamination, and/or deterioration. Thus, the use of paint films reveals to be an advantage in the prevention of the catalyst/support aging.

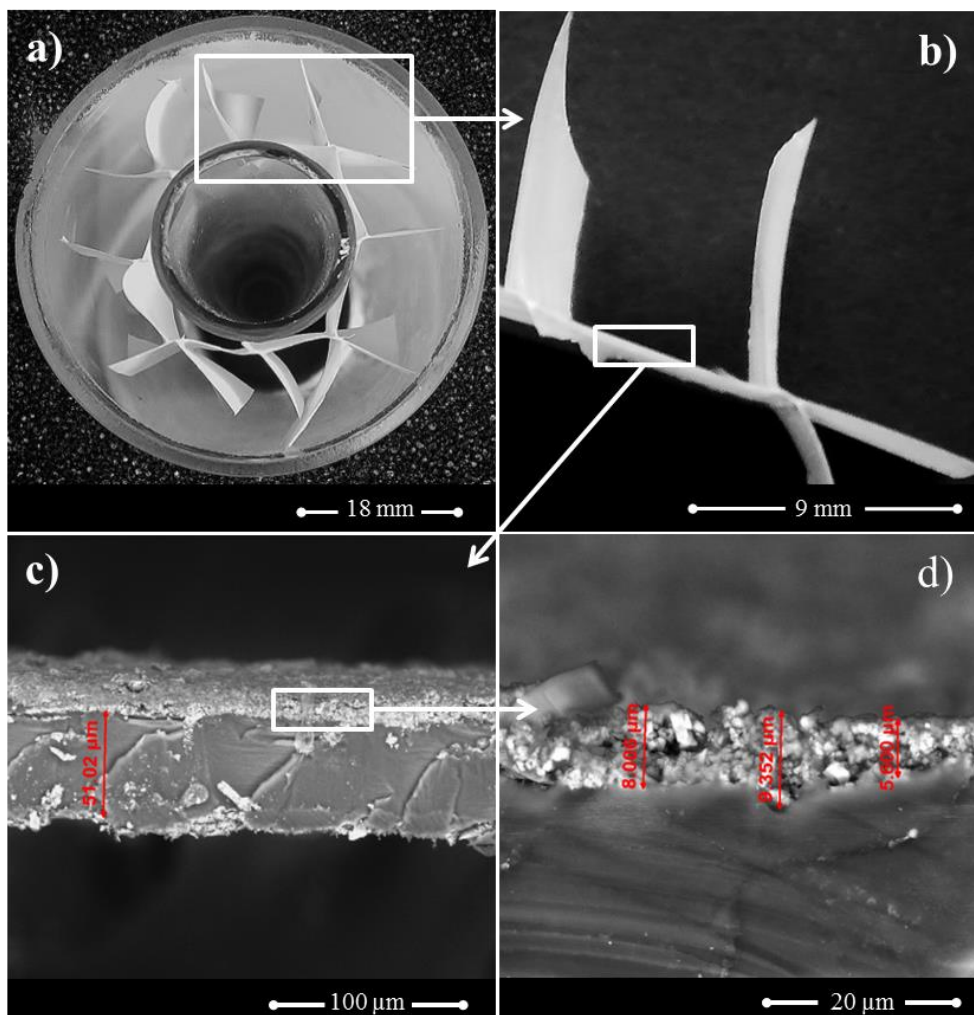


Figure 5.4. Photographs (a-b) and SEM micrographs (c-d) of PC used in PCO of *n*-decane.

5.3.1.2. Operating parameters effect on *n*-decane photoconversion

At steady-state conditions, *n*-decane photoconversion fraction ($C_{\text{dec, exit}} / C_{\text{dec, feed}}$) was obtained for four experimental conditions (Figures 5.5 – 5.7). Figure 5.5 shows the effect of the feed flow rate (Q_{feed}) on the *n*-decane conversion fraction. *n*-Decane conversion decreases as Q_{feed} increases, since a higher feed flow rate results in a lower residence time, reducing the pollutant-catalyst contact period. Thereby, for a 4-fold increase in Q_{feed} , the photocatalytic process is 1.6, 1.9, and 2.3 times less effective, respectively, for incident irradiances of 38.4, 29.1 and 18.9 W_{UV} m⁻² (Table 5.2: runs 4 and 7, runs 5 and 8, and runs 6 and 9, respectively).

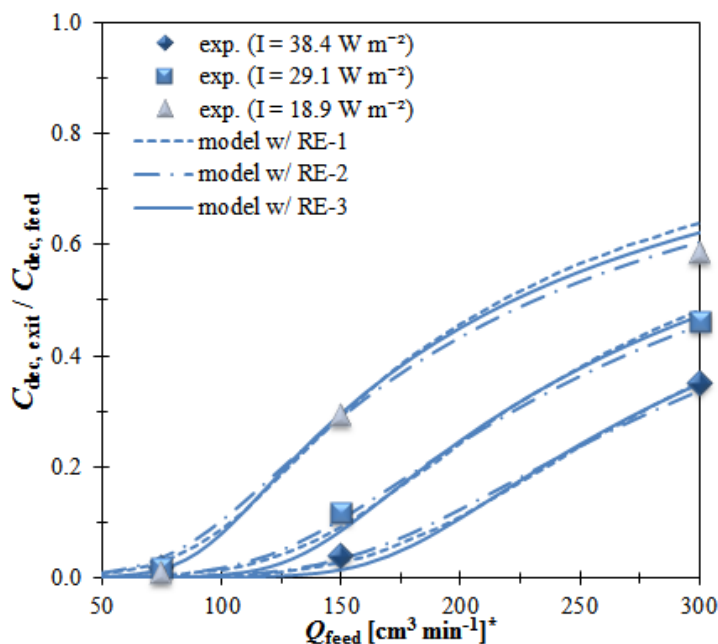


Figure 5.5. Influence of feed flow rate (Q_{feed}) on n -decane conversion fraction ($C_{\text{dec, exit}} / C_{\text{dec, feed}}$ at steady-state conditions): experimental points for incident irradiance measured within 280 – 400 nm (sunlight UV fraction) of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ ($\blacklozenge$), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ ($\blacksquare$), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ ($\blacktriangle$), and RE-1 (---), RE-2 (— · —), and RE-3 (—); $C_{\text{dec, feed}} = 73 \text{ ppm}$, $RH^* = 40 \%$, and $T = 298 \text{ K}$; operation conditions reported in Table 5.2; * measured at 298 K and 1 bar.

On the other hand, the organic load entering the reactor increases with the Q_{feed} , which means that, although the reduced conversion at higher Q_{feed} , the photocatalytic reaction rate of n -decane, r_{dec} , increases. In this sense, under the highest incident irradiance ($38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$), the r_{dec} is maximized (ca. $11.5 \times 10^{-6} \text{ mol min}^{-1}$) for $Q_{\text{feed}} = 300 \text{ cm}^3 \text{ min}^{-1}$ followed by $9.6 \times 10^{-6} \text{ mol min}^{-1}$ for $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$. The highest conversion was attained for $Q_{\text{feed}} = 75 \text{ cm}^3 \text{ min}^{-1}$ (conversion of ca. 99 %) however its reaction rate was the lowest ($4.4 \times 10^{-6} \text{ mol min}^{-1}$). A similar behaviour was observed for all the irradiances employed as shown in Figure 5.6. The results suggest that increasing the Q_{feed} from $75 \text{ cm}^3 \text{ min}^{-1}$ to $300 \text{ cm}^3 \text{ min}^{-1}$, the mass transfer between the n -decane molecules and the surface of the catalyst is enhanced due to a higher organic load; however the residence time at $Q_{\text{feed}} = 300 \text{ cm}^3 \text{ min}^{-1}$ ($\tau = 44 \text{ s}$) seems insufficient to convert n -decane molecules in the same proportion as at $Q_{\text{feed}} = 75 \text{ cm}^3 \text{ min}^{-1}$, resulting in a reduction of the n -decane conversion at higher Q_{feed} .

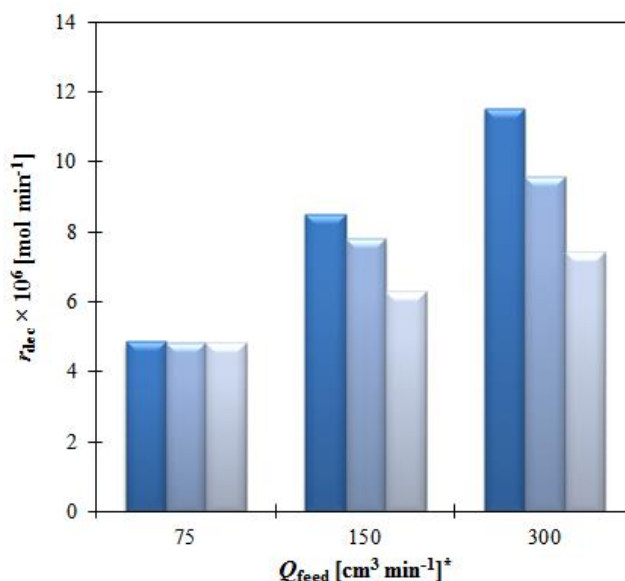


Figure 5.6. Influence of feed flow rate (Q_{feed}) on *n*-decane photocatalytic reaction rate (r_{dec}), at steady-state conditions: experimental points for incident irradiance measured within 280 – 400 nm (sunlight UV fraction) of $38.4 \text{ W}_{\text{UV}} \text{m}^{-2}$ (■), $29.1 \text{ W}_{\text{UV}} \text{m}^{-2}$ (▒), and $18.9 \text{ W}_{\text{UV}} \text{m}^{-2}$ (□); $C_{\text{dec, feed}} = 73 \text{ ppm}$, $RH^* = 40 \%$, and $T = 298 \text{ K}$; operation conditions reported in Table 5.2; * measured at 298 K and 1 bar.

It is also worth noting that the incident irradiance on the catalyst surface becomes more relevant for higher feed flow rates. As seen before, higher Q_{feed} mean higher organic load and, thus, more molecules are available to be converted. However, these molecules are in a higher number than the photons generated for each employed irradiance. Consequently, the PCO of *n*-decane depends more on the irradiance at higher organic load, *i.e.*, higher Q_{feed} than at low Q_{feed} .

In Figure 5.7 is shown the influence of the feed concentration on the *n*-decane conversion fraction. Results show a decrease in the conversion fraction with an increase of *n*-decane concentration. In fact, for a 3.4-fold increase in $C_{\text{dec, feed}}$ (from 41 to 138 ppm), 1.8, 2.4, and 3.6 times lower conversion fractions were observed for incident irradiances of 38.4, 29.1 and $18.9 \text{ W}_{\text{UV}} \text{m}^{-2}$, respectively (Table 5.2: runs 4 and 7, runs 5 and 8, and runs 6 and 9, respectively).

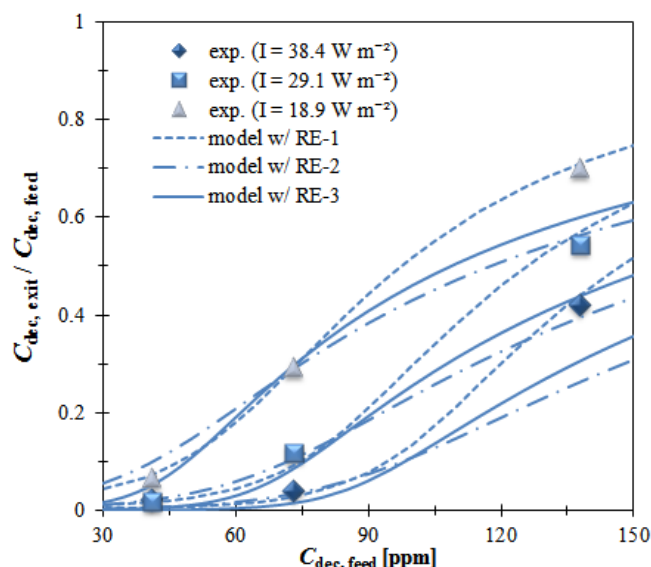


Figure 5.7. Influence of the feed concentration ($C_{\text{dec, feed}}$) on n -decane conversion fraction ($C_{\text{dec, exit}} / C_{\text{dec, feed}}$) at steady-state conditions: experimental points for incident irradiance measured within 280 – 400 nm (sunlight UV fraction) of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ ($\blacklozenge$), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ ($\blacksquare$), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ ($\blacktriangle$), and RE-1 (---), RE-2 (— · —), and RE-3 (—); $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$, $RH^* = 40 \%$, and $T = 298 \text{ K}$; operation conditions reported in Table 5.2; * measured at 298 K and 1 bar.

Regarding the photocatalytic reaction rate of n -decane, Figure 5.8 shows that increasing the $C_{\text{dec, feed}}$ so does the r_{dec} . In other words, under the same irradiance and for a given Q_{feed} , higher $C_{\text{dec, feed}}$ enhances the mass transfer between the feed gas stream and the catalyst surface increasing the amount of converted n -decane. However, increasing the number of n -decane molecules entering the reactor per unit of time, a higher number of photons/hydroxyl radicals are necessary to achieve the same conversion fraction which means that higher $C_{\text{dec, feed}}$ promotes higher reaction rate of n -decane but lower values of conversion.

The results above also suggest that the feed concentration has a more important influence on the PCO of n -decane than the feed flow rate which is related to the following: the number of moles of n -decane entering the reactor increases linearly with Q_{feed} (4.79×10^{-6} , 8.86×10^{-6} and $1.77 \times 10^{-5} \text{ mol min}^{-1}$ for 75, 150 and $300 \text{ cm}^3 \text{ min}^{-1}$, respectively) while increasing the $C_{\text{dec, feed}}$ the number of n -decane moles per minute is proportional to $C_{\text{dec, feed}}^2$ (2.76×10^{-6} , 8.86×10^{-6} and $3.36 \times 10^{-5} \text{ mol min}^{-1}$ for 41, 73 and 138 ppm, respectively). In this sense, higher $C_{\text{dec, feed}}$ provides more n -decane molecules adsorbed per surface area than higher Q_{feed} , restricting the generation of oxidant species from adsorbed water and oxygen (namely, hydroxyl radicals, peroxide radicals, and superoxide radicals) ultimately resulting of losses of n -decane conversion.

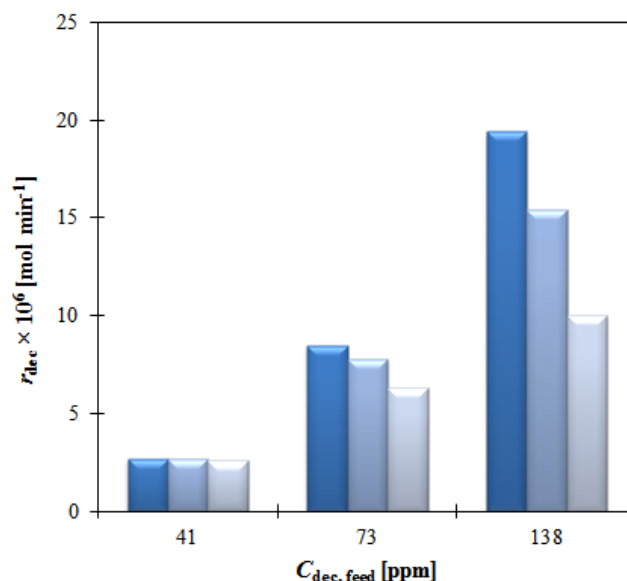


Figure 5.8. Influence of feed concentration ($C_{dec, feed}$) on the photocatalytic reaction rate (r_{dec}), at steady-state conditions: experimental points for incident irradiance measured within 280 – 400 nm (sunlight UV fraction) of 38.4 W_{UV} m⁻² (■), 29.1 W_{UV} m⁻² (▒), and 18.9 W_{UV} m⁻² (□); $C_{dec, feed} = 73$ ppm, $RH^* = 40\%$, and $T = 298$ K; operation conditions reported in Table 5.2; * measured at 298 K and 1 bar.

Although there are plenty of studies describing the influence of feed relative humidity on the photoconversion of alkanes, conclusions are still not clear [10, 43]. Twesme *et al.* [44] and Zhang and Liu [45] pointed out 40 % and 20 % of relative humidity, respectively, as the optimum conditions regarding water content to obtain the highest conversion rates in their studies. Shang *et al.* [46] demonstrated in their studies that the conversion rate of *n*-heptane decreases as the relative humidity was increased from 0 to 60 %. In fact, the presence of vapour water molecules has two opposing effects: *i*) inhibits the conversion by competitive adsorption to the photocatalyst surface (for feed streams with high water vapour content) [6, 47]; *ii*) accelerates the conversion by promoting hydroxyl radicals formation [48]. Figure 5.9 shows a slight relative increase (3 %) of the *n*-decane photoconversion fraction for the highest irradiance value (38.4 W_{UV} m⁻²) and within the relative humidity range of 3 % to 40 %. On the other hand, it was found that for the lower irradiance values, particularly for 18.9 W_{UV} m⁻², its effect on the *n*-decane photoconversion becomes more relevant: for the same relative humidity increment, the *n*-decane photoconversion is 3 % (from run 16 to run 1) to 25 % (from run 18 to run 3) more efficient with a 2-fold reduction of the incident radiation (from 38.4 to 18.9 W_{UV} m⁻²). This supports the important role of hydroxyl radicals in photocatalytic processes due to the lower amount of surface electron-hole pairs available on the catalyst surface to react with the pollutant molecules.

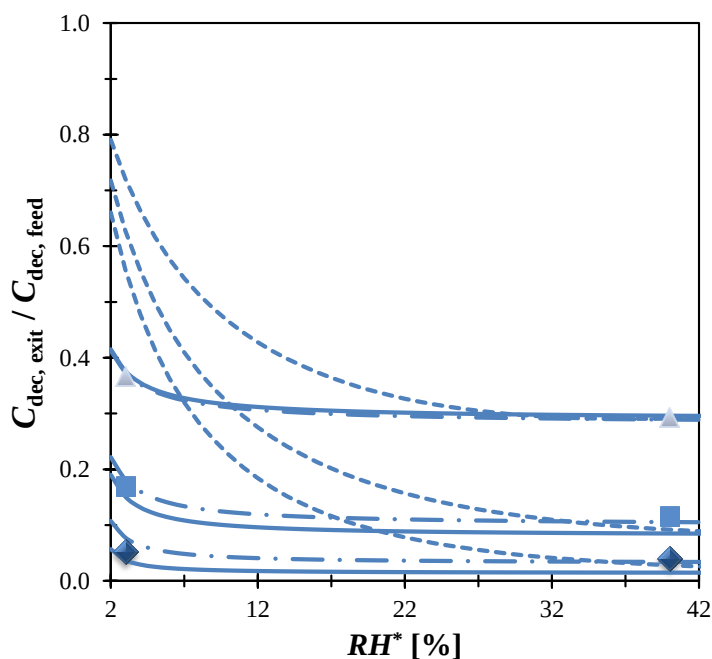


Figure 5.9. Influence of the feed relative humidity (RH) on n -decane conversion fraction ($C_{\text{dec, exit}} / C_{\text{dec, feed}}$) at steady-state conditions: experimental points for incident irradiance measured within 280 – 400 nm (sunlight UV fraction) of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ ($\blacklozenge$), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ ($\blacksquare$), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ ($\blacktriangle$), and RE-1 (---), RE-2 (— · —), and RE-3 (—); $Q_{\text{feed}}^* = 150 \text{ cm}^3 \cdot \text{min}^{-1}$, $C_{\text{dec, feed}} = 73 \text{ ppm}$, and $T = 298 \text{ K}$; operation conditions reported in Table 5.2; * measured at 298 K and 1 bar.

It should be pointed out that after 50 h under simulated solar radiation and continuous feed (humid air contaminated with n -decane), similar photoconversion fractions were obtained under the same operating conditions (data not shown). Considering the up-stated for SEM analysis (see section 5.3.1.1), it is suggested that PC deterioration was negligible.

5.3.1.3. Simulation and predictive studies of n -decane kinetics through PCO

Several models have been proposed in the literature for simulating VOC photocatalytic oxidation kinetics [42, 49]. Table 5.3 describes the complete mathematical model combined with three different Langmuir-Hinshelwood reactions rate expressions.

Table 5.3. Mathematical model, boundary conditions, kinetic reaction rate expressions used for estimation of the kinetic and adsorption equilibrium parameters of the PCO of n-decane; Estimated kinetic and adsorption equilibrium parameters resulting of the mathematical model.

Mathematical model, correlations, parameters, and boundary conditions [42, 49]				
Material balance for each component i		$\frac{d}{dz} \left(\varepsilon D_{ax} \frac{dC_i}{dz} \right) - \frac{d}{dz} (\bar{u}_{0, ch} C_i) - \nu_i r = 0$		
Axial dispersion (laminar flow) [50-53]		$D_{ax} = D_m + (1/192) \left[(\bar{u}_{0, ch}^2 d_{ch}^2) / (\varepsilon D_m) \right]$		
Molecular diffusivity of the mixture		$D_m \cong \frac{1}{N} \sum_{i=1}^N D_{m, i}, \text{ with } D_{m, i} = (1 - y_i) \sum_{\substack{i=1 \\ j \neq i}}^n \frac{D_{ij}}{y_i}$		
Binary diffusion coefficient [54-57]		$D_{ij} = \frac{1.41 \times 10^{-7} T^{1.75} \left[\frac{1}{2} (M_i^{-1} + M_j^{-1}) \right]^{1/2}}{p \left[(\Sigma_v)_i^{1/3} + (\Sigma_v)_j^{1/3} \right]^2}$		
Superficial velocity (in the cross-section of each channel)		$\bar{u}_{0, ch} = Q_{feed} \left[\pi (1/2 d_{ot, i})^2 - \pi (1/2 d_{in, e})^2 \right]^{-1}$		
Component i	N ₂	O ₂	H ₂ O	Dec
M_i [g·mol ⁻¹]	28.01	32.00	18.02	142.28
$(\Sigma_v)_i$	18.5	16.3	13.1	209.8
Boundary conditions	Photoreactor feed ($z = 0$)		Photoreactor exit ($z = L_R$)	
	$u_{0, feed} C_{i, feed} = \bar{u}_{0, ch} C_i - \varepsilon D_{ax} \frac{dC_i}{dz} \Big _{z=0}$		$\frac{dC_i}{dz} \Big _{z=L_R} = 0$	
Kinetic reaction rate expressions [3, 6, 42, 49, 58-64]				
RE-1	$r_{dec} = I^n \cdot k \left(\frac{K_{dec} K_{H_2O} C_{dec} C_{H_2O}}{(1 + K_{dec} K_{H_2O} C_{dec} C_{H_2O})^2} \right)$ <i>Langmuir-Hinshelwood bimolecular competitive one type of sites</i>			
RE-2	$r_{dec} = I^n \cdot k \left(\frac{K_{dec} C_{dec}}{1 + K_{dec} C_{dec}} \right) \left(\frac{K_{H_2O} C_{H_2O}}{1 + K_{H_2O} C_{H_2O}} \right)$ <i>Langmuir-Hinshelwood bimolecular non-competitive two types of sites</i>			
RE-3	$r_{dec} = I^n \cdot k \left(\frac{K_{dec, 1} C_{dec}}{1 + K_{dec, 1} C_{dec} + K_{H_2O, 1} C_{H_2O}} \right) \left(\frac{K_{H_2O, 2} C_{H_2O}}{1 + K_{dec, 2} C_{dec} + K_{H_2O, 2} C_{H_2O}} \right)$ <i>Langmuir-Hinshelwood bimolecular competitive two types of sites</i>			
Estimated parameters				
Kinetic reaction rate expressions		RE-1	RE-2	RE-3
Kinetic and adsorption equilibrium parameters	n	0.8	0.8	0.8
	k [mol m ⁻² s ⁻¹ (W ⁻¹ m ²) ^{n}]	1.0×10^{-5}	3.2×10^{-6}	2.8×10^{-6}
	K_{dec} ($K_{dec, 1}$) [M ⁻¹]	13	2205	4498
	K_{H_2O} ($K_{H_2O, 1}$) [M ⁻¹]	9.7×10^{-5}	1.5×10^{-4}	1.0×10^{-8}
	$K_{dec, 2}$ [M ⁻¹]	—	—	905
	$K_{H_2O, 2}$ [M ⁻¹]	—	—	4.6×10^{-4}
Statistics	R^2	0.764	0.912	0.954
	$S_R^2 \times 10^7$ [mol ² m ⁻⁴ s ⁻²]	3.84	1.43	0.874

Note: all variables herein presented were already described in Chapter 2.

The numerical solution of the mathematical model was performed in gPROMS environment (Process System Enterprise, London, UK) using the orthogonal collocation on finite elements method. The number of elements used was 90 with two interior collocation points (third order polynomials) in each element of the photocatalytic bed. The simulations were performed with an absolute and relative tolerance of 1×10^{-5} . First, parameters were estimated using a sequential quadratic programming algorithm [42]; then, the mathematical model was employed for simulating the PCO of *n*-decane. Table 5.3 reports the estimated kinetic and adsorption equilibrium parameters.

Results shows that the mathematical model with the Langmuir-Hinshelwood kinetic reaction rate expression RE-3 (bimolecular competitive two types of sites rate expression) generally produced better fitting results within the operational conditions studied than models RE-1 or RE-2 (bimolecular competitive one type of sites or bimolecular non-competitive two types of sites rate expressions) (Figures 5.5 - 5.7). This means that both *n*-decane and water molecules must be considered independent and targeting different active sites of the catalyst surface. The surface active sites competition between the two types of molecules cannot be disregarded because, despite the higher number of parameters required by RE-3, this rate expression is more suitable to describe the experimental data (see the statistical analysis reported in Table 5.3). Contrarily to the previous reported models of PCO [42, 49], it was necessary to include an incident irradiance exponential order constant (n). The radial effect of the UV radiation passing through the PC samples and its consequent reflection and refraction were not considered; moreover, the mathematical model neglects any partial UV absorption by the PC samples. Nevertheless, the UV irradiance on PCO of *n*-decane could be fitted by an irradiance exponential order constant $n = 0.8$, as can be seen throughout this chapter (Figures 5.5 - 5.7).

The closest results to our data regarding gas-phase PCO of *n*-decane were obtained by Debono *et al.* [65]. However, these authors performed UVA-photocatalytic experiments of *n*-decane over TiO₂ powder dispersed at the bottom of a batch reactor, and employing *n*-decane-polluted air stream at ppb level. Therefore and only for these conditions Debono *et al.* [65] were able to provide a photocatalytic lab-scale setup effective for complete *n*-decane photoconversion.

Considering that the mathematical model described successfully the reported experiments, simulations can now be performed to obtain insights concerning the effect of each operating variable on the process performance. The effect of the lab-unit geometrical parameters on the PCO of *n*-decane was assessed (*e.g.*, photoreactor length L_R) within the operating condition studied, aiming unit geometric optimization and re-scaling. Figure 5.10 shows the *n*-decane photoconversion fraction profiles, considering photoreactors of different lengths (L_R).

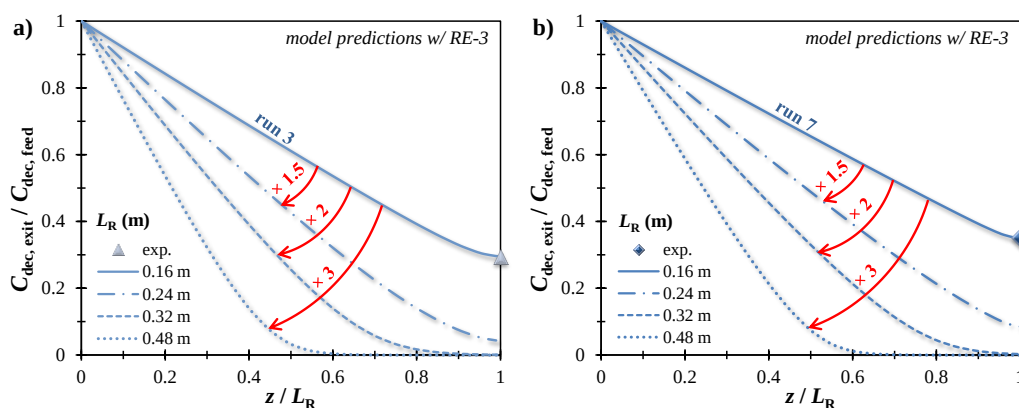


Figure 5.10. *n*-Decane photoconversion fraction profiles ($C_{\text{dec, exit}}/C_{\text{dec, feed}}$, at steady-state conditions) for photoreactors with different lengths [L_R]: 0.16 (—), 0.24 (---), 0.32 (- · -), and 0.48 m (· · ·); (a) $C_{\text{dec, feed}} = 73$ ppm, $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$, and $I = 18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (measured within 280 – 400 nm: sunlight UV fraction); (b) $C_{\text{dec, feed}} = 73$ ppm, $Q_{\text{feed}}^* = 300 \text{ cm}^3 \text{ min}^{-1}$, and $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (measured within 280 – 400 nm: sunlight UV fraction); $RH^* = 30 \%$, and $T = 298 \text{ K}$; operation conditions reported in Table 5.2 (runs 3 and 7, respectively) (* measured at 298 K and 1 bar); experimental data (points); mathematical modelling with RE-3 (lines).

It can be seen that, when the operating conditions of run 3 are employed (lowest incident irradiance, and intermediate feed flow rate and *n*-decane concentration), a 1.5-fold increase of the photoreactor length yields to a *n*-decane photoconversion enhancement of 85 % (see Figure 5.10a). Moreover, for a photoreactor 2× longer, complete *n*-decane photoconversion is attained (Figure 5.10a). On the other hand, Figure 5.10b predicts how *n*-decane photoconversion fraction is affected as a function of the photoreactor length when the highest incident irradiance and feed flow rate are employed (run 7). For a 1.5 times longer photoreactor than the experimentally employed, a 76 % *n*-decane photoconversion enhancement is observed. If the reactor is twice the length ($L_R = 0.32 \text{ m}$), only 1 % of *n*-decane feed is predictively unreacted; complete *n*-decane photoconversion is attained when using a ~3 times longer photoreactor.

5.3.2. Reaction mechanism for the PCO of *n*-decane

The conversion mechanisms of alkanes and the corresponding formation of its by-products have been studied recently [43, 46, 65-68]. According to the previously cited authors it was found that ketones and aldehydes are the main intermediates of *n*-decane photochemical reaction. Minabe *et al.* [69] reported that gas-phase photooxidation of long organic chains over TiO₂ thin-films only produces CO₂ and H₂O. It was suggested that both reactants and intermediates were continuously adsorbed on the TiO₂ surface. Within this work, identification and quantification of the *n*-decane photocatalytic reaction by-products were monitored by GC/MSD (Table 5.4), for the experimental conditions of run 1 (Table 5.2).

Table 5.4. Reaction by-products identified and quantified in the gas-phase photoconversion of *n*-decane (experimental conditions reported in Table 5.2: run 1).

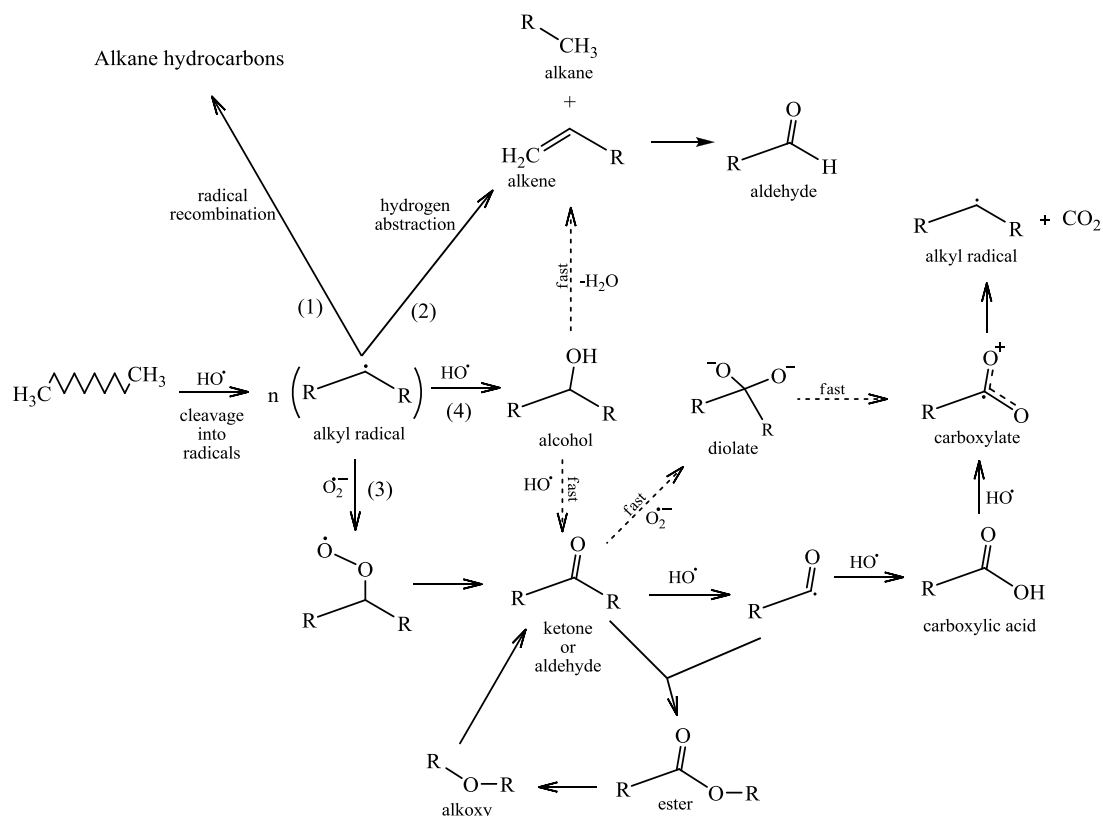
Compound <i>i</i>	Molecular		M_i [g mol ⁻¹]	C_i [ppm] ^a	$C_{i, C-dec}$ [ppm] ^c
	Formula	Structure			
decane ^b	C ₁₀ H ₂₂		142.3	4.32	3.65
hexane	C ₆ H ₁₄		86.18	0.035	0.029
heptane	C ₇ H ₁₆		100.2	0.028	0.023
octane	C ₈ H ₁₈		114.2	0.007	0.006
nonane	C ₉ H ₂₀		128.3	0.036	0.030
undecane	C ₁₁ H ₂₄		156.3	0.005	0.004
4-methylnonane	C ₁₀ H ₂₂		142.3	0.006	0.005
2,6-dimethyloctane	C ₁₀ H ₂₂		142.3	0.009	0.008
butanoic acid	C ₄ H ₈ O ₂		88.11	0.022	0.012
propanoic acid	C ₃ H ₆ O ₂		74.08	0.072	0.035
butanal	C ₄ H ₈ O		72.11	0.016	0.005

^a the concentration of the major compounds, C_i , was calculated using the response factor of toluene, except for decane for which specific response factors were used (calibration solutions).

^b decane concentration of the feed and exit streams were analysed by MGC: $C_{dec, feed} = 73$ ppm; $C_{C-dec, feed} = 62$ ppm where $C_{C-dec, feed}$ is the carbon atoms concentration of *n*-decane on the feed stream.

^c $C_{i, C-dec}$ stands for carbon atoms concentration of compound *i* formed by *n*-decane conversion (ppm).

The identified by-products (and their concentration) were: unreacted *n*-decane (4.32 ppm), *n*-hexane (0.035 ppm), *n*-heptane (0.028 ppm), *n*-octane (0.007 ppm), *n*-nonane (0.036 ppm), *n*-undecane (0.005 ppm), 4-methylnonane (0.006 ppm), 2,6-dimethyloctane (0.009 ppm), butanoic acid (0.022 ppm), propanoic acid (0.072 ppm), and butanal (0.016 ppm). Therefore and based on the nature of the identified compounds, a reaction mechanism under wet air (40 %) is proposed and schematized in Scheme 5.1. According to Scheme 5.1, *n*-decane undergoes a cleavage into radicals – cracking – by a hydroxyl radical. Taking into consideration that alkyl radical stability increases along the series from methyl to primary, followed by secondary, and then by tertiary carbon, the energy required to create them decreases [70]. So, in the case of straight-chain alkanes, secondary carbons are oxidized by hydroxyl radical rather than primary ones. Nonetheless, from Scheme 5.1 and supported by literature [46, 70-72], it is assumed the formation of both primary and secondary alkyl radicals. After homolytic cleavage of *n*-decane four paths can take place: 1) radical recombination generating new alkane hydrocarbons such as *n*-hexane, *n*-octane, or 2,6-dimethyloctane (Table 5.4); 2) hydrogen abstraction reactions leading to the formation of alkanes and alkenes; 3) reaction with adsorbed O₂ producing a highly reactive superoxide radicals; 4) oxidation by hydroxyl radicals forming alcohols.



Scheme 5.1. Schematic representation of the reaction pathways proposed for the gas-phase conversion of *n*-decane under simulated solar radiation (R: alkyl roots or hydrogen).

Several authors [46, 66, 72, 73] reported the rapid dehydration of alcohols into alkenes or oxidation into corresponding ketones or aldehydes (see Scheme 5.1, path 4); alkenes could be degraded into aldehydes as reported by Djeghri and Teichner [71] whereas aldehydes could suffer double oxidation by hydroxyl radicals into carboxylic acid [73-75] as it was detected the presence of propanoic and butanoic acid. An alternative approach was suggested by Kominami *et al.* [76] after observing the formation of an ester from the recombination of the aldehyde and its intermediate. Then, according to Augugliaro *et al.* and Peral *et al.* [48, 73], ester could be adsorbed on the TiO₂ surface where it would be dissociated into alkoxy and carboxylate radical. The alkoxy form an aldehyde and the carboxylate radical could produce alkyl radicals and carbon dioxide leading to alkanes after radical recombination or alkenes after hydrogen abstraction reaction. Carboxylate radical could also be formed by oxidation by hydroxyl radical of carboxylic acid which would lead to the formation of alkyl radicals and CO₂ in a process called decarboxylative dimerization. On the other hand, several authors [77-79] have proposed the reaction between ketones and adsorbed O₂, forming an unstable ketone diolate complex onto the TiO₂ surface. Consequently, the diolate complex would rapidly be dissociated into carboxylate which would lead to the formation of alkyl radicals and carbon dioxide. These radicals would be rapidly oxidized into alcohols and, then, aldehydes [80]. This approach may explain the absence

of ketones and presence of butanal.

Considering that $C_{i, \text{C-dec}}$ refers to the carbon atoms concentration of compound i formed by n -decane conversion (all unreacted n -decane and its by-products produced), it can be defined as:

$$C_{i, \text{C-dec}} = \frac{C_i}{M_i} \cdot n(C) \cdot M(C) \quad 5.1$$

where C_i [ppm] and M_i [g mol⁻¹] are the gas phase concentration and molecular weight of compound i , respectively, $n(C)$ is the number of carbon atoms of each component i molecule, and $M(C)$ [g mol⁻¹] is the molecular weight of a carbon atom. Thus, the mineralization efficiency ($\eta_{\min}$ in %) can be determined through eq. 5.2.

$$\eta_{\min} [\%] = \left[1 - \frac{\sum_i (C_{i, \text{C-dec}})_{\text{exit}}}{\sum_i (C_{i, \text{C-dec}})_{\text{feed}}} \right] \quad 5.2$$

Thus, considering the carbon atoms concentration of each identified and quantified by-product resulting from the n -decane molecules conversion (experimental conditions reported in Table 1: run 1) more than 99 % of the n -decane converted (~94 % of n -decane fed) was completely mineralized into CO₂ and H₂O. This result is in agreement to what Debono *et al.* [65] disclosed in their previous work: the total carbon atoms concentration of all by-products formed by n -decane conversion is lower than 5 %.

5.4. Conclusions

The use of an annular lab-photoreactor under simulated solar radiation has shown to be extremely efficient on the photocatalytic process over a photo-TiO₂ paint. Under simulated solar radiation, the gas-phase photocatalytic experiments showed that highest n -decane conversion (98 %) was attained at the lowest Q_{feed} (75 cm³ min⁻¹) and $C_{\text{dec, feed}}$ (41 ppm), and highest RH (40 %) and I (38.4 W_{UV} m⁻²). Feeding the photoreactor with the double flow rate, the n -decane conversion decreases from 96 to 62 % (run 1 and 7). Alternatively, when the n -decane concentration on the feed stream is doubled, the remaining unreacted n -decane fed increases from 4 to 46 % (run 1 and 13). It was also observed that the water vapour content effect on the PCO of n -decane is more pronounced under lower irradiances ($I = 18.9$ W_{UV} m⁻²), *i.e.*, from ~71 to 56 % (run 3 and 18).

A phenomenological model, assuming a Langmuir-Hinshelwood mechanism (bimolecular competitive with two types of sites) was able to describe the n -decane

photoconversion. It was proposed that both species compete for adsorption within different specific active sites (type 1 and 2) of the catalyst surface. Considering the type of by-products identified, a reaction mechanism for *n*-decane photoconversion under the conditions used was proposed.

For all reasons stated before and considering the well-known wide range of paint applications, the results reported seem quite promising for the treatment of indoor and outdoor air. Further research should focus in studying the role of interfering pollutants, as NO₂, and also the eventual production of acetaldehyde and formaldehyde as sub-products.

5.5. References

- [1] C.H. Ao, S.C. Lee, C.L. Mak, L.Y. Chan, *Appl. Catal. B: Environ.* 42 (2003) 119-129.
- [2] A.T. Hodgson, H. Destailats, D.P. Sullivan, W.J. Fisk, *Indoor Air* 17 (2007) 305-316.
- [3] J. Mo, Y. Zhang, Q. Xu, J.J. Lamson, R. Zhao, *Atmos. Environ.* 43 (2009) 2229-2246.
- [4] S.A. Grinshpun, A. Adhikari, T. Honda, K.Y. Kim, M. Toivola, K.S. Ramchander Rao, T. Reponen, *Environ. Sci. Technol.* 41 (2006) 606-612.
- [5] M.A. Isbell, R.J. Stolzberg, L.K. Duffy, *Sci. Total Environ.* 345 (2005) 31-40.
- [6] S. Wang, H.M. Ang, M.O. Tade, *Environ. Int.* 33 (2007) 694-705.
- [7] J. Zhao, X. Yang, *Build. Environ.* 38 (2003) 645-654.
- [8] C. Srinivasan, N. Somasundaram, *Curr. Sci.* 85 (2003) 1431-1438.
- [9] D.Y. Goswami, *J. Sol. Energy Eng.* 119 (1997) 101-107.
- [10] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69-96.
- [11] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, *J. Chem. Technol. Biotechnol.* 77 (2002) 102-116.
- [12] C. McCullagh, J. Robertson, D. Bahnemann, P. Robertson, *Res. Chem. Intermed.* 33 (2007) 359-375.
- [13] D. Bahnemann, *Sol. Energy* 77 (2004) 445-459.
- [14] R.W. Matthews, *J. Chem. Soc. Faraday Trans. 1* 80 (1984) 457-471.
- [15] J.-M. Herrmann, *Top. Catal.* 34 (2005) 49-65.
- [16] A.L. Linsebigler, G. Lu, J.T. Yates, *Chem. Rev.* 95 (1995) 735-758.
- [17] M. Hernandez-Alonso, I. Tejedor-Tejedor, J. Coronado, J. Soria, M. Anderson, *Thin Solid Films* 502 (2006) 125-131.
- [18] C. Guillard, J. Disdier, C. Monnet, J. Dussaud, S. Malato, J. Blanco, M.I. Maldonado, J.-M. Herrmann, *Appl. Catal. B: Environ.* 46 (2003) 319-332.
- [19] M.L. Satuf, R.J. Brandi, A.E. Cassano, O.M. Alfano, *Appl. Catal. B: Environ.* 82 (2008) 37-49.
- [20] E.M. Rossi, L. Pylkkänen, A.J. Koivisto, M. Vippola, K.A. Jensen, M. Miettinen, K. Sirola, H. Nykäsenoja, P. Karisola, T. Stjernvall, E. Vanhala, M. Kiilunen, P. Pasanen, M. Mäkinen, K. Hämeri, J. Joutsensaari, T. Tuomi, J. Jokiniemi, H. Wolff, K. Savolainen, S. Matikainen, H. Alenius, *Toxicol. Sci.* 113 (2010) 422-433.
- [21] C.M. Sayes, R. Wahi, P.A. Kurian, Y. Liu, J.L. West, K.D. Ausman, D.B. Warheit, V.L. Colvin, *Toxicol. Sci.* 92 (2006) 174-185.
- [22] R. Zhang, Y. Bai, B. Zhang, L. Chen, B. Yan, *J. Hazard. Mater.* 211-212 (2012) 404-413.
- [23] A. Fujishima, K. Hashimoto, T. Watanabe, *TiO₂ Photocatalysis: Fundamentals and Applications*, Bkc, Incorporated, Tokyo, 1999.
- [24] E. Keidel, *Furben Zeitung* 34 (1929) 1242.
- [25] C.F. Goodeve, J.A. Kitchener, *Trans. Faraday Soc.* 34 (1938) 570-579.
- [26] H. Gerischer, in: H. Eyring, D. Henderson, W. Jost (Eds.), *Physical Chemistry: An Advanced Treatise*, Academic Press, New York, 1970, pp. 463-542.
- [27] V.A. Myamlin, Y.V. Pleskov, *Electrochemistry of Semiconductors*, Plenum Press, New York, 1967.

- [28] S. Kato, F. Mashio, Abstr. Book Annu. Meet. Chem. Soc. Jpn. (1956) 223.
- [29] A. Fujishima, K. Honda, *Nature* 238 (1972) 37-38.
- [30] C.E. Bygott, J.E. Maltby, J.L. Stratton, R. McIntyre, Photocatalytic coatings for the construction industry International RILEM Symposium on Photocatalysis, Environment and Construction Materials, 8–9 October, Florence, Italy, 2007, pp. 251-258.
- [31] O. d'Hennezel, P. Pichat, D.F. Ollis, *J. Photochem. Photobiol. A* 118 (1998) 197-204.
- [32] A. Bouzaza, A. Laplanche, *J. Photochem. Photobiol. A* 150 (2002) 207-212.
- [33] C. Águia, J. Ângelo, L.M. Madeira, A. Mendes, *Catal. Today* 151 (2010) 77-83.
- [34] J. Chen, C.-s. Poon, *Build. Environ.* 44 (2009) 1899-1906.
- [35] T. Salthammer, F. Fuhrmann, *Environ. Sci. Technol.* 41 (2007) 6573-6578.
- [36] T. Maggos, J.G. Bartzis, M. Liakou, C. Gobin, *J. Hazard. Mater.* 146 (2007) 668-673.
- [37] J. Kolarik, J. Toftum, *Build. Environ.* 57 (2012) 396-402.
- [38] E. Uhde, T. Salthammer, *Atmos. Environ.* 41 (2007) 3111-3128.
- [39] J. Auvinen, L. Wirtanen, *Atmos. Environ.* 42 (2008) 4101-4112.
- [40] O. Geiss, C. Cacho, J. Barrero-Moreno, D. Kotzias, *Build. Environ.* 48 (2012) 107-112.
- [41] C. Águia, J. Ângelo, L.M. Madeira, A. Mendes, *J. Environ. Manage.* 92 (2011) 1724-1732.
- [42] F.V.S. Lopes, S.M. Miranda, R.A.R. Monteiro, S.D.S. Martins, A.M.T. Silva, J.L. Faria, R.A.R. Boaventura, V.J.P. Vilar, *Appl. Catal. B: Environ.* 140-141 (2013) 444-456.
- [43] A.K. Boulamanti, C.J. Philippopoulos, *Atmos. Environ.* 43 (2009) 3168-3174.
- [44] T.M. Twesme, D.T. Tompkins, M.A. Anderson, T.W. Root, *Appl. Catal. B: Environ.* 64 (2006) 153-160.
- [45] P. Zhang, J. Liu, *J. Photochem. Photobiol. A* 167 (2004) 87-94.
- [46] J. Shang, Y. Du, Z. Xu, *Chemosphere* 46 (2002) 93-99.
- [47] S. Yamazaki, H. Tsukamoto, K. Araki, T. Tanimura, I. Tejedor-Tejedor, M.A. Anderson, *Appl. Catal. B: Environ.* 33 (2001) 109-117.
- [48] V. Augugliaro, S. Coluccia, V. Loddo, L. Marchese, G. Martra, L. Palmisano, M. Schiavello, *Appl. Catal. B: Environ.* 20 (1999) 15-27.
- [49] F.V.S. Lopes, R.A.R. Monteiro, A.M.T. Silva, G.V. Silva, J.L. Faria, A.M. Mendes, V.J.P. Vilar, R.A.R. Boaventura, *Chem. Eng. J.* 204–206 (2012) 244-257.
- [50] T. Valdés-Solís, M.J.G. Linders, F. Kapteijn, G. Marbán, A.B. Fuertes, *Chem. Eng. Sci.* 59 (2004) 2791-2800.
- [51] G.I. Taylor, *P. Roy. Soc. Lond. A. Mat.* 219 (1953) 186-203.
- [52] A. Aris, *P. Roy. Soc. Lond. A. Mat.* 235 (1956) 67-77.
- [53] D.M. Ruthven, *Principals of adsorption and adsorption processes*, John Wiley & Sons, New York, 1984.
- [54] B.E. Poling, J.M. Prausnitz, J.P. O'Connell, *The properties of gases and liquids*, 5th Edition ed., McGraw-Hill, New York, 2001.
- [55] E.N. Fuller, K. Ensley, J.C. Giddings, *J. Phys. Chem.* 73 (1969) 3679-3685.
- [56] E.N. Fuller, J.C. Giddings, *J. Chromatogr. Sci.* 3 (1965) 222-227.
- [57] E.N. Fuller, P.D. Schettler, J.C. Giddings, *Ind. Eng. Chem.* 58 (1966) 18-27.

- [58] C.N. Satterfield, Mass transfer in heterogeneous catalysis, MIT Press, Massachusetts Institute of Technology, Cambridge, MA, USA, 1970.
- [59] G. Li Puma, I. Salvadó-Estivill, T.N. Obee, S.O. Hay, Sep. Purif. Technol. 67 (2009) 226-232.
- [60] K.-H. Wang, H.-H. Tsai, Y.-H. Hsieh, Appl. Catal. B: Environ. 17 (1998) 313-320.
- [61] T.N. Obee, R.T. Brown, Environ. Sci. Technol. 29 (1995) 1223-1231.
- [62] T.N. Obee, Environ. Sci. Technol. 30 (1996) 3578-3584.
- [63] T.N. Obee, S.O. Hay, Environ. Sci. Technol. 31 (1997) 2034-2038.
- [64] J. Peral, X. Domènech, D.F. Ollis, J. Chem. Technol. Biotechnol. 70 (1997) 117-140.
- [65] O. Debono, F. Thévenet, P. Gravejat, V. Héquet, C. Raillard, L. Le Coq, N. Locoge, J. Photochem. Photobiol. A 258 (2013) 17-29.
- [66] N. Djeghri, M. Formenti, F. Juillet, S.J. Teichner, Faraday Discuss. Chem. Soc. 58 (1974) 185-193.
- [67] R. Nakamura, S. Sato, J. Phys. Chem. B 106 (2002) 5893-5896.
- [68] W. Balcerski, S.Y. Ryu, M.R. Hoffmann, Int. J. Photoenergy 2008 (2008).
- [69] T. Minabe, D.A. Tryk, P. Sawunyama, Y. Kikuchi, K. Hashimoto, A. Fujishima, J. Photochem. Photobiol. A 137 (2000) 53-62.
- [70] K.P.C. Vollhardt, N.E. Schore, Organic chemistry: structure and function, 3rd Edition ed., W. H. Freeman and company, New York, 1999.
- [71] N. Djeghri, S.J. Teichner, J. Catal. 62 (1980) 99-106.
- [72] C. Häggglund, B. Kasemo, L. Österlund, J. Phys. Chem. B 109 (2005) 10886-10895.
- [73] J. Peral, D.F. Ollis, J. Catal. 136 (1992) 554-565.
- [74] E. Obuchi, T. Sakamoto, K. Nakano, F. Shiraishi, Chem. Eng. Sci. 54 (1999) 1525-1530.
- [75] X. Ye, D. Chen, J. Gossage, K. Li, J. Photochem. Photobiol. A 183 (2006) 35-40.
- [76] H. Kominami, H. Sugahara, K. Hashimoto, Catal. Commun. 11 (2010) 426-429.
- [77] C. Raillard, V. Héquet, P. Le Cloirec, J. Legrand, Water Sci. Technol. 53 (2006) 107.
- [78] M.A. Henderson, Surf. Sci. 602 (2008) 3188-3193.
- [79] M.A. Henderson, J. Catal. 256 (2008) 287-292.
- [80] E. Piera, J.A. Ayllón, X. Doménech, J. Peral, Catal. Today 76 (2002) 259-270.

Part IV

Chapter 6. N-modified TiO₂ photocatalytic activity towards organics degradation

Chapter 7. Visible-light-driven photocatalytic properties of N-modified titania nanotubes toward air purification

6. N-modified TiO₂ photocatalytic activity towards organics degradation

*In the present chapter, nitrogen modified TiO₂ samples were prepared by grinding the benchmark TiO₂ photocatalyst (P25, Evonik®) with different amounts of urea and applying calcination temperatures between 340 - 420 °C. As far as XRD analysis concerns, nitrogen modification did not affect the crystalline phase of TiO₂ P25; on the other hand the modified materials developed an absorption in the visible part of the electromagnetic spectrum. The TiO₂ P25 modified with urea materials, under simulated solar radiation, induced a reduction in the photocatalytic activity towards degradation of gas-phase PCE in comparison to bare TiO₂ P25. The material with a urea:TiO₂ weight ratio of 1:2, calcined at 380 °C, exhibited the highest photocatalytic activity under visible light illumination ($\lambda > 430$ nm), towards degradation of diphenhydramine, an emerging water pollutant of pharmaceutical origin. In addition, this photocatalyst was also the most efficient for complete inactivation of *Escherichia coli* in aqueous solution when ultraviolet radiation ($\lambda = 365$ nm) was used. From the XPS analysis on the chemical states of this photocatalyst it is concluded that nitrogen is interstitial to the TiO₂ structure.*

This chapter is based on the research article “Monteiro, R.A.R., Miranda, S.M., Vilar, V.J.P., Pastrana-Martínez, L.M., Tavares, P.B., Boaventura, R.A.R., Faria, J.L., Pinto, E., Silva, A.M.T., N-modified TiO₂ photocatalytic activity towards diphenhydramine degradation and *Escherichia coli* inactivation in aqueous solutions, Applied Catalysis B: Environmental, 162 (2015), 66-74, DOI: 10.1016/j.apcatb.2014.06.017”.

6.1. Introduction

TiO₂ is a semiconductor with unique optoelectronic and physiochemical properties, which have been, since the early of the 20th century, alluring the industry in many different applications [1-3]. In 1956, Kato and Mashio [4] conducted several studies dealing with oxidation reactions induced by TiO₂ under illumination. Later, in the 1960s, the TiO₂ photochemical effect was also explored to induce electrochemical reactions [5, 6]. Following the example of natural photosynthesis, Fujishima succeeded in 1969 to photoelectrochemically decompose water over TiO₂, a breakthrough finding published in a restricted Japanese journal [7]. Only in 1972, Fujishima and Honda described for the first time the photoelectrochemical decomposition of water under light radiation and without any applied electric current, using a single TiO₂-rutile crystal (*n*-type semiconductor) as photoanode and a Pt counter electrode [8]. The interest of photocatalytic processes on environmental applications escalated after Frank and Bard [9] in 1977 examined the possibilities of using TiO₂ to decompose cyanide in water. Thereafter, photocatalytic reactions have attracted increasing attention not only for many different water/wastewater treatment applications but also in the fields of energy conversion and air purification [10-17].

With a band gap of 3.2 eV, the photocatalytic activation of TiO₂ under solar irradiance is limited to the UV fraction of natural sunlight ($\lambda < 400$ nm), which represents roughly ~4% of the total Sun irradiance reaching Earth's surface. In recent years, lot of attention has been paid towards shifting the absorption of TiO₂ based materials deeper into the visible region of the electromagnetic spectrum, where lies near 42% of the Sun's total irradiance. Several approaches have been described in the literature to achieve this goal, including doping or impregnation of metal ions into TiO₂ [18-21], reduction of TiO₂ via plasma treatments [22, 23], combination of TiO₂ with other semiconductors or with carbon materials [24-27], and non-metallic doping of TiO₂ (C, F, N, S) [28-39].

Theoretical calculations for substitutional doping of C, N, F, P or S for O in the TiO₂ anatase phase, later confirmed by spectroscopic techniques [28], pointed out TiO_{2-x}N_x (powders and films) as very promising photocatalysts for visible light activation (>500 nm). As early as 1986, Sato [37] reported the superior photoactivity of the nitrogen modified TiO₂ with relation to the benchmark TiO₂ (P25) material under visible light illumination. Since then, several methods for doping TiO₂ with nitrogen have been developed, such as ion implantation [38, 40-42], sputtering [43-45], mechanical milling [46-48], chemical vapour deposition [49, 50], sol-gel synthesis [37, 51-55] and decomposition of nitrogen-containing metallorganic precursors [56-58].

Despite the general agreement found in the literature regarding the improvement of the

TiO₂ photocatalytic activity driven by the incorporation of nitrogen, this enhancement has not been always observed. For example, the incorporation of β -substitutional nitrogen in N-doped TiO₂ was confirmed by XPS in the study of Yates *et al.* [59]. However, no relevant photocatalytic activity under visible light was observed. Frach *et al.* [60] also reported a lack of visible light activity for N-doped TiO₂. In fact, the photocatalytic activity of N-doped TiO₂ materials depends on several factors, with the preparation methods and precursors employed playing an unequivocally critical role on the resulting photocatalytic properties [57].

In this context, there is an on-going discussion on how nitrogen incorporation enhances the photocatalytic activity of TiO₂ under visible illumination [54, 61-65]. Due to the different chemical nature of nitrogen doping species [52, 53, 66-69], it is important to understand the following concepts: a) whether the incorporation is interstitial or substitutional; b) if these species will diffuse to the surface of TiO₂; or c) will be incorporated at the sub-surface or in bulk sites [55, 70]. The location of the nitrogen species into the TiO₂ structure and their interaction with material matrix will strongly affect the material photocatalytic activity.

The electronic structure of the doped material has also been an issue in discussion. One point of view states that nitrogen incorporation shifts the adsorption edge to lower energies narrowing its band gap [28, 43, 71]; other authors opposed that the absorption in the visible region is due to the electronic transitions, from localized impurity states in the band gap to the conduction band [33, 54, 61, 72]. Moreover, Livraghi *et al.* [70] found that N-doped TiO₂ contains a single atom nitrogen centre in the bulk of TiO₂, promoting absorption in the visible region and electron transfer from the band gap to the conduction band, as well as electron scavengers adsorbed at the surface of TiO₂.

The majority of these studies has been performed with organic pollutants, whereas the anti-microbial properties of N-doped TiO₂ materials have received much less attention [30, 73-75]. Liu *et al.* [73] compared N-doped TiO₂ materials prepared by the sol-gel method and TiO₂ P25 towards *Escherichia coli* inactivation under visible light illumination; the results showed higher efficiency of the N-doped TiO₂. Rizzo *et al.* [75] also showed the higher photocatalytic inactivation of an *E. coli* strain, that is antibiotic resistant, when using N-doped TiO₂ in comparison to commercially available TiO₂ photocatalysts (Cristal[®] PC50 and PC100). Cheng *et al.* [74] reported the inactivation of more than 99% of *E. coli* and *Staphylococcus aureus* over N-doped TiO₂. Rengifo-Herrera and Pulgarin [30] also reported a high photocatalytic activity of N,S co-doped and N-doped commercial anatase TiO₂ powders towards *E. coli* inactivation under visible light illumination; in this case, the efficiency of such materials was similar to that obtained with the benchmark TiO₂ P25.

In the present chapter, nitrogen modified TiO₂ powders were prepared with different urea amounts and calcined at different temperatures, in order to optimize the method for the synthesis of an active photocatalyst. Scanning electron microscopy (SEM), diffuse reflectance UV-Vis spectroscopy (UV-DRS), *X-ray diffraction* (XRD), X-ray photoelectron spectroscopy (XPS), surface area and porosity measurements, were performed on the as-prepared samples. The photocatalytic activity of these nitrogen modified TiO₂ materials was assessed, under simulated solar radiation, in the degradation of gas-phase perchloroethylene (PCE). Furthermore, the photocatalytic activity of these materials under visible light illumination was systematically studied in aqueous-phase for the degradation of diphenhydramine which is an emerging water pollutant. The selected samples were also tested under ultraviolet radiation, towards the inactivation of *E. coli*.

6.2. Experimental

6.2.1. Chemicals and materials

TiO₂ P25 (80 % anatase, 20 % rutile) from Evonik[®], urea (reagent grade, 98%) from Sigma-Aldrich and ethanol (99.8 %) from AGA were employed without further purification. Ultrapure water was produced in a Direct-Q Millipore[®] system.

Honeycomb cellulose acetate structures (TIMax CA50-9/S – $L_C = 80$ mm, $d_{ch}^2 = 9$ mm $\times$ 9 mm, $e_{w,ch} = 0.1$ mm; Wacotech GmbH & Co. KG.) were used as substrate to immobilize the powders for the gas-phase photocatalytic experiments.

The reagents used for the generation of humidified air streams contaminated with PCE as well as the gases provided by Air Liquide are described in sub-section 2.2.1. of Chapter 2.

The high-purity (99 %) analytical grade pharmaceutical selected for this study, diphenhydramine (DP) hydrochloride (2-diphenylmethoxy-*N,N*-dimethylethanamine hydrochloride), was supplied by Sigma–Aldrich. The properties of DP are already listed elsewhere [76]. Potassium hydroxide (> 90 %) and tert-butanol (≥ 99.7 %) were obtained from Fluka, Sigma–Aldrich. Hydrochloric acid (37 %) was purchased from Pronalab. EDTA (ethylenediaminetetraacetic acid, > 99 %) was supplied by Fisher Scientific. Acetonitrile ($\geq 99.8\%$) was used with HPLC grade (Chromanorm).

6.2.2. Catalyst preparation and characterization

The nitrogen modification of TiO₂ P25 was accomplished by classical impregnation with urea. An amount of 1.0 g TiO₂ P25 was mixed with 0.10 – 3.0 g of urea and then 60 mL of ethanol were added under stirring until complete evaporation of the solvent. A calcination step of 2 h was also performed. Samples were labelled as N_xP25-y where x represents the weight of urea in grams (up to 3.0 g) and y represents the calcination temperature in °C (typically 380 °C). To investigate the effect of the calcination temperature, the sample prepared with 0.50 g of urea was also thermally treated at 340 °C and 420 °C. These samples were respectively denoted as N_{0.50}P25-340 and N_{0.50}P25-420.

The optical properties of the samples were analysed by UV/Vis diffuse reflectance spectroscopy (UV-DRS) using a JASCO V-560 UV/Vis spectrophotometer, equipped with an integrating sphere attachment (JASCO ISV-469). The reflectance spectra were converted by the instrument software (JASCO) to equivalent absorption Kubelka-Munk units. Barium sulphate was used as a reference.

The surface area measurements were performed in a Quantachrome NOVA 4200e porosimeter using N₂ at – 196 °C. Before analysis, the samples were outgassed overnight at 150 °C. Surface areas were calculated from the N₂ adsorption isotherms using the Brunauer–Emmett–Teller (BET) method (S_{BET}). The micropore surface areas were calculated using the *t*-plot method and the pore size distribution was obtained using the Barrett-Joyner-Halenda (BJH) analysis from the desorption branch [77-79]; while this method is more appropriate for type IV isotherms, it was used in the present work to compare the samples.

The morphology of the samples was observed by scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDS) analysis, using a FEI Quanta 400 FEG ESEM / EDAX Genesis X4M apparatus equipped with a Schottky field emission gun (for optimal spatial resolution). The samples were mounted on a carbon double-sided adhesive tape and observed at different magnifications.

X-ray diffraction (XRD) analysis was carried out in a PANalytical X'Pert MPD equipped with a X'Celerator detector and secondary monochromator (Cu K α λ = 0.154 nm, 50 kV, 40 mA; data recorded at a 0.017°/step size, 1 s/step). Rietveld refinement with Powder Cell software (CCP14, UK) was used to identify the crystallographic phases and to calculate the crystallite size from the XRD diffraction patterns.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos AXIS

Ultra HSA, with VISION software for data acquisition and CASAXPS software for data analysis. The analysis was carried out with a monochromatic Al K α X-ray source (1486.7 eV), operating at 15 kV (90 W), in FAT mode (Fixed Analyser Transmission), with a pass energy of 40 eV for regions ROI and 80 eV for survey. Data acquisition was performed with a pressure lower than 1×10^{-6} Pa, and it was used a charge neutralization system. The deconvolution of the spectra was performed using the XPSPEAK41 program, in which an adjustment of the peaks was considered using peak fitting with Gaussian-Lorentzian peak shape and Shirley type background subtraction.

6.2.3. Photocatalytic experiments

6.2.3.1. Gas-phase photocatalytic experiments

The lab-scale facility described in Chapters 2 and 3 (sub-sections 2.2.2. and 3.2.2, respectively) was employed in gas-phase photocatalytic experiments. The experimental procedure followed to prepare the photocatalytic films onto the cellulose acetate honeycomb structures was already described in sub-section 3.2.1. of Chapter 3. The mass of photocatalyst affixed on each supporting substrate as well as the corresponding surface density, ρ_A , are listed in Table 6.1. The experimental conditions employed in this study are summarized in Table 6.1.

Table 6.1. Mass of photocatalyst (m) affixed onto the substrates surface and corresponding surface density (ρ_A); experimental conditions employed in the gas-phase PCO of PCE under simulated solar radiation.

<i>Photocatalysts</i>			
Sample	m [mg]	ρ_A [mg cm ⁻²]	
TiO ₂ P25	100.4	0.124	
N _{0.50} P25-380	143.1	0.177	
N _{1.0} P25-380	155.5	0.193	
N _{2.0} P25-380	122.2	0.152	
N _{3.0} P25-380	137.6	0.171	
<i>Experimental conditions</i>			
Q_{feed}^* [cm ³ min ⁻¹]	$C_{\text{feed, PCE}}$ [ppm]	RH^* [%]	$I^\#$ [W _{UV} m ⁻²]
300	1100	40	38.4

* measured at 1 bar and 298 K.

measured for the spectral range between 280 - 400 nm: UV fraction of the incident solar radiation.

All experiments were conducted inside the chamber of the solar simulator and using the CPC photoreactor. The description of the lab-scale prototype was already presented in sub-section 3.2.2. of Chapter 3.

The photolytic oxidation of PCE was already evaluated within the study described in Chapter 2.

The performance of each photocatalyst towards PCE photocatalytic degradation was compared in similar operational conditions and calculated as described in eq. 6.1.

$$\text{Conversion (\%)} = \left(1 - \frac{C_{\text{PCE, exit}}}{C_{\text{PCE, feed}}} \right) \times 100 \quad 6.1$$

6.2.3.2. Diphenhydramine photocatalytic degradation

The photocatalytic efficiencies of the samples were evaluated in the degradation of 10 mg L^{-1} DP (absorption at $\lambda < 280 \text{ nm}$) at room temperature (25°C) under visible light illumination. A Heraeus TQ 150 medium-pressure mercury vapour lamp ($\lambda_{\text{exc}} = 254, 313, 366, 436 \text{ and } 546 \text{ nm}$) was held in a quartz immersion tube located inside a DURAN[®] glass water-cooling jacket. A cut-off long pass filter ($\lambda > 430 \text{ nm}$) was used to block the shorter wavelengths. The photon flow entering the reactor was *ca.* 2.86 mW cm^{-2} determined by integrating the irradiance spectrum using a UV-vis spectroradiometer (USB2000+, OceanOptics, USA).

The batch experiments were performed in a glass reactor filled with 7.5 mL of DP solution. The initial pH of the DP solution was 5.9 (variations lower than 0.4 were observed at the end of the experiments) and at these pH values (*i.e.* below 7.0) DP protonated form is the only specie present in solution [26]. The suspension was magnetically stirred and continuously purged with an oxygen flow to maintain oxygen saturation. The load of catalyst was kept at the optimal value of 1.0 g L^{-1} determined for degradation of DP with $\text{TiO}_2 \text{ P25}$ [26]. A schematic representation of the experimental unit can be found in Figure 6.1.

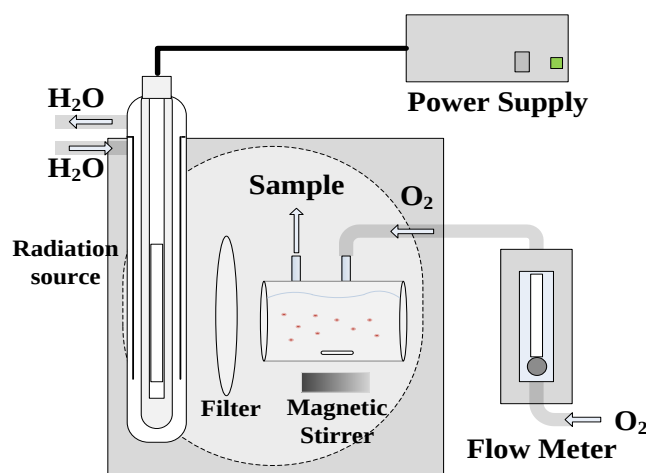


Figure 6.1. Schematic representation of the experimental unit used in DP photocatalytic degradation experiments (adapted from Gomes da Silva [80]).

Prior to irradiation, the suspension was magnetically stirred for 30 min under dark conditions to establish the adsorption–desorption equilibrium. The concentration of the substrate measured after equilibration was established as the initial substrate concentration ($C_{DP,0}$). The dark adsorption (discarded by this method) was never larger than 20 % of the initial amount of pollutant loaded. Then, the lamp was turned on. Samples were taken from the reactor at different reaction times and centrifuged at 14000 rpm for 10 min to separate the catalyst particles before being analysed. A control experiment, in the absence of catalyst, was also performed as a blank run in order to account for direct photolysis. A pseudo-first order kinetic model, often used in photocatalysis as a mathematical equation able to describe the experimental results [81-83], was used as follow:

$$C_{DP,t} = C_{DP,0} e^{-kt} \quad 6.2$$

where k is the apparent pseudo-first order kinetic constant, t is the reaction time and $C_{DP,0}$ and $C_{DP,t}$ denote the DP concentration at $t = 0$ and $t = t$, respectively.

The k constants obtained by fitting the model described in eq. 6.2 to the normalized DP concentration histories ($C_{DP,t}/C_{DP,0}$) as well as the coefficient of variation, CV (standard error $\times 100$ /parameter value) and the corresponding regression coefficient (r^2), are gathered in Table 6.2.

Table 6.2. Pseudo first-order kinetic constant (k), respective coefficient of variation (CV) and regression coefficient (r^2) of DP degradation under visible light illumination.

Catalyst	$k \times 10^3 [\text{min}^{-1}]$	CV [%]	r^2
None	0.30 ± 0.05	6.1	0.97
N _{0.10} P25-380	3.2 ± 0.2	5.8	0.96
N _{0.25} P25-380	4.2 ± 0.3	6.8	0.95
N _{0.40} P25-380	5.6 ± 0.2	3.1	0.99
N _{0.50} P25-380	8.7 ± 0.5	5.3	0.97
N _{0.60} P25-380	7.1 ± 0.4	5.6	0.97
N _{0.75} P25-380	6.2 ± 0.5	7.9	0.94
N _{1.0} P25-380	6.2 ± 0.2	3.9	0.98
N _{2.0} P25-380	1.6 ± 0.1	4.5	0.98
N _{3.0} P25-380	0.7 ± 0.4	6.0	0.96
TiO ₂ P25	0.51 ± 0.06	12	0.90
N _{0.50} P25-340	4.6 ± 0.1	2.0	0.99
N _{0.50} P25-420	2.7 ± 0.1	2.3	0.99

The concentration of DP was analysed by HPLC with a Hitachi Elite LaChrom system equipped with a Hydrosphere C18 column (250 mm $\times$ 4.6 mm; 5 μm particles) maintained at room temperature, a Diode Array Detector (L-2450) and a solvent delivery pump (L-2130). An

isocratic method set at a flow rate of 1 mL min^{-1} was used with the eluent consisting of an A:B (70:30) mixture of 20 mM NaH_2PO_4 acidified with H_3PO_4 at pH 2.80 (A) and acetonitrile (B). Absorbance was found to be linear over the whole range of measurement. The maximum relative standard deviation of HPLC measurements was never larger than 2 %.

6.2.3.3. Bacterial inactivation tests

E. coli ATCC 25922 was used for the microbiological tests and the “spread plate method” was employed to evaluate the photocatalysts antibacterial activity. This method consisted of spreading 100 μL of a suspension of a given photocatalyst (0.125 mg mL^{-1} and 0.500 mg mL^{-1}) and *E. coli* cells into Mueller-Hinton agar (MH, Merck, Germany) plates. Before each experiment, *E. coli* was inoculated into MH agar and incubated overnight at 37°C . A suspension of *E. coli* cells was prepared and diluted in saline solution to approximately 10^3 - 10^4 colony-forming units (CFU) mL^{-1} .

Inactivation tests were carried out in a 6 wells microtiter plate where 1 cm^3 of the photocatalyst suspension was added to 1 mL of the *E. coli* cells suspension. The microtiter plate was placed at a distance of 3.60 cm from a UVA lamp (Sylvania Lynx-s 11 W blacklight blue lamp with a spectral peak of 365 nm; photon flux of $25 \text{ W}_{\text{UV}} \text{ m}^{-2}$) (see Figure 6.2).

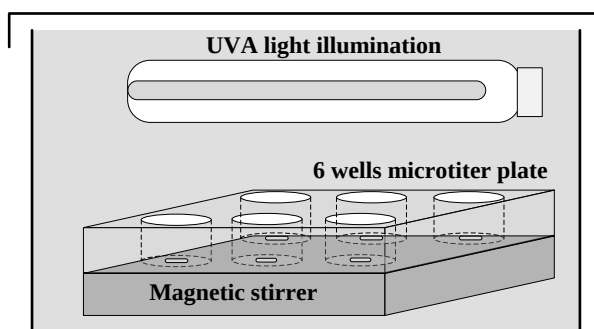


Figure 6.2. Schematic representation of the experimental unit used for the *E. coli* inactivation experiments.

The UVA photon flux was measured in several points located at 3.6 cm of the UVA lamp, using a broadband UV radiometer (CUV 5, Kipp & Zonen B.V.); the radiometer was plugged to a handheld display unit (Meteon, Kipp & Zonen B.V.) to produce readings in terms of UVA photon flux. All experiments were performed at room temperature and the suspensions magnetically stirred throughout the experimental period to ensure adequate mixing and contact between the photocatalyst and *E. coli* cells. Under UVA light radiation, samples for cell counting were collected at $t = 0, 5, 10, 15$ and 20 min . Samples without growth after photocatalytic

treatment were re-suspended in MH broth for evaluation of the photocatalyst bactericidal effect: the cultures were incubated at 37 °C during 24 h and 100 µL were spread into MH agar plates to evaluate viable bacteria. Control experiments in the dark and under UVA light in the absence of photocatalyst were also performed. All the results obtained were confirmed in triplicate.

6.3. Results and discussion

6.3.1. Characterization

The XRD patterns of the different N_xP25-y samples as well as of the bare TiO₂ P25 sample, used as reference, are shown in Figure 6.3. In comparison with TiO₂ P25, no new diffraction peaks were observed in the samples prepared with different amounts of urea (Figure 6.3a). Apparently, the modification with nitrogen does not affect the crystalline TiO₂ forms of TiO₂ P25 (anatase and rutile), which is in agreement with results previously described in the literature [33, 84, 85]. However, for the nitrogen-containing samples it is visible that the intensities of the peaks are slightly different from those of bare TiO₂ P25, suggesting some modification by the treatment performed. Figure 6.3b shows that the crystalline forms of TiO₂ also remained similar when samples were subjected to different calcination temperatures (*i.e.*, N_{0.50}P25-340, N_{0.50}P25-380 and N_{0.50}P25-420).

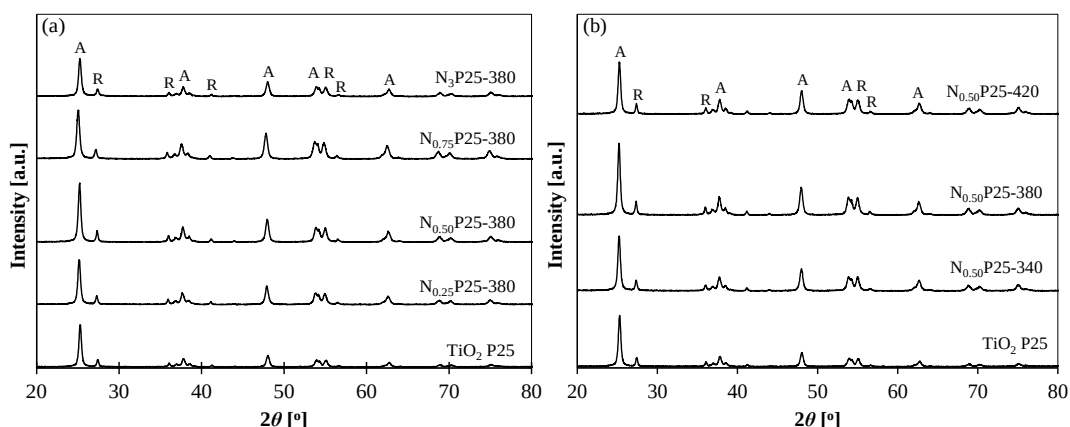


Figure 6.3. XRD patterns of the powder samples synthesized with different (a) urea contents and (b) calcination temperatures. XRD pattern of TiO₂ P25 is also shown as reference. A: anatase; R: rutile.

The phase composition and crystallite sizes of the different samples, estimated by the Williamson–Hall equation [86] are listed in Table 6.3. All nitrogen-containing samples present lower percentage of anatase crystalline phase and higher percentage of rutile crystalline phase when compared with TiO₂ P25. At the same time, the anatase and rutile crystallites are in general

smaller than those of TiO₂ P25 (as observed previously when hydrothermal/solvothermal methods were used to prepare TiO₂ and nitrogen-modified TiO₂ samples [35, 87]), except for the N_{0.50}P25-380 sample in which the rutile crystallite size is, by far, the highest (50 nm) among all the samples.

Table 6.3. Optical, structural and textural properties of N_xP25-y and bare TiO₂ P25.

Sample	N ₂ physisorption		XRD		UV-Vis	
	S _{BET} ^a [m ² g ⁻¹]	r _{p, BJH} ^a [nm]	Phase composition ^b [v/v %]	Crystallite size ^b [nm]	Absorption threshold [nm]	E _g [eV]
TiO ₂ P25	61	15	86 (A), 14 (R)	32 (A), 44 (R)	382	3.25
N _{0.25} P25-380	63	12	82 (A), 18 (R)	28 (A), 37 (R)	397	3.13
N _{0.50} P25-380	61	10	85 (A), 15 (R)	30 (A), 50 (R)	415	2.99
N _{0.75} P25-380	63	13	82 (A), 18 (R)	26 (A), 30 (R)	403	3.08
N _{0.50} P25-340	-	-	81 (A), 19 (R)	32 (A), 32 (R)	412	3.02
N _{0.50} P25-420	-	-	84 (A), 16 (R)	29 (A), 45 (R)	405	3.07

^a BET surface area (S_{BET}) calculated by Brunauer-Emmet-Teller (BET) formula and average pore diameter ($r_{p, \text{BJH}}$) calculated by

Barrett-Joyner-Halenda (BJH) formula.

^b A: anatase; R: rutile

Figure 6.4 shows the nitrogen adsorption-desorption isotherms of N_xP25-380 samples. The pore size distributions were computed by the BJH analysis method from the desorption branch of the isotherm (Figure 6.4 inset). All samples have similar specific surface areas (around 62 m² g⁻¹, Table 6.3) and the isotherms are of type II [88], exhibiting a hysteresis loop at high relative pressures between 0.8 and 1.0 indicating the presence of mesopores. In the inset of Figure 6.4, a clear pore size distribution with maximum pore radius between 10 and 15 nm is observed.

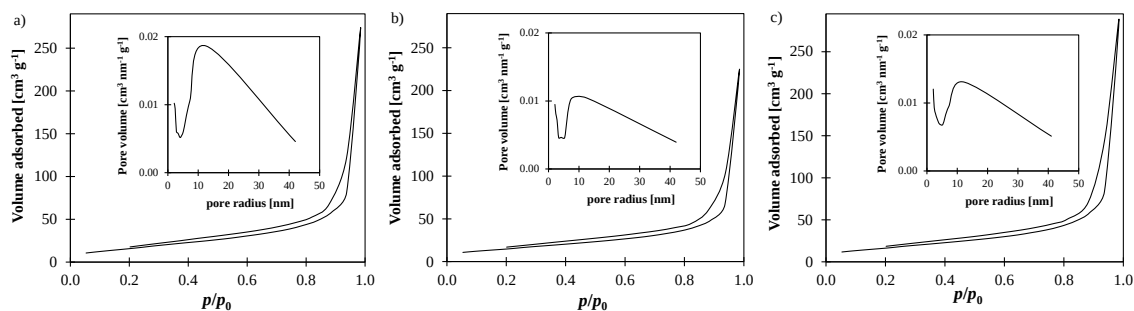


Figure 6.4. N₂ adsorption-desorption isotherms and pore size distribution (inset) of: a) N_{0.75}P25-380, b) N_{0.50}P25-380 and c) N_{0.25}P25-380.

The spectra obtained through UV-DRS for bare TiO₂ P25 and N_xP25-380 samples prepared with different amounts of urea are depicted in Figure 6.5a. The samples N_{0.50}TiO₂-380 and N_{0.75}P25-380 presented a significant absorption tail in the visible region between 400 and 600 nm, which is the typical absorption feature of N-doped TiO₂ materials. Thus, for these samples, the modification of TiO₂ with nitrogen resulted in a red shift of the absorbance region. According to some authors [1, 2, 61], this phenomenon is due to the substitution on the lattice of oxygen by nitrogen during the TiO₂ nitridation, narrowing the band gap by mixing the N2p and the O2p states. Another hypothesis, reported by Irie *et al.* [61] and by Sathish *et al.* [33], suggests the presence of an isolated narrow band above the valence band. In contrast, no significant absorption above 400 nm was observed for N_{0.25}P25-380, which may imply an ineffective modification of TiO₂ due to the low amount of urea used in this case.

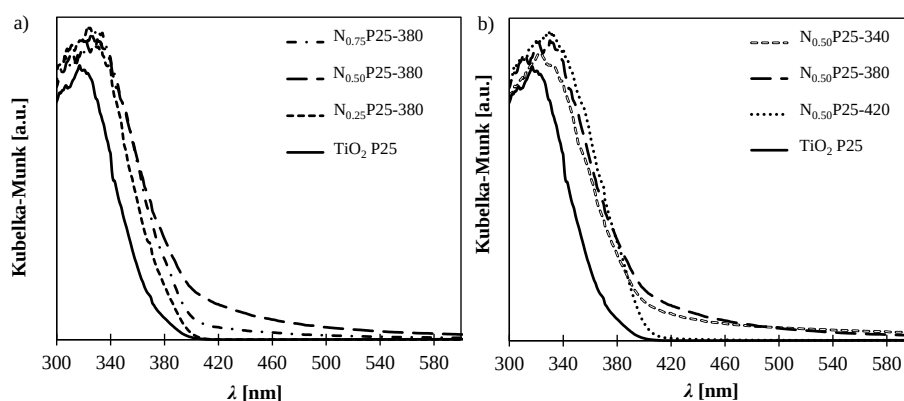


Figure 6.5. UV-Vis absorption spectra of: a) N_{0.25}P25-380, N_{0.50}P25-380, N_{0.75}P25-380 and bare P25 and b) N_{0.50}P25-340, N_{0.50}P25-380, N_{0.50}P25-420 and bare TiO₂ P25.

The influence of the calcination temperature on the optical properties of N_{0.50}P25-y is shown in Figure 6.5b. It can be observed that only the samples N_{0.50}P25-380 and N_{0.50}P25-340 present an absorption in the visible region, while no significant absorption was found for the sample calcined at the highest temperature (420 °C). The N_{0.50}P25-380 sample also presents the

lowest band gap energy (2.99 eV in Table 6.3), making it potentially the most active photocatalyst. Figure 6.6 shows SEM micrographs for this particular sample and the corresponding EDS spectrum. Agglomerates of spherical-like particles are observed on the micrographs while EDS analysis confirmed the presence of nitrogen on this sample. In addition, the particles size seems to be lower than 50 nm, in agreement with the XRD data and pore size distributions presented above.

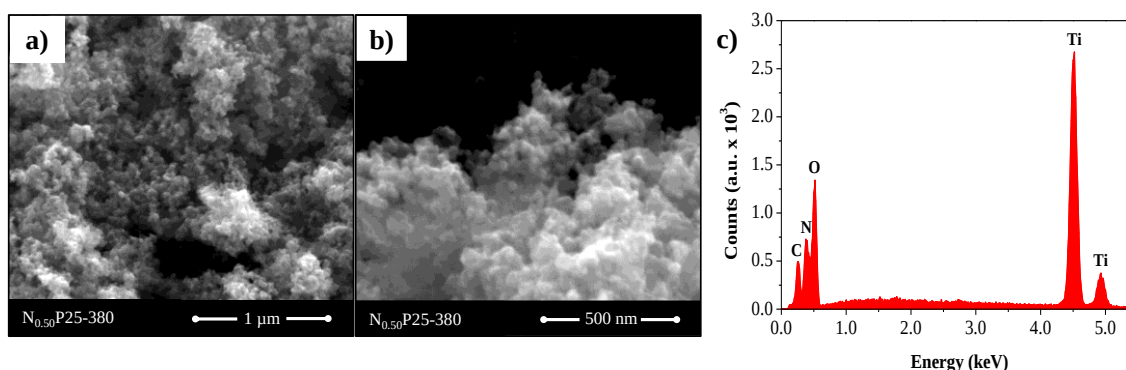


Figure 6.6. (a-b) SEM micrographs at different magnifications, and (c) EDS spectrum of $N_{0.50}P25-380$.

XPS analysis was also performed for this sample, and the results are shown in Figure 6.7, together with those obtained for bare P25. N1s peaks in the range of 396–404 eV are considered typical of N-TiO₂ materials [5, 6, 33, 47, 54, 56, 89, 90]. A N1s peak at 396–397 eV is often considered characteristic of Ti-N-Ti-N or Ti-N-Ti-O linkages, thus attributed to nitrogen replacing oxygen in the crystal lattice of TiO₂ [33, 47, 54, 89, 90]. A N1s peak at higher binding energy (398–400 eV) [33, 89] is generally assigned to the presence of Ti–O–N and/or Ti–N–O bonds [33, 54, 89] where the electronic status of nitrogen is anion-like (N⁻). Figure 6.7a shows the deconvoluted N1s spectrum, where two peaks (at 399.0 and 400.3 eV) are observed. Considering the above mentioned discussion, these peaks may be attributed to Ti–O–N and/or Ti–N–O bonds, in this way suggesting nitrogen substitution into TiO₂ [33, 87, 91]. Bare P25 sample did not reveal any peak associated to N1s core level (data not shown). Regarding Ti2p and O1s core levels, respectively Figures 6.7b and 6.7c, no differences were observed when comparing the $N_{0.50}P25-380$ sample and bare P25.

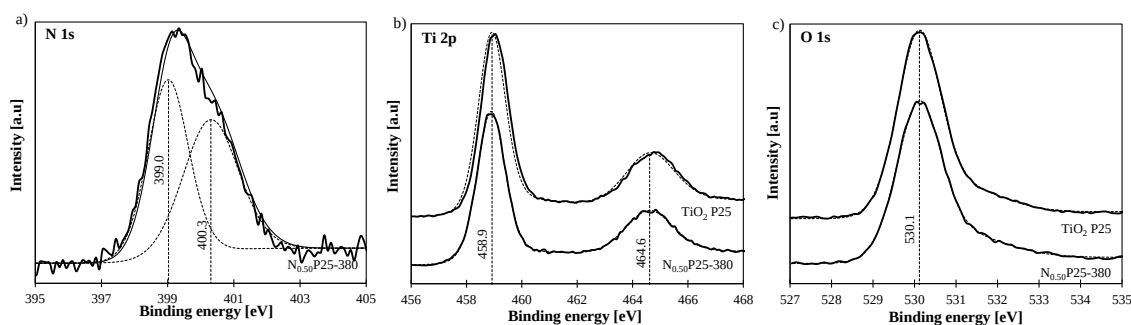


Figure 6.7. X-ray photoelectron spectra of $N_{0.50}P25-380$ and bare TiO₂ P25 samples: (a) N1s, (b) Ti2p and (c) O1s core levels.

6.3.2. Gas-phase PCO of PCE under simulated solar light

The samples obtained with a wide range of urea:TiO₂ weight ratios (up to 3:1), together with bare P25, were studied in the photodegradation of gas-phase PCE under simulated solar radiation, *i.e.*, $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (measured within 280 - 400 nm: solar UV fraction)

The photocatalytic activity as a function of nitrogen content is shown in Figure 6.8. Bare P25 presented the highest activity (67 % conversion of initial PCE concentration) in comparison to nitrogen containing samples. N_{0.5}P25-380 was able to convert around 35 % of the PCE feed while N_{1.0}P25-380, N_{2.0}P25-380 and N_{3.0}P25-380 converted respectively *ca.* 24 %, 18 % and 13 %. The results show that N-doping induced a reduction in photocatalytic activity being more marked as the nitrogen content increases.

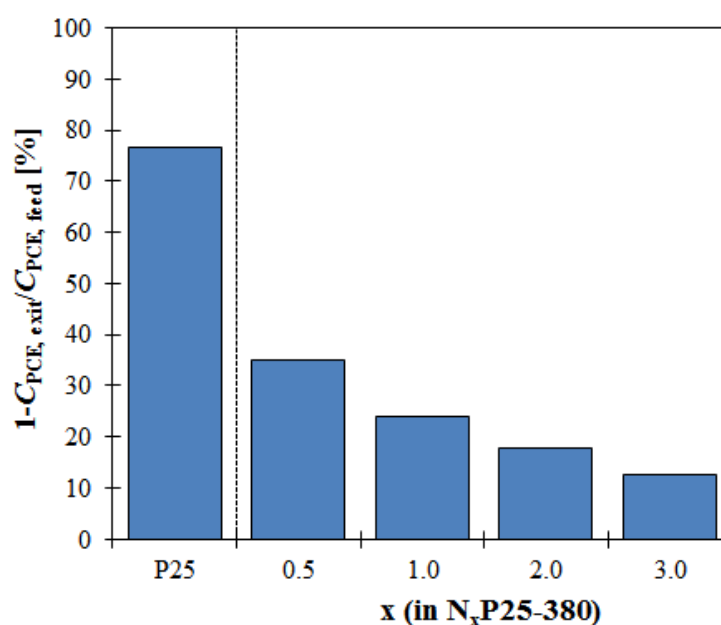


Figure 6.8. Gas-phase PCO of PCE ($C_{\text{PCE, feed}} = 1100 \text{ ppm}$; $Q_{\text{feed}}^* = 300 \text{ cm}^3 \text{ min}^{-1}$; $RH^* = 40 \%$) at steady-state conditions, under simulated solar radiation ($I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$, measured within the spectral range of 280 – 400 nm) for materials prepared with different urea content and bare P25 * measured at 298 K and 1 bar.

Disregarding the bare TiO₂ P25 photocatalytic activity, the observation of a more pronounced activity as the nitrogen content decreases is noteworthy: further investigation of such phenomenon should enlighten the overall photocatalytic mechanism of N-modified TiO₂ materials prepared in this study.

6.3.3. Diphenhydramine photocatalytic degradation under visible light

The samples obtained with a wide range of urea:TiO₂ weight ratios (up to 3:1), and also those treated at three different temperatures, together with bare TiO₂ P25, were studied in the photodegradation of DP under visible light illumination, *i.e.* at $\lambda > 430$ nm (Figure 6.9). The respective pseudo-first order rate constants are shown in Table 6.2. It is worthy of note that DP is a very resistant pollutant in the absence of a catalyst, since the DP conversion observed in such case is less than 3 % in 60 min (Figure 6.9a).

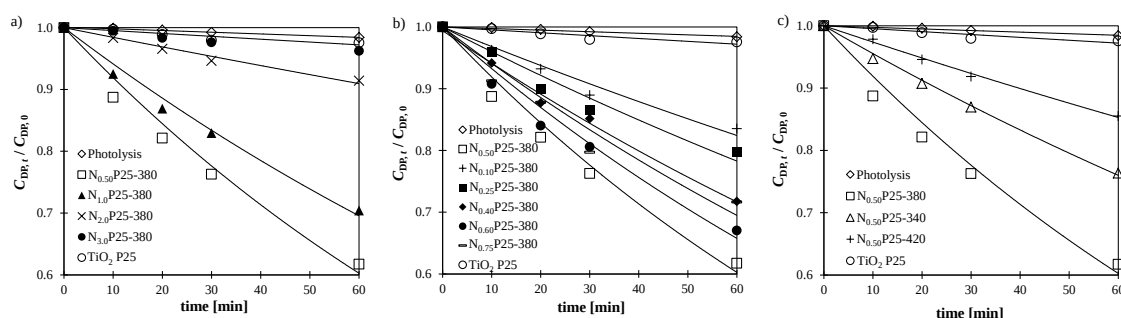


Figure 6.9. Photocatalytic degradation of DP (10 mg L⁻¹) under visible light illumination for (a)-(b) materials prepared with different urea contents and (c) different temperatures (340, 380 and 420 °C). Catalyst load = 1.0 g L⁻¹. Curves represent the fitting of the pseudo-first order equation to the experimental data.

The activity of the catalysts prepared with different amounts of urea follows the sequence (Figures 6.9a and 6.9b respectively for small and large amounts of urea, and Table 6.2): N_{0.50}P25-380 ($8.7 \times 10^{-3} \text{ min}^{-1}$) > N_{0.60}P25-380 ($7.1 \times 10^{-3} \text{ min}^{-1}$) > N_{0.75}P25-380 ($6.2 \times 10^{-3} \text{ min}^{-1}$) ~ N_{1.0}P25-380 ($6.2 \times 10^{-3} \text{ min}^{-1}$) > N_{0.40}P25-380 ($5.6 \times 10^{-3} \text{ min}^{-1}$) > N_{0.25}P25-380 ($4.2 \times 10^{-3} \text{ min}^{-1}$) > N_{0.10}P25-380 ($3.2 \times 10^{-3} \text{ min}^{-1}$) > N_{2.0}P25-380 ($1.6 \times 10^{-3} \text{ min}^{-1}$) > N_{3.0}P25-380 ($0.7 \times 10^{-3} \text{ min}^{-1}$) > TiO₂ P25 ($0.51 \times 10^{-3} \text{ min}^{-1}$), where the values in brackets refer to the pseudo-first order rate constants. The results indicate the superior activity of all modified samples compared to TiO₂ P25 towards DP degradation under visible light illumination, and that the catalytic activity depends on the amount of urea employed in the preparation method, *i.e.* in the nitrogen content in TiO₂, considering that these materials were calcined at the same temperature. For instance, it is shown a clear increase in the pseudo-first order rate constant with the amount of urea (N_{0.10}P25-380 and N_{0.50}P25-380 samples), until a certain point where a clear decrease in pseudo-first order rate constants is then observed when the amount of urea is further increased (N_{0.50}P25-380 and N_{3.0}P25-380 samples). Thus, among the nitrogen modified samples, the highest pseudo-first order rate constant was obtained when 0.50 g of urea was used ($8.7 \times 10^{-3} \text{ min}^{-1}$). The high photocatalytic activity of N_{0.50}P25-380 towards degradation of DP can be justified by the highest red-shift of the absorption to the visible range

observed in Figure 6.5, corresponding to the lowest band gap energy (Table 6.3), originated by the substitution on the lattice of oxygen by nitrogen during the TiO₂ nitridation. In fact, the efficiency of these materials ($N_{0.50}P25-380 > N_{0.75}P25-380 > N_{0.25}P25-380 > TiO_2 P25$) followed the opposite trend with respect to the band gap energies indicated in brackets: $N_{0.50}P25-380$ (2.99 eV) < $N_{0.75}P25-380$ (3.08 eV) < $N_{0.25}P25-380$ (3.13 eV) < $TiO_2 P25$ (3.25 eV).

It is widely accepted that the treatment temperature used to prepare N-doped TiO₂ catalysts influences the photocatalytic activity [33, 92]. Figure 6.9c shows the effect of the thermal treatment on DP photocatalytic degradation with the samples prepared with a fixed amount of urea (0.50 g) and different calcination temperatures, *i.e.* 340, 380, and 420 °C. The photocatalytic activity was influenced by the calcination temperature, wherein the pseudo-first order rate constant increases from 340 °C to 380 °C but decreases from 380 °C to 420 °C (*i.e.*, $k = 4.6 \times 10^{-3}$, 8.7×10^{-3} and $2.7 \times 10^{-3} \text{ min}^{-1}$ for $N_{0.50}P25-340$, $N_{0.50}P25-380$ and $N_{0.50}P25-420$, respectively, Table 6.2). Among these three samples, the lowest photocatalytic activity was found for $N_{0.50}P25-420$, being related with a lower amount of nitrogen in the TiO₂ structure due to the highest calcination temperature [93]. In fact, the sample calcined at 420 °C is less yellowish than those calcined at 340 °C and 380 °C, which may implies nitrogen depletion from the photocatalyst [92, 93]. In contrast, the calcination at 340 °C may be not enough to decompose the nitrogen-precursor and incorporate nitrogen in the structure of TiO₂. Once again, the efficiency of the materials ($N_{0.50}P25-380 > N_{0.50}P25-340 > N_{0.50}P25-420 > TiO_2 P25$) followed the opposite trend of the band gap energies shown in brackets: $N_{0.50}P25-380$ (2.99 eV) < $N_{0.50}P25-340$ (3.02 eV) < $N_{0.50}P25-420$ (3.07 eV) < $TiO_2 P25$ (3.25 eV).

6.3.4. *Escherichia coli* inactivation

Figure 6.10 summarizes the photocatalytic effect of bare TiO₂ P25, $N_{0.25}P25-380$, $N_{0.50}P25-380$ and $N_{0.75}P25-380$ on the growth inhibition of *E. coli* under UVA. Two different photocatalyst loads were tested in order to assess their influence on the *E. coli* growth inhibition. All the photocatalysts tested showed very good antimicrobial activity against *E. coli* bacteria at the highest photocatalyst load tested (0.500 mg mL⁻¹), reducing more than 95 % of CFU in 5 min and 100 % in 10 min.

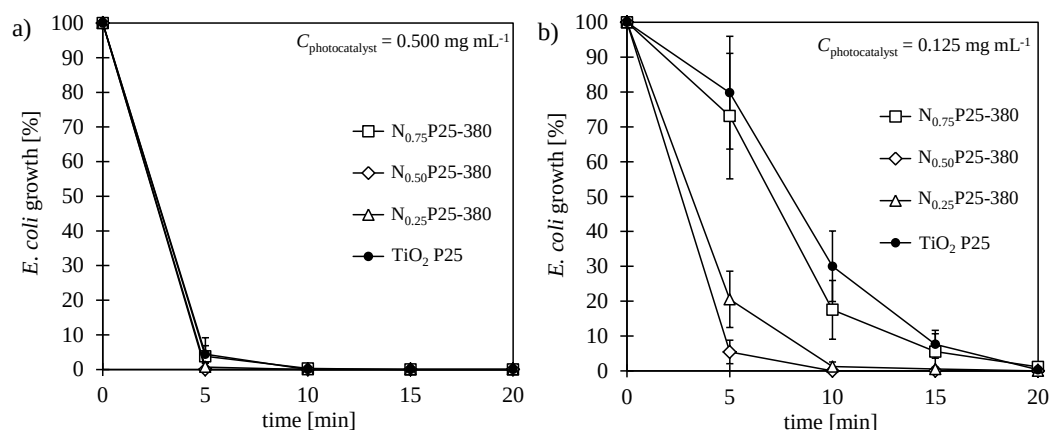


Figure 6.10. *E. coli* growth under UVA for photocatalyst loads of (a) 0.500 mg mL⁻¹ and (b) 0.125 mg mL⁻¹. Results are mean values ($n = 3$) and the error bars represent the standard deviation.

Reducing the photocatalyst load to 0.125 mg mL⁻¹, becomes evident that N_{0.50}P25-380 presents the highest inactivation efficiency towards *E. coli*, whereas TiO₂ P25 showed the lowest. Interestingly, these results for *E. coli* inactivation under UVA correlate well to those obtained for DP degradation under visible light illumination, where N_{0.50}P25-380 stands out as a better photocatalyst for the experimental conditions employed. The tested photocatalysts showed no effect under dark conditions as no *E. coli* inactivation was observed after 20 min without UVA light; the effect of the UVA lamp was also assessed and negligible *E. coli* inactivation was observed in the experiments performed under UVA light radiation without photocatalyst (data not shown). Furthermore, no bacteria growth was observed in the re-suspended samples incubated at 37 °C during 24 h. These results show the bactericidal effect of the photocatalyst on *E. coli*.

Rengifo-Herrera *et al.* [94] monitored the formation of hydroxyl (HO[•]) and superoxide (O₂^{•-}) radicals by using electron spin resonance (ESR) studies with bare TiO₂ and N, S co-doped TiO₂ samples. The authors concluded that HO[•] radicals were the main species involved in *E. coli* inactivation under UV (330–400). It was also suggested that the O₂^{•-} radical and its oxidation product (¹O₂) were responsible for a marked *E. coli* inactivation with N, S co-doped TiO₂ under visible (400 – 500 nm) illumination. These conclusions are in agreement with other publications of the same authors dealing with (N-, S- and N-/S-) doped TiO₂ samples [30, 95, 96]. Therefore, the mechanisms involved under UV and visible light can be different; however, *E. coli* inactivation was observed in both cases regardless the main species involved. Since reactive species are produced with the N_{0.50}P25-380 sample under visible illumination (as shown by the significant DP degradation obtained in Figure 6.9), *E. coli* inactivation under such conditions is also expected.

6.4. Conclusions

Effective visible light active nitrogen modified TiO₂ P25 photocatalysts were synthesized by a simple and low-cost preparation method, well suited for scale-up mass production.

From XPS analyses, it is shown that anion-like nitrogen (N⁻) is present in the structure of TiO₂, as O–Ti–N and Ti–O–N linkages.

The catalytic activity of N-modified TiO₂ materials for the degradation of PCE indoor air pollutant under simulated solar radiation, and for the inactivation of *E. coli* bacteria in aqueous solutions, under UVA radiation was found to depend on the amount of urea used in the preparation method. The calcination temperature also influences the catalytic activity, as observed in the aqueous-phase degradation experiments with the pharmaceutical pollutant, DP, under visible light illumination.

In this study, N-modified TiO₂ materials revealed lower photocatalytic activity towards the degradation of gas-phase PCE under simulated solar radiation than bare TiO₂ P25. Regarding the aqueous-phase experiments, the material prepared with a urea:TiO₂ weight ratio of 1:2, and calcined at 380 °C, exhibits the highest photocatalytic efficiency for DP degradation and completely inactivates *E. coli* bacteria in 10 min. Further tests are needed in order to clarify the overall photocatalytic mechanism of nitrogen modified TiO₂ samples towards the elimination of harmful organic molecules and microorganisms inactivation whether present in air or water media.

6.5. References

- [1] E. Keidel, *Furben Zeitung* 34 (1929) 1242.
- [2] C.F. Goodeve, J.A. Kitchener, *Trans. Faraday Soc.* 34 (1938) 570-579.
- [3] A. Fujishima, K. Hashimoto, T. Watanabe, *TiO₂ Photocatalysis: Fundamentals and Applications*, Bkc, Incorporated, Tokyo, 1999.
- [4] S. Kato, F. Mashio, *Abtr. Book Annu. Meet. Chem. Soc. Jpn.* (1956) 223.
- [5] H. Gerischer, in: H. Eyring, D. Henderson, W. Jost (Eds.), *Physical Chemistry: An Advanced Treatise*, Academic Press, New York, 1970, pp. 463–542.
- [6] V.A. Myamlin, Y.V. Pleskov, *Electrochemistry of Semiconductors*, Plenum Press, New York, 1967.
- [7] A. Fujishima, K. Honda, S. Kikuchi, *J. Chem. Soc. Jpn. (Kogyo Kagaku Zasshi)* 72 (1969) 108-113.
- [8] A. Fujishima, K. Honda, *Nature* 238 (1972) 37-38.
- [9] S.N. Frank, A.J. Bard, *J. Am. Chem. Soc.* 99 (1977) 303-304.
- [10] C. Srinivasan, N. Somasundaram, *Curr. Sci.* 85 (2003) 1431-1438.
- [11] D.Y. Goswami, *J. Sol. Energy Eng.* 119 (1997) 101-107.
- [12] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69-96.
- [13] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, *J. Chem. Technol. Biotechnol.* 77 (2002) 102-116.
- [14] C. McCullagh, J. Robertson, D. Bahnemann, P. Robertson, *Res. Chem. Intermed.* 33 (2007) 359-375.
- [15] D. Bahnemann, *Sol. Energy* 77 (2004) 445-459.
- [16] R.W. Matthews, *J. Chem. Soc. Faraday Trans. 1* 80 (1984) 457-471.
- [17] J.-M. Herrmann, *Top. Catal.* 34 (2005) 49-65.
- [18] A.K. Ghosh, H.P. Maruska, *J. Electrochem. Soc.* 124 (1977) 1516-1522.
- [19] E. Borgarello, J. Kiwi, M. Graetzel, E. Pelizzetti, M. Visca, *J. Am. Chem. Soc.* 104 (1982) 2996-3002.
- [20] M. Anpo, *Pure Appl. Chem.* 72 (2000) 1787-1792.
- [21] H. Yamashita, M. Harada, J. Misaka, M. Takeuchi, Y. Ichihashi, F. Goto, M. Ishida, T. Sasaki, M. Anpo, *J. Synchrotron Radiat.* 8 (2001) 569-571.
- [22] K. Takeuchi, I. Nakamura, O. Matsumoto, S. Sugihara, M. Ando, T. Ihara, *Chem. Lett.* 29 (2000) 1354-1355.
- [23] T. Ihara, M. Miyoshi, M. Ando, S. Sugihara, Y. Iriyama, *J. Mater. Sci.* 36 (2001) 4201-4207.
- [24] T. Hirai, K. Suzuki, I. Komasa, J. Colloid Interface Sci. 244 (2001) 262-265.
- [25] D. Chatterjee, A. Mahata, *Appl. Catal. B: Environ.* 33 (2001) 119-125.
- [26] L.M. Pastrana-Martínez, S. Morales-Torres, V. Likodimos, J.L. Figueiredo, J.L. Faria, P. Falaras, A.M.T. Silva, *Appl. Catal. B: Environ.* 123–124 (2012) 241-256.
- [27] L.M. Pastrana-Martínez, S. Morales-Torres, S.K. Papageorgiou, F.K. Katsaros, G.E. Romanos, J.L. Figueiredo, J.L. Faria, P. Falaras, A.M.T. Silva, *Appl. Catal. B: Environ.* 142–143 (2013) 101-111.
- [28] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* 293 (2001) 269-271.
- [29] T. Ohno, T. Mitsui, M. Matsumura, *Chem. Lett.* 32 (2003) 364-365.

- [30] J.A. Rengifo-Herrera, C. Pulgarin, *Sol. Energy* 84 (2010) 37-43.
- [31] Q. Xiao, L. Ouyang, *J. Phys. Chem. Solids* 72 (2011) 39-44.
- [32] C. Burda, Y. Lou, X. Chen, A.C.S. Samia, J. Stout, J.L. Gole, *Nano Lett.* 3 (2003) 1049-1051.
- [33] M. Sathish, B. Viswanathan, R.P. Viswanath, C.S. Gopinath, *Chem. Mater.* 17 (2005) 6349-6353.
- [34] M. Mrowetz, W. Balcerski, A.J. Colussi, M.R. Hoffmann, *J. Phys. Chem. B* 108 (2004) 17269-17273.
- [35] G. Yang, Z. Jiang, H. Shi, T. Xiao, Z. Yan, *J. Mater. Chem.* 20 (2010) 5301-5309.
- [36] T. Cottineau, N. Bealu, P.-A. Gross, S.N. Pronkin, N. Keller, E.R. Savinova, V. Keller, *J. Mater. Chem. A* 1 (2013) 2151-2160.
- [37] S. Sato, *Chem. Phys. Lett.* 123 (1986) 126-128.
- [38] O. Diwald, T.L. Thompson, T. Zubkov, S.D. Walck, J.T. Yates, *J. Phys. Chem. B* 108 (2004) 6004-6008.
- [39] V. Likodimos, C. Han, M. Pelaez, A.G. Kontos, G. Liu, D. Zhu, S. Liao, A.A. de la Cruz, K. O'Shea, P.S.M. Dunlop, J.A. Byrne, D.D. Dionysiou, P. Falaras, *Ind. Eng. Chem. Res.* 52 (2013) 13957-13964.
- [40] M. Batzill, E.H. Morales, U. Diebold, *Phys. Rev. Lett.* 96 (2006) 026103.
- [41] A. Ghicov, J.M. Macak, H. Tsuchiya, J. Kunze, V. Haeublein, L. Frey, P. Schmuki, *Nano Lett.* 6 (2006) 1080-1082.
- [42] K. Yang, Y. Dai, B. Huang, *J. Phys. Chem.* 111 (2007) 12086-12090.
- [43] Y. Nakano, T. Morikawa, T. Ohwaki, Y. Taga, *Appl. Phys. Lett.* 86 (2005) 132104.
- [44] S.-Z. Chen, P.-Y. Zhang, D.-M. Zhuang, W.-P. Zhu, *Catal. Commun.* 5 (2004) 677-680.
- [45] J. Premkumar, *Chem. Mater.* 16 (2004) 3980-3981.
- [46] I.-C. Kang, Q. Zhang, S. Yin, T. Sato, F. Saito, *Appl. Catal. B: Environ.* 84 (2008) 570-576.
- [47] S. Yin, K. Ihara, M. Komatsu, Q. Zhang, F. Saito, T. Kyotani, T. Sato, *Solid State Commun.* 137 (2006) 132-137.
- [48] B. Liu, S. Yin, R. Li, Y. Wang, T. Sato, *J. Ceram. Soc. Jpn.* 115 (2007) 692-696.
- [49] O. Diwald, T.L. Thompson, E.G. Goralski, S.D. Walck, J.T. Yates, *J. Phys. Chem. B* 108 (2003) 52-57.
- [50] T. Tachikawa, Y. Takai, S. Tojo, M. Fujitsuka, H. Irie, K. Hashimoto, T. Majima, *J. Phys. Chem. B* 110 (2006) 13158-13165.
- [51] C. Di Valentin, G. Pacchioni, A. Selloni, S. Livraghi, E. Giamello, *J. Phys. Chem. B* 109 (2005) 11414-11419.
- [52] T. Imao, T. Horiuchi, N. Noma, S. Ito, *J. Sol-Gel Sci. Technol.* 39 (2006) 119-122.
- [53] N. Venkatachalam, A. Vinu, S. Anandan, B. Arabindoo, V. Murugesan, *J. Nanosci. Nanotechnol.* 6 (2006) 2499-2507.
- [54] S. Sakthivel, M. Janczarek, H. Kisch, *J. Phys. Chem. B* 108 (2004) 19384-19387.
- [55] C. Di Valentin, E. Finazzi, G. Pacchioni, A. Selloni, S. Livraghi, M.C. Paganini, E. Giamello, *Chem. Phys.* 339 (2007) 44-56.
- [56] C. Bolver, R. Bellod, A. Fuerte, M. Fernández-García, *Appl. Catal. B: Environ.* 65 (2006) 301-308.
- [57] D. Li, H. Haneda, S. Hishita, N. Ohashi, *Mater. Sci. Eng. B-Adv.* 117 (2005) 67-75.

- [58] T. Sano, N. Negishi, K. Koike, K. Takeuchi, S. Matsuzawa, J. Mater. Chem. 14 (2004) 380-384.
- [59] H.M. Yates, M.G. Nolan, D.W. Sheel, M.E. Pemble, J. Photochem. Photobiol. A 179 (2006) 213-223.
- [60] P. Frach, D. Glöß, M. Vergöhl, F. Neumann, K. Hund-Rinke, Proceeding of the 4th International Workshop on the Utilization and Commercialisation of Photocatalytic Systems (EJIPAC '04) (2004).
- [61] H. Irie, Y. Watanabe, K. Hashimoto, J. Phys. Chem. B 107 (2003) 5483-5486.
- [62] R. Nakamura, T. Tanaka, Y. Nakato, J. Phys. Chem. B 108 (2004) 10617-10620.
- [63] C. Di Valentin, G. Pacchioni, A. Selloni, Phys. Rev. B 70 (2004) 085116.
- [64] N. Serpone, J. Phys. Chem. B 110 (2006) 24287-24293.
- [65] A.V. Emeline, N.V. Sheremetyeva, N.V. Khomchenko, V.K. Ryabchuk, N. Serpone, J. Phys. Chem. 111 (2007) 11456-11462.
- [66] R. Bacsa, J. Kiwi, T. Ohno, P. Albers, V. Nadtochenko, J. Phys. Chem. B 109 (2005) 5994-6003.
- [67] J.-h. Xu, W.-L. Dai, J. Li, Y. Cao, H. Li, H. He, K. Fan, Catal. Commun. 9 (2008) 146-152.
- [68] H. Li, J. Li, Y. Huo, J. Phys. Chem. B 110 (2006) 1559-1565.
- [69] K. Yamada, H. Nakamura, S. Matsushima, H. Yamane, T. Haishi, K. Ohira, K. Kumada, C. R. Chim. 9 (2006) 788-793.
- [70] S. Livraghi, M.C. Paganini, E. Giamello, A. Selloni, C. Di Valentin, G. Pacchioni, J. Am. Chem. Soc. 128 (2006) 15666-15671.
- [71] T. Morikawa, R. Asahi, T. Ohwaki, K. Aoki, Y. Taga, Jpn. J. Appl. Phys. 40 (2001) L561-L563.
- [72] S. Sato, R. Nakamura, S. Abe, Appl. Catal. A: Gen. 284 (2005) 131-137.
- [73] Y. Liu, J. Li, X. Qiu, C. Burda, Water Sci. Technol. 54 (2006) 47-54.
- [74] X.L. Cheng, Y.J. Hu, S.J. Hu, L. Yu, G.R. Xie, Adv. Mater. Res. 189 (2011) 1258-1262.
- [75] L. Rizzo, D. Sannino, V. Vaiano, O. Sacco, A. Scarpa, D. Pietrogiacomini, Appl. Catal. B: Environ. 144 (2014) 369-378.
- [76] J.P. Berninger, B. Du, K.A. Connors, S.A. Eytcheson, M.A. Kolkmeier, K.N. Prosser, T.W. Valenti, C.K. Chambliss, B.W. Brooks, Environ. Toxicol. Chem. 30 (2011) 2065-2072.
- [77] S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc. 60 (1938) 309-319.
- [78] E.P. Barrett, L.G. Joyner, P.P. Halenda, J. Am. Chem. Soc. 73 (1951) 373-380.
- [79] R.S. Mikhail, S. Brunauer, E.E. Bodor, J. Colloid Interface Sci. 26 (1968) 45-53.
- [80] C.S.C.G.d.S. Gomes da Silva, Synthesis, Spectroscopy and Characterization of Titanium Dioxide Based Photocatalysts for the Degradative Oxidation of Organic Pollutants, PhD dissertation, Faculdade de Engenharia da Universidade do Porto, Porto, Portugal, 2008.
- [81] P. Zhang, J. Liu, J. Photochem. Photobiol. A 167 (2004) 87-94.
- [82] B. Ohtani, J. Photochem. Photobiol. C 11 (2010) 157-178.
- [83] J.-M. Herrmann, Environ. Sci. Pollut. Res. 19 (2012) 3655-3665.
- [84] Y.V. Pleskov, Solar Energy Conversion: A Photochemical Approach, Springer Verlag, Berlin, 1990.
- [85] J. Yuan, M. Chen, J. Shi, W. Shangguan, Int. J. Hydrogen Energy 31 (2006) 1326-1331.
- [86] H. Bi, S. Li, Y. Zhang, Y. Du, J. Magn. Magn. Mater. 277 (2004) 363-367.
- [87] F. Peng, L. Cai, L. Huang, H. Yu, H. Wang, J. Phys. Chem. Solids 69 (2008) 1657-1664.

- [88] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouqueról, T. Siemieniowska, *Pure Appl. Chem.* 57 (1985) 603-619.
- [89] X. Chen, C. Burda, *J. Phys. Chem. B* 108 (2004) 15446-15449.
- [90] Y. Cong, J. Zhang, F. Chen, M. Anpo, *J. Phys. Chem.* 111 (2007) 6976-6982.
- [91] H.U. Lee, S.C. Lee, S. Choi, B. Son, S.M. Lee, H.J. Kim, J. Lee, *Chem. Eng. J.* 228 (2013) 756-764.
- [92] S. Yin, Y. Aita, M. Komatsu, T. Sato, *J. Eur. Ceram. Soc.* 26 (2006) 2735-2742.
- [93] D. Wu, M. Long, W. Cai, C. Chen, Y. Wu, *J. Alloys Compd.* 502 (2010) 289-294.
- [94] J.A. Rengifo-Herrera, K. Pierzchała, A. Sienkiewicz, L. Forró, J. Kiwi, C. Pulgarin, *Appl. Catal. B: Environ.* 88 (2009) 398-406.
- [95] J.A. Rengifo-Herrera, J. Kiwi, C. Pulgarin, *J. Photochem. Photobiol. A* 205 (2009) 109-115.
- [96] J.A. Rengifo-Herrera, E. Mielczarski, J. Mielczarski, N.C. Castillo, J. Kiwi, C. Pulgarin, *Appl. Catal. B: Environ.* 84 (2008) 448-456.

7. Visible-light-driven photocatalytic properties of N-modified titania nanotubes toward air purification

In the present chapter, the modification of titanate nanotubes (TiNT) with nitrogen (NTiNT) was accomplished through impregnation method. Titanate nanotubes were synthesized via hydrothermal treatment of titania powders in NaOH solution at 130 °C for 48 h. The obtained samples were characterized by UV–Vis absorption spectroscopy, BET surface area, XRD, TEM, XPS, and TG analysis. Structure, morphology, composition, and visible light absorption property of nitrogen-modified TiO₂ nanotubes are found depend on the nitrogen content and not so on the calcination temperature for the range used in this work. The photocatalytic activity of these nanotubes was investigated for the degradation of methylethylketone (MEK) and hydrogen sulfide (H₂S) under ultraviolet and solar light radiation. MEK is very resistant to photocatalytic degradation with the prepared materials. However, the results show that modification of the titanate nanotubes with nitrogen in a proportion of 1 to 1 (TiNT to urea weight ratio) and calcination at 400 °C lead to materials with high photocatalytic activity under ultraviolet radiation and moderate photocatalytic activity under solar radiation for degradation of H₂S.

7.1. Introduction

Since the work published in 1972 by Fujishima and Honda [1], heterogeneous photocatalytic oxidation (PCO) processes have become a research topic of growing interest, mostly in the treatment of indoor air contaminated with volatile organic compounds (VOCs) and microorganisms [2, 3], water purification and disinfection, sensing, solar cells antibacterial protection, among others [4-7].

The most widely used catalyst in PCO is titanium dioxide (TiO_2) because it is inexpensive, resistant to photocorrosion, has high oxidative power and relatively low toxicity [8, 9]. Despite the enormous potential of TiO_2 as semiconductor photocatalyst, there are some well-known drawbacks that have to be taken into account. For instance, its wide band gap (~ 3.2 eV) requires ultraviolet (UV) radiation, and consequently the need of UV lamps significantly increases the process operation cost [10]. For this reason, the use of sunlight is particularly more interesting for real case applications. However, only a small fraction of solar energy is useful in the TiO_2 photocatalytic reaction (*i.e.*, only 4% corresponds to UV). Another important disadvantage of titania is the reduced surface area and mass transfer limitation [11, 12]. In order to overcome these obstacles, different ways to prepare titanate nanostructures have been investigated, aiming the intensification of the photocatalytic process under solar light [13-15].

Nanotubular materials have been considered important for photocatalytic applications, owing to their special electronic and mechanical properties. Their high photocatalytic activity, surface area and high pore volume [16, 17], as well as a wall thickness smaller than the minority charge carrier mean pathway (holes), allow highly efficient electron-hole charge separation and reduced recombination rate [18, 19]. However, as commonly observed for TiO_2 nanoparticles, TiO_2 nanotubes can only be excited under UV radiation [20]. In order to lower the threshold energy for photoexcitation, several authors have developed nitrogen-modified titanium dioxide nanotubes which showed a relevant catalytic activity in various reactions performed under visible light [21-24], of particular interest for solar applications.

In this chapter, high aspect ratio titanate nanotubes (TiNT) [18, 25, 26] were synthesized with an alkaline hydrothermal treatment using the benchmark TiO_2 P25 photocatalyst Evonik® and NaOH at 130 °C for 48h. The modification of TiNT with nitrogen was performed impregnating urea followed by thermal treatment. The effect of calcination temperature and nitrogen content on the structure of these nanotubes was assessed. The obtained yellow samples were characterized by UV-Vis absorption spectroscopy, BET specific surface area, transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and thermogravimetric (TG) analysis. The photocatalytic efficiency of the prepared materials was

evaluated for degradation of methylethylketone (MEK) and hydrogen sulfide (H_2S) under both ultraviolet and solar light radiation. These gas-phase photooxidation reactions were performed *on-stream* in a single-pass annular concentric photoreactor.

7.2. Experimental

7.2.1. Hydrothermal synthesis of titanate nanotubes (TiNT)

Titanate nanotubes (TiNT) were synthesized by hydrothermal treatment of 3.0 g of TiO_2 powder (P25, benchmark TiO_2 photocatalyst from Evonik®) in 180 cm^3 of 10 M NaOH solution in a Teflon autoclave, orbitally stirred for 1 h, and further digested at 130 °C for 48 h [18, 25-27]. After the hydrothermal treatment, the obtained white powder was rinsed with distilled water, filtered under vacuum and further washed with HCl. The material was once again rinsed with distilled water and filtrated under reduced pressure until neutral pH. Then, it was dried overnight at 50 °C.

7.2.2. Nitrogen-modified TiO_2 nanotubes (NTiNT)

TiNT were modified with nitrogen by mixing TiNT and urea, in ethanol, with 1:1, 1:2, 1:3, and 1:4 weight ratios, under stirring until full evaporation, and further calcination at 380 or 400 °C in flowing air. The samples were labelled as $\text{N}_x\text{TiNT-y}$, where x refers to the urea proportion with respect to TiNT (*i.e.*, 1, 2, 3 or 4) and y corresponds to the calcination temperature (*i.e.*, 380 or 400 °C). Eight nitrogen-modified TiNT samples were synthesized and stored for further characterization.

7.2.3. Characterization of N-modified TiO_2 nanotubes

Surface area and porosimetry measurements were carried out on an accelerated surface area and porosimetry system (ASAP2010, Micromeritics Instrument Corporation), using nitrogen as adsorbent at liquid N_2 temperature. Before N_2 adsorption, the material was degassed overnight at 150 °C for removing impurities and moisture from the surface. The specific surface areas were calculated from N_2 adsorption isotherms using the Brunauer-Emmett-Teller (BET) method [28]; the micropore surface areas were derived using the t -plot method [29]; finally, the pore size distribution of each sample was obtained using the Barrett-Joyner-Halenda (B.J.H.) method [30]. The UV-Vis absorption spectra of the materials were recorded on a Cary 100 Scan UV/Vis

spectrophotometer (Varian, Inc.) equipped with a DRA-CA-301 diffuse reflectance cell (Labsphere, Inc.). Barium sulphate (BaSO_4) was used as reference. X-ray diffraction (XRD) analysis was performed using a D8 Advance Bruker diffractometer, with a Cu K α radiation source in a $\theta/2\theta$ mode, with a duration scan of 0.5 s and a small step scan (0.04° 2θ). Also, thermogravimetric (TG) analysis was carried out on an IR-analyser (Q5000, TA Instruments). Each sample was placed in a platinum crucible heated from room temperature to 900 °C with a heating rate of 10 °C min⁻¹, using a 20/80 vol.% O₂/N₂ mixture at a flow rate of 25 cm³ min⁻¹ (measured at 298 K and 1 atm).

X-ray photoelectron spectroscopy (XPS) surface characterization was performed on a Multilab 2000 spectrometer (Thermo Fisher Scientific) equipped with Al K α anode ($h\nu = 1486.6$ eV). Peak deconvolution was made with Advantage program (Thermo Electron Company). The subtraction of the energy shift due to electrostatic charging was determined using the carbon C1s band at 284.6 eV as reference. Doniach-Sunjić shape [31] and Shirley backgrounds subtraction [32] were assumed to obtain the C1s peak areas from the raw data. Argon-ion bombardment procedure was also performed in order to clean the N_xTiNT-y samples surfaces. Samples morphology was also observed with a transmission electron microscope (TEM 002B, TOPCON Corporation) under an accelerating voltage of 200 kV and with a point-to-point resolution of 0.17 nm. Each sample was sonically dispersed in an ethanol solution; then, a drop of the final solution was deposited onto a copper grid covered by a holey carbon membrane for observation.

7.2.4. Gas-phase photocatalytic experiments

The lab-scale facility employed in gas-phase photocatalytic experiments is schematically represented in Figure 7.1. These experiments were carried out in a 265 mm length single-pass annular Pyrex reactor made of two coaxial tubes ($d_{\text{in,e}} = 22$ mm, $d_{\text{ot,i}} = 29$ mm where $d_{\text{in,e}}$ and $d_{\text{ot,i}}$ are the external diameter of the inner tube and the internal diameter of the outer tube, respectively) as represented in Figure 7.1. The reactant mixture flows between the internal (quartz) and the external (Pyrex) concentric tubes, far-off from 3.5 mm. The light source was provided by commercial 8 W UVA (45.3 W m^{-2}) blacklight lamp (spectral peak centred at 365 nm) or, alternatively, an 8 W daylight lamp (42.5 W m^{-2} of visible light and of 0.7 W m^{-2} of UVA), placed inside the inner tube of the reactor. For experiments with MEK, 400 mg of photocatalytic material (N₁TiNT-380 sample) – corresponding to a TiO₂ surface density of 1.67 mg cm^{-2} – were evenly coated on the inner wall of the external reactor glass tube by evaporating a catalyst-suspended aqueous solution while continuously spinning the tube. The same procedure was used for degradation experiments of H₂S, but in this case only 50 mg of

catalyst ($\text{N}_1\text{TiNT-400}$ sample) – corresponding to a TiO_2 surface density of 0.21 mg cm^{-2} – were used to coat the inner wall of the external reactor glass tube.

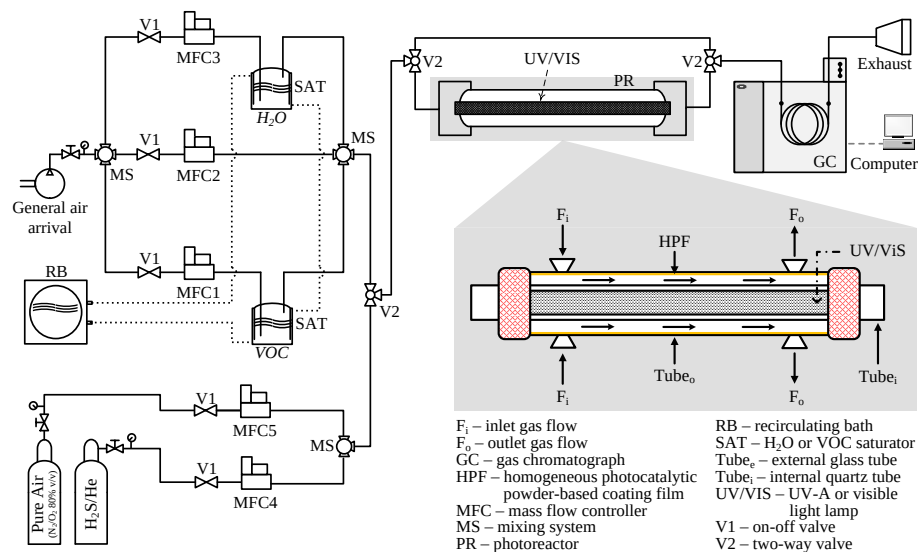


Figure 7.1. Lab-scale facility employed in MEK or H_2S degradation experiments comprising a photocatalytic annular concentric reactor

As represented in Figure 7.1, for gas-phase photooxidation experiments of MEK, the incoming air flow is separated into three ways, each one controlled by different mass flow controllers (MFCs). Air is continuously bubbling through two saturators, one containing MEK and other containing de-ionized water. The final flow of air containing MEK and water vapour (500 ppm of MEK and 50 % of relative humidity, measured at 298 K and 1 atm) continuously fed the reactor with a total flow rate of $300 \text{ cm}^3 \text{ min}^{-1}$ (measured at 298 K and 1 atm). The feed and exit streams of the photoreactor were analysed by thermal conductivity detectors (TCD) installed in a gas microchromatography (micro CG M200H, Agilent Technologies, Inc.), able to quantify organics, H_2O and CO_2 . For gas-phase photooxidation experiments of H_2S , a reactant stream (15 ppm of H_2S content) was generated by mixing a pure air stream (10 vol.%) with another stream of H_2S balanced in He, separately controlled by two MFCs; this final stream fed the photoreactor with a continuous total flow of $500 \text{ cm}^3 \text{ min}^{-1}$ (measured at 298 K and 1 atm). H_2S and SO_2 were analysed *on-line* by a pulsed flame photometric detector (PFPD) within in a gas chromatograph (GC CP3800, Varian, Inc.) equipped with a CP-Sil 5 CB fused silica capillary column for quantification of all sulfide products.

Before each photocatalytic reaction, the catalyst was exposed to the polluted air streams in the absence of radiation until reaching adsorption equilibrium (after which the illumination is switched on).

7.3. Results and discussion

7.3.1. Material characterization

BET surface areas, S_{BET} , of the eight synthesized $N_x\text{TiNT}$ samples are shown in Figure 7.2a. Results indicate that the specific surface area decreases as the N content increases from $314 \text{ m}^2 \text{ g}^{-1}$ to $94 \text{ m}^2 \text{ g}^{-1}$ for 400°C and from $314 \text{ m}^2 \text{ g}^{-1}$ to $50 \text{ m}^2 \text{ g}^{-1}$ for 380°C . As the nitrogen content increases, more nanotube surface can be occupied until a monolayer of nitrogen is formed at the whole surface, consequently reducing the accessibility of the gas during the analysis [33]. Nitrogen adsorption-desorption isotherms of samples prepared at both temperatures with the lowest and highest TiNT to urea weight ratios (namely $N_1\text{TiNT-380}$, $N_4\text{TiNT-380}$, $N_1\text{TiNT-400}$, and $N_4\text{TiNT-400}$) are shown in Figure 7.2b. All samples exhibit typical IUPAC [34] type IV pattern and very narrow hysteresis loops at relative pressures (mesoporous solid with pore sizes between 2 and 50 nm), which is related to capillary condensation throughout filling-emptying of mesopores. From the desorption curves presented in Figure 7.2b, the pore-size distribution plots were calculated by the Barret-Joyner-Halenda formula (Figure 7.2c). For all samples, two peaks were obtained: one with an median pore diameter of 3.6 nm and a second peak at ~ 13 nm, corresponding to the nanotubes inner diameter and to the voids between nanotubes [35], respectively. However, for the samples calcined at 400°C , a decrease in the pore volume was evident which may correspond to a collapse of the nanotube structure as it was already reported by Geng *et al.* [36].

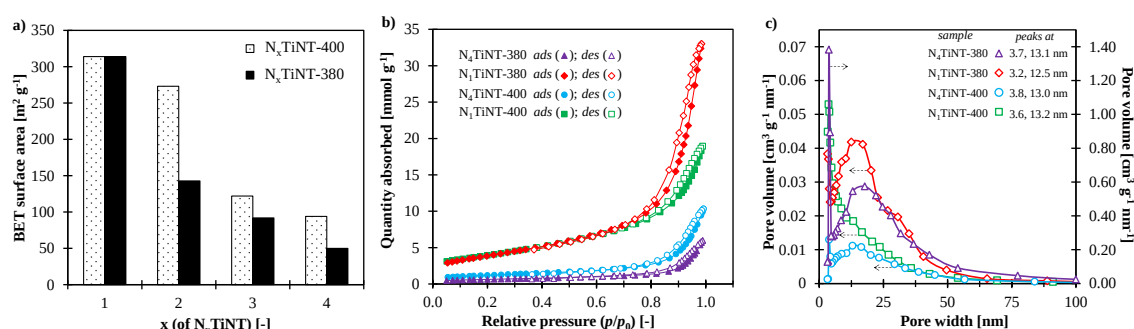


Figure 7.2. BET surface area (S_{BET}) calculated by Brunauer-Emmet-Teller (BJH) formula (a), N_2 adsorption-desorption isotherms (b), and median pore diameter ($d_{p, \text{BJH}}$) calculated by Barret-Joyner-Halenda (BJH) formula (c) of $N_1\text{TiNT}$ to $N_4\text{TiNT}$ samples calcined at 380 and 400°C .

According to several authors [37-39], doping TiO_2 with non-metal species is usually followed by changes in light absorption properties. Figure 7.3 shows the UV/Vis diffuse reflectance spectra of TiO_2 , TiNT, and different $N_x\text{TiNT}$ samples. TiO_2 P25 and TiNT have negligible adsorption in the visible range ($\lambda > 400 \text{ nm}$) and the absorption edge red shift to the visible region observed for $N_x\text{TiNT-y}$ samples is related to the presence of nitrogen species. This

phenomenon has been attributed to the substitution on the lattice of oxygen by nitrogen during the TiO_2 nitridation, narrowing the band gap by mixing the $\text{N}2\text{p}$ and the $\text{O}2\text{p}$ states [40, 41], as well as to the presence of an isolated narrow band above the valence band [40, 42]. It was also observed that increasing the amount of dopant (from 1:1 to 1:4) leads to a higher absorption in visible range, regardless the calcination temperature used, which is consistent with the intensification of the yellow colour observed from N_1TiNT to N_4TiNT observed (data not shown).

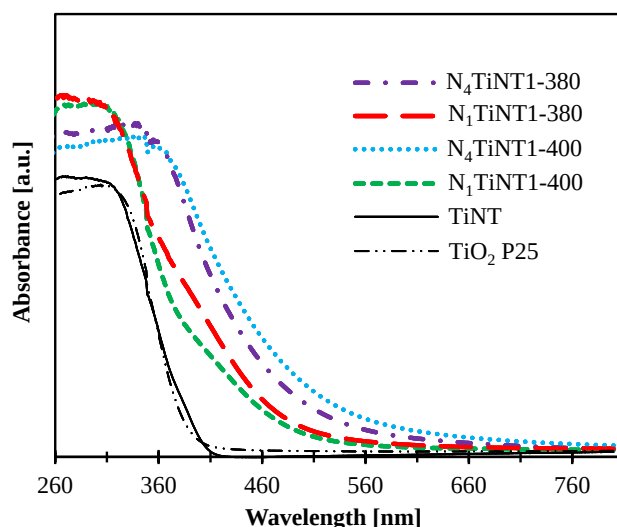


Figure 7.3. UV-Vis absorption spectra of N_4TiNT and N_1TiNT calcined at 380 °C and 400 °C, TiNT and bare TiO_2 P25 without thermal treatment.

XRD was carried out to the samples before (TiNT) and after (N_4TiNT -380 and N_4TiNT -400) the thermal treatment and nitrogen modification (data not shown). The XRD pattern of TiNT suggests layered protonic titanate typically assigned as $\text{H}_2\text{Ti}_3\text{O}_7$ phase [43-45]. After thermal treatment, peaks of TiO_2 anatase form are observed by XRD, in particular for the sample treated at the highest temperature (400 °C), indicating that anatase is formed from $\text{H}_2\text{Ti}_3\text{O}_7$ phase. No nitrogen related phase was identified suggesting that the nitrogen elements were moved into interstitial or substitutional sites of the TiO_2 lattice [46].

Thermogravimetric (TG) analysis was performed for TiNT , urea and N_4TiNT samples without calcination. Figure 7.4 indicates that raw TiO_2 nanotubes have a slight weight loss of 13 % at low temperature due to molecularly adsorbed water loss and dehydroxylation surface. Thermal degradation of urea (nitrogen source) results in a sharp N_4TiNT weight loss, starting at near 120 °C until 350 °C (see Figure 7.4).

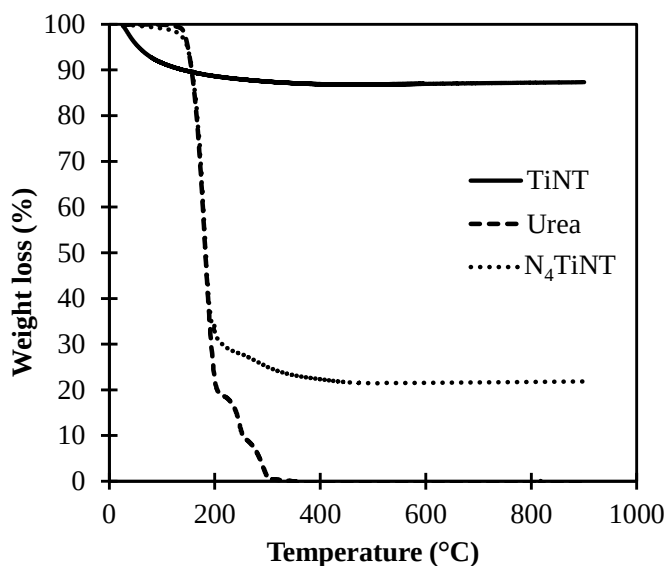


Figure 7.4. TG curves of TiNT, urea, and N₄TiNT samples without thermal treatment.

N1s region XPS of different N_xTiNT-y samples (N₁TiNT-380, N₃TiNT-380, N₁TiNT-400, N₂TiNT-400, and N₃TiNT-400) are reported in Figure 7.5a. A broad band from 396 to 403 eV which is typical of N-modified TiO₂ [47-49] can be observed. Two peaks were obtained by deconvolution at 398 - 399 eV (peak 1) and 400 - 401 eV (peak 2). The peaks obtained at these binding energies have been assigned by several authors [42, 49, 50] to the oxidized Ti-N formation, leading to as Ti-O-N and/or Ti-N-O linkages. It has also been reported the presence of another peak at 396 - 397 eV attributed to nitrogen replacing the oxygen in the crystal lattice of TiO₂ [42, 49-52] resulting in Ti-N-Ti-N or Ti-N-Ti-O linkages. In this study no peak at 396 eV was detected. Figure 7.5b reports the N/Ti and O/Ti ratios during argon ion bombardment for the same samples. Regardless calcination temperature, both O/Ti and N/Ti ratio decrease from the highest to the lowest nitrogen content sample. Most probably, the decrease of the O/Ti ratio is related to a better incorporation of the nitrogen anion in the TiO₂ structure, replacing each oxygen atom; the N/Ti decrease occurs due an obvious reduction in nitrogen atoms amount added to the catalyst during its synthesis. Regarding N₃TiNT samples calcined at 380 and 400 °C, it can be observed a drastic reduction of the N/Ti area ratio after starting the Ar⁺ bombardment, indicating that nitrogen is concentrated at the catalyst surface; however, a similar behaviour was not observable for the other samples, suggesting that nitrogen was not only present at catalyst surface but also incorporated into modified structure sub-layers. In addition, O/Ti reduction during the Ar⁺ bombardment may be justified with the preferential sputtering of oxygen under the bombardment, leading to formation of a high number of oxygen vacancies on the catalyst surface [53].

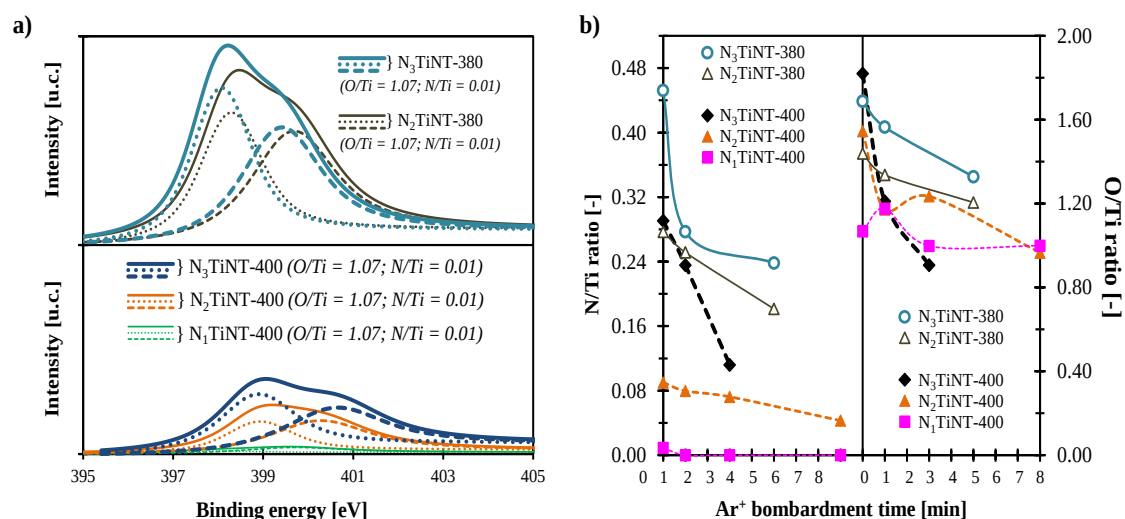


Figure 7.5. N1s X-ray photoelectron spectral details (a) and N/Ti and O/Ti area ratios during argon ion bombardment (b) of N₂TiNT-380, N₃TiNT-380, N₁TiNT-400, N₂TiNT-400, and N₃TiNT-400 samples.

Finally, Figure 7.6 shows TEM images of N₄TiNT-380 and N₄TiNT-400 samples, where nanotubes appear in both samples; however, they are less evident in micrographs of the sample calcined at the higher temperature which may be due to the fact that TiO₂ is no longer a nanotubular structure. These results correlates well with the results obtained for nitrogen adsorption-desorption isotherms (N₄TiNT-400). Concerning N₄TiNT-380 sample, a tubular morphology with open ends between 50 – 100 nm long and *ca.* 3 - 5 and 10 – 15 nm of inner and outer diameter, respectively, can be observed.

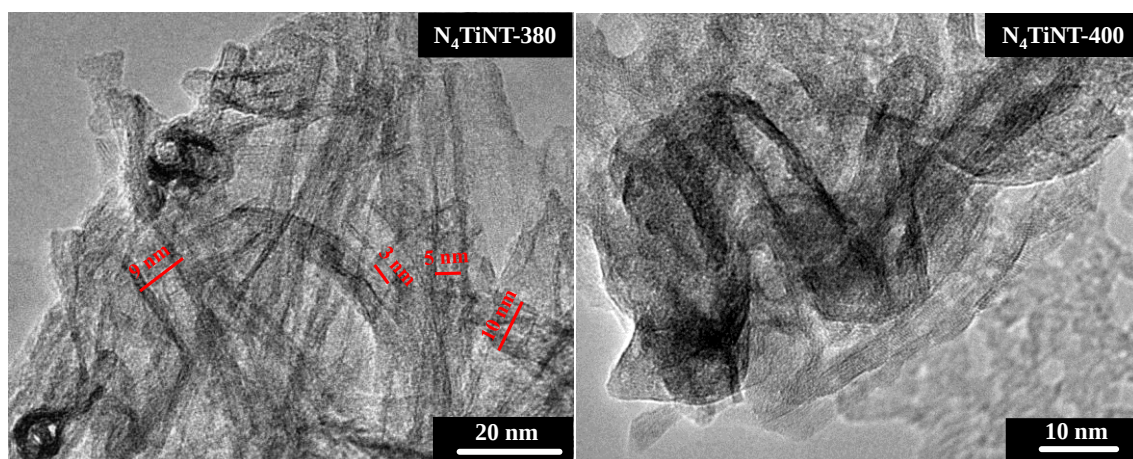


Figure 7.6. TEM images of N₄TiNT-380 (left side) and N₄TiNT-400 (right side).

7.3.2. Photocatalytic tests

Prior to the photocatalytic tests, a blank test consisting in an experiment without photocatalyst was performed, showing no measurable MEK or H₂S concentration decrease (data

not shown).

The photocatalytic activity of N₁TiNT-380 sample was evaluated under two different radiation sources (UVA and solar light lamps) using methylethylketone (MEK) as model pollutant (Figure 7.7a). For both radiation sources, a maximum of MEK degradation was observed between 10 – 20 minutes (ca. 30 % under solar radiation and ca. 45 % under UVA radiation) followed by a strong decrease of the MEK conversion until steady-state is reached. After 60 minutes (at steady-state), conversion was negligible under solar radiation and ~10 % of MEK degradation was attained under UVA radiation. Moreover, no conversion into CO₂ was observed allowing the assumption that intermediates are formed and they can even remain at the catalyst surface. The last hypothesis may also leads to catalyst deactivation, as already reported in literature for photocatalytic gas-phase studies. For instance, Piera *et al.* [54] reported TiO₂ P25 deactivation after 40 h for the photocatalytic degradation of ethanol. Alberici *et al.* [55] showed TiO₂ deactivation when using nitrogen-containing pollutants. More recently, in a study conducted by Yamin *et al.* [56] deactivation of WO₃-modified TiO₂ nanotubes was observed in experiments performed with MEK under both UVA and artificial solar radiation. Grandcolas *et al.* [57] also reported a strong deactivation of WO₃-modified TiO₂ nanotubes when using diethylsulfide under solar radiation.

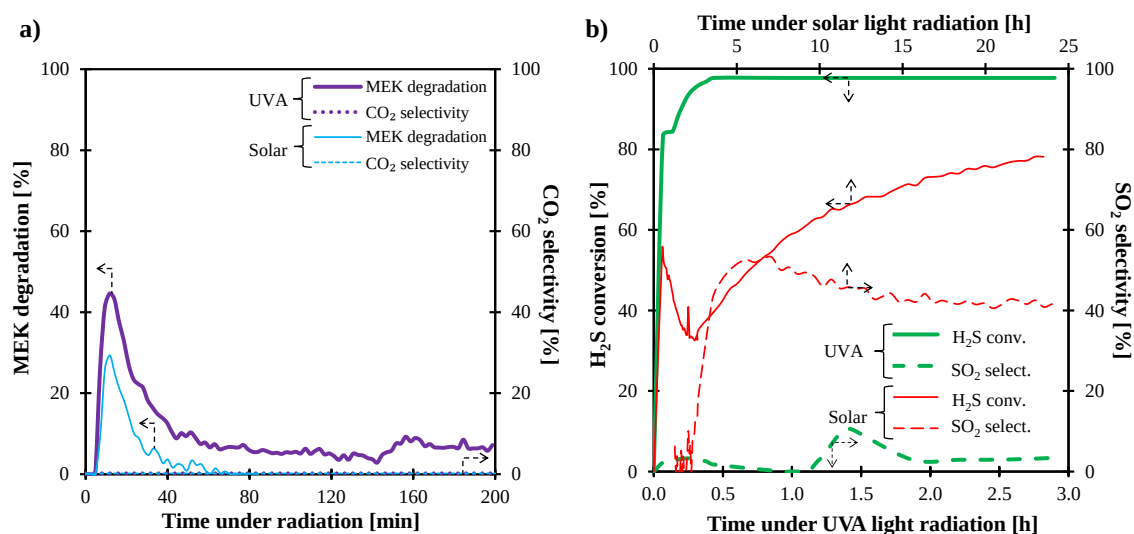


Figure 7.7. Gas-phase photooxidation under UVA or solar radiation of: a) MEK with N₁TiNT-380 photocatalyst ($\rho_A = 1.67 \text{ mg cm}^{-2}$, $C_{\text{MEK, feed}} = 500 \text{ ppm}$, $RH^* = 50 \%$, $Q_{\text{feed}}^* = 300 \text{ cm}^3 \text{ min}^{-1}$); b) H₂S with N₁TiNT-400 ($\rho_A = 0.21 \text{ mg} \cdot \text{cm}^{-2}$, $C_{\text{H}_2\text{S, feed}} = 15 \text{ ppm}$, $RH^* = 0\%$, $Q_{\text{feed}}^* = 500 \text{ cm}^3 \text{ min}^{-1}$). [* - measured at 298 K and 1 atm].

The main pathways for MEK gas-phase photooxidation are the photocatalytic hydroxyl radicals' formation, the mineralization of MEK (CO₂ and H₂O) and its intermediates, and termination reactions. A reaction mechanism of MEK degradation under UV-Vis radiation was

already proposed [58, 59] and it is illustrated in Fig. 8a. The reaction may initiate with the addition of coadsorbed oxygen to MEK resulting in butanone diolate complex formation. This complex is rapidly dissociated into alkyl radicals and carbon dioxide [58, 60]. Combining the radicals produced along the reaction may form intermediates such as ethane (C_2H_6), ethylene (C_2H_4) ethanol (C_2H_6OH) and methanol (CH_3OH) [58-60]. Alternatively, MEK can be oxidized by $\cdot OH$ radical producing aldehydes and carboxylic acids via carbonyl radical formation [58-60]. Regarding the relevance of the mechanism initiated by the attack of $HO\cdot$ radical, it must be pointed out the pioneer work of Xiang *et al.* [61]. They reported for the first time the measurement and comparison of the formation rates of $HO\cdot$ over several semiconductor surfaces during photocatalysis using coumarin ($HO\cdot$ radical scavenger) as a fluorescence probe. In a different research work related with N-doped TiO_2 nanosheets, Xiang *et al.* [62] reported a linear response between fluorescence intensity and radiation time. It was concluded that the amount of $\cdot OH$ radical generated at the catalyst surface is proportional to the radiation time during the photocatalytic process. In addition, it was stated that the rate of photocatalytic formation of $\cdot OH$ radicals over N-doped TiO_2 nanosheets is much higher than for N-doped TiO_2 microcrystals. In the present study, photocatalytic experiments were also performed with samples prepared with higher nitrogen content. It was observed that higher nitrogen content leads to lower specific surface area and to less photocatalytic performance. A lower initial maximum MEK degradation followed by a strong deactivation of the catalyst until no evident photocatalytic activity under UVA or solar light radiation was always observed (data not shown).

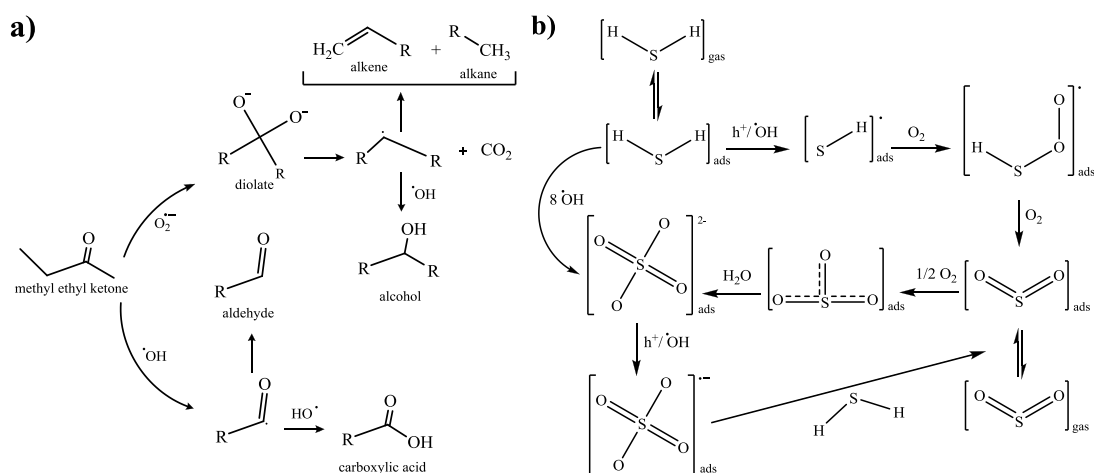


Figure 7.8. Schematic representation of reaction pathways for the photocatalytic degradation under UVA or solar radiation of MEK [58, 59] (a) and H₂S [63-66] (b).

As example, the photocatalytic activity of the N₁TiNT-400 sample for H₂S degradation under UVA and solar light radiation is shown in Figure 7.7b. N₁TiNT-400 is very active for H₂S degradation under UV radiation (about 98 % after reaching steady-state: ~23 min). The SO₂

selectivity remained low, as a result from the wanted oxidation of H_2S into sulfates. When solar light as radiation source was used, 78 % of H_2S was degraded in 24 h. In this case, the generation of SO_2 was much higher than the experiment under UVA radiation, with a SO_2 selectivity of about 40 %, although the main part of H_2S was still converted into sulfates (Figure 7.7b). The enhanced photocatalytic activity observed in both experiments may be attributed to the presence of surface SO_4^{2-} or oxygen vacancy which can also capture photogenerated electrons [67]. Thus, the recombination of photogenerated carriers can be successfully inhibited, leading to the formation of $\text{O}_2^{\bullet-}$ and $\text{HO}^{\bullet}$, increasing, in this way, the quantum efficiency of photocatalytic reaction catalysed by N-modified TiO_2 nanotubes.

One should keep in mind that the reaction mechanism remains till now not fully understood; nevertheless, a possible general reaction mechanism of H_2S degradation under UV/Vis radiation based on the literature [63-66] can be illustrated as shown in Figure 7.8b.

H_2S may be oxidized by $\text{HO}^{\bullet}$ radicals into SO_2 through $\text{HS}^{\bullet}$ radical formation (Canela *et al.* [63, 65], Vorontsov *et al.* [69]). This radical could be generated by the reaction between H_2S and the hole or by reaction with $\text{HO}^{\bullet}$ radical formed by the oxidation of adsorbed water by the holes. Then, $\text{HO}^{\bullet}$ radical undergoes oxidation by oxygen producing SO_2 which forms SO_3 by reacting with oxygen. Due to SO_3 hygroscopic properties, H_2SO_4 can be rapidly produced. An alternative mechanism was previously proposed by Canela *et al.* [63] where H_2S would be oxidized by $\text{HO}^{\bullet}$ radicals into sulfates bypassing the formation of HS radicals. However, this fact implies the presence of eight $\text{HO}^{\bullet}$ radicals for each H_2S molecule making this mechanism unfavourable [63-66].

As a final step of the mechanism, SO_4^{2-} ions can also be oxidized by $\text{HO}^{\bullet}$ radicals or by photogenerated holes producing $\text{SO}_4^{\bullet-}$ radical known as a strong oxidizing agent with a reduction potential of $E^\circ = 2.4 \text{ V}$ [68]. According to Alonso-Tellez *et al.* [64] this mechanism may also explain the long-term photocatalyst reactivation behaviour increasing the H_2S conversion to 100 % as well as SO_2 selectivity to 100 % and at the same time, preventing the photocatalyst deactivation.

7.4. Conclusions

In this work, N-modified TiO_2 nanotubes exhibiting visible-light photocatalytic properties were synthesized at low temperature by the hydrothermal treatment method owning significant absorbance in the visible-light range. Transmission electron microscopy evidenced the

unidimensional nature of the TiO_2 materials; however, their structure seems to be sensible to a high calcination temperature (400 °C). From BET surface area results specific surface area of the nitrogen-modified TiNT increases as TiNT/urea weight ratio becomes closer to one. This fact suggest a commitment between the amount of doping and the treatment temperature in order to define the optimal doping conditions of the catalyst. X-ray photoelectron spectroscopy indicates that the chemical states of the nitrogen in TiO_2 nanotubes may coexist in the form of N-Ti-O and Ti-O-N. Although for higher N/Ti ratio nitrogen seems to be concentrated at surface being more easily sputtered through Ar^+ ion bombardment. MEK was poorly degraded over synthesised materials and its mineralization was not efficient generating intermediates: probably ethane, ethylene, formic acid, and/or formaldehyde. These formed compounds remained in the surface of the photocatalyst leading to its drastic deactivation. Nevertheless, it was found that nitrogen-modified TiNT material is an active photocatalyst for H_2S degradation under UV radiation. A moderate photocatalytic activity was also observed under solar light. In both cases, SO_2 was generated (with low concentration under UV radiation) and should be kept as low as possible since it still is a hazardous gas.

7.5. References

- [1] A. Fujishima, K. Honda, *Nature* 238 (1972) 37-38.
- [2] J. Mo, Y. Zhang, Q. Xu, J.J. Lamson, R. Zhao, *Atmos. Environ.* 43 (2009) 2229-2246.
- [3] Y. Paz, *Appl. Catal. B: Environ.* 99 (2010) 448-460.
- [4] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69-96.
- [5] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, *J. Chem. Technol. Biotechnol.* 77 (2002) 102-116.
- [6] D. Bahnemann, *Sol. Energy* 77 (2004) 445-459.
- [7] J.-M. Herrmann, *Top. Catal.* 34 (2005) 49-65.
- [8] C.M. Sayes, R. Wahi, P.A. Kurian, Y. Liu, J.L. West, K.D. Ausman, D.B. Warheit, V.L. Colvin, *Toxicol. Sci.* 92 (2006) 174-185.
- [9] R. Zhang, Y. Bai, B. Zhang, L. Chen, B. Yan, *J. Hazard. Mater.* 211-212 (2012) 404-413.
- [10] W.A. Jacoby, D. Blake, R.D. Noble, C.A. Koval, *J. Catal.* 157 (1995) 87-96.
- [11] X.Z. Li, F.B. Li, *J. Appl. Electrochem.* 32 (2002) 203-210.
- [12] H. Hidaka, T. Shimura, K. Ajisaka, S. Horikoshi, J. Zhao, N. Serpone, *J. Photochem. Photobiol. A* 109 (1997) 165-170.
- [13] A. Kodama, S. Bauer, A. Komatsu, H. Asoh, S. Ono, P. Schmuki, *Acta Biomater.* 5 (2009) 2322-2330.
- [14] Z. Jing, D. Guo, W. Wang, S. Zhang, W. Qi, B. Ling, *Solid State Sci.* 13 (2011) 1797-1803.
- [15] L.L. Costa, A.G.S. Prado, *J. Photochem. Photobiol. A* 201 (2009) 45-49.
- [16] J. Yu, H. Yu, B. Cheng, M. Zhou, X. Zhao, *J. Mol. Catal. A-Chem.* 253 (2006) 112-118.
- [17] L. Dong, Y. Ma, Y. Wang, Y. Tian, G. Ye, X. Jia, G. Cao, *Mater. Lett.* 63 (2009) 1598-1600.
- [18] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihar, *Adv. Mater.* 11 (1999) 1307-1311.
- [19] B.D. Yao, Y.F. Chan, X.Y. Zhang, W.F. Zhang, Z.Y. Yang, N. Wang, *Appl. Phys. Lett.* 82 (2003) 281-283.
- [20] D.V. Bavykin, S.N. Gordeev, A.V. Moskalenko, A.A. Lapkin, F.C. Walsh, *J. Phys. Chem. B* 109 (2005) 8565-8569.
- [21] L.H. Huang, C. Sun, Y.L. Liu, *Appl. Surf. Sci.* 253 (2007) 7029-7035.
- [22] H. Tokudome, M. Miyauchi, *Chem. Lett.* 33 (2004) 1108-1109.
- [23] A.G. Kontos, A. Katsanaki, T. Maggos, V. Likodimos, A. Ghicov, D. Kim, J. Kunze, C. Vasilakos, P. Schmuki, P. Falaras, *Chem. Phys. Lett.* 490 (2010) 58-62.
- [24] P. Zhou, J. Yu, Y. Wang, *Appl. Catal. B: Environ.* 142-143 (2013) 45-53.
- [25] J. Yu, Q. Xiang, M. Zhou, *Appl. Catal. B: Environ.* 90 (2009) 595-602.
- [26] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Langmuir* 14 (1998) 3160-3163.
- [27] Z.R. Tian, J.A. Voigt, J. Liu, B. McKenzie, H. Xu, *J. Am. Chem. Soc.* 125 (2003) 12384-12385.
- [28] S. Brunauer, P.H. Emmett, E. Teller, *J. Am. Chem. Soc.* 60 (1938) 309-319.
- [29] R.S. Mikhail, S. Brunauer, E.E. Bodor, *J. Colloid Interface Sci.* 26 (1968) 45-53.
- [30] E.P. Barrett, L.G. Joyner, P.P. Halenda, *J. Am. Chem. Soc.* 73 (1951) 373-380.
- [31] S. Doniach, M. Sunjic, *J. Phys. C Solid State* 3 (1970) 285.

- [32] J.E. Castle, A.M. Salvi, *J. Vac. Sci. Technol. A* 19 (2001) 1170-1175.
- [33] Y.-C. Xie, Y.-Q. Tang, in: H.P. D.D. Eley, B.W. Paul (Eds.), *Adv. Cat.*, Academic Press, 1990, pp. 1-43.
- [34] J. Wilks, in: J. Wilhelm (Ed.), *Physical Chemistry: An Advanced Treatise*, Academic Press, 1971, pp. 437-488.
- [35] J. Yu, H. Yu, B. Cheng, X. Zhao, Q. Zhang, *J. Photochem. Photobiol. A* 182 (2006) 121-127.
- [36] J. Geng, D. Yang, J. Zhu, D. Chen, Z. Jiang, *Mater. Res. Bull.* 44 (2009) 146-150.
- [37] J. Yu, M. Zhou, B. Cheng, X. Zhao, *J. Mol. Catal. A-Chem.* 246 (2006) 176-184.
- [38] M. Zhou, J. Yu, *J. Hazard. Mater.* 152 (2008) 1229-1236.
- [39] Q. Xiang, J. Yu, M. Jaroniec, *Phys. Chem. Chem. Phys.* 13 (2011) 4853-4861.
- [40] H. Irie, Y. Watanabe, K. Hashimoto, *J. Phys. Chem. B* 107 (2003) 5483-5486.
- [41] S. Sato, *Chem. Phys. Lett.* 123 (1986) 126-128.
- [42] M. Sathish, B. Viswanathan, R.P. Viswanath, C.S. Gopinath, *Chem. Mater.* 17 (2005) 6349-6353.
- [43] S. Zhang, Q. Chen, L.M. Peng, *Phys. Rev. B* 71 (2005) 014104.
- [44] G.H. Du, Q. Chen, R.C. Che, Z.Y. Yuan, L.-M. Peng, *Appl. Phys. Lett.* 79 (2001) 3702-3704.
- [45] M.H. Razali, A.-F. Mohd Noor, A.R. Mohamed, S. Sreekantan, *Journal of Nanomaterials* 2012 (2012) 10.
- [46] Z. Wang, W. Cai, X. Hong, X. Zhao, F. Xu, C. Cai, *Appl. Catal. B: Environ.* 57 (2005) 223-231.
- [47] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* 293 (2001) 269-271.
- [48] O. Diwald, T.L. Thompson, T. Zubkov, S.D. Walck, J.T. Yates, *J. Phys. Chem. B* 108 (2004) 6004-6008.
- [49] S. Sakthivel, M. Janczarek, H. Kisch, *J. Phys. Chem. B* 108 (2004) 19384-19387.
- [50] X. Chen, C. Burda, *J. Phys. Chem. B* 108 (2004) 15446-15449.
- [51] S. Yin, K. Ihara, M. Komatsu, Q. Zhang, F. Saito, T. Kyotani, T. Sato, *Solid State Commun.* 137 (2006) 132-137.
- [52] Y. Cong, J. Zhang, F. Chen, M. Anpo, *J. Phys. Chem.* 111 (2007) 6976-6982.
- [53] S. Pétigny, H. Mostéfa-Sba, B. Domenichini, E. Lesniewska, A. Steinbrunn, S. Bourgeois, *Surf. Sci.* 410 (1998) 250-257.
- [54] E. Piera, J.A. Ayllón, X. Doménech, J. Peral, *Catal. Today* 76 (2002) 259-270.
- [55] R.M. Alberici, M.C. Canela, M.N. Eberlin, W.F. Jardim, *Appl. Catal. B: Environ.* 30 (2001) 389-397.
- [56] Y. Yamin, N. Keller, V. Keller, *J. Photochem. Photobiol. A* 245 (2012) 43-57.
- [57] M. Grandcolas, T. Cottineau, A. Louvet, N. Keller, V. Keller, *Appl. Catal. B: Environ.* 138-139 (2013) 128-140.
- [58] M.A. Henderson, *Surf. Sci.* 602 (2008) 3188-3193.
- [59] G. Glowa, P. Driver, J.C. Wren, *Radiat. Phys. Chem.* 58 (2000) 49-68.
- [60] G. Vincent, A. Queffeuilou, P.M. Marquaire, O. Zahraa, *J. Photochem. Photobiol. A* 191 (2007) 42-50.
- [61] Q. Xiang, J. Yu, P.K. Wong, *J. Colloid Interface Sci.* 357 (2011) 163-167.
- [62] Q. Xiang, J. Yu, W. Wang, M. Jaroniec, *Chem. Commun.* 47 (2011) 6906-6908.

- [63] M.C. Canela, R.M. Alberici, W.F. Jardim, J. Photochem. Photobiol. A 112 (1998) 73-80.
- [64] A. Alonso-Tellez, D. Robert, N. Keller, V. Keller, Appl. Catal. B: Environ. 115–116 (2012) 209-218.
- [65] M.C. Canela, R.M. Alberici, R.C.R. Sofia, M.N. Eberlin, W.F. Jardim, Environ. Sci. Technol. 33 (1999) 2788-2792.
- [66] R. Portela, S. Suárez, S.B. Rasmussen, N. Arconada, Y. Castro, A. Durán, P. Ávila, J.M. Coronado, B. Sánchez, Catal. Today 151 (2010) 64-70.
- [67] H. Li, G. Li, J. Zhu, Y. Wan, J. Mol. Catal. A-Chem. 226 (2005) 93-100.
- [68] B.C. Gau, H. Chen, Y. Zhang, M.L. Gross, Anal. Chem. 82 (2010) 7821-7827.
- [69] A.V. Vorontsov, E.V. Savinov, L. Davydov, P.G. Smirniotis, Appl. Catal. B: Environ. 32 (2001) 11-24.

Part V

*Chapter 8. Evaluation of a solar/UV annular
pilot scale reactor for 24 h
continuous PCO of n-decane*

*Chapter 9. Final remarks and suggestions
for future work*

8. Evaluation of a solar/UV annular pilot scale reactor for 24 h continuous PCO of n-decane

In this chapter, a pilot scale single-pass continuous-flow annular photoreactor ($r = 32.8$ mm) was designed and manufactured based on lab-scale fixed-bed experimental data, modelling simulations, and predictions of PCO of pure-targeted VOCs reported in the previous chapters. The photoreactor features a CPC to capture both direct and diffuse solar radiation and, simultaneously, artificial UVA lamps, in order to examine the possibility of working continuously day and night. The PCO of n-decane ($C_{dec, feed} = 10$ ppm, $Q_{feed} = 2$ L min⁻¹, $\tau = 44$ s) over cellulose acetate monolithic structures coated with different TiO₂-based photocatalytic films ($L_R = 144$ cm) was studied under solar and artificial UVA radiation. Gas-phase n-decane conversions up to 100 %, were attained using P25 or PC500 photocatalytic films under solar irradiances of 15 W_{UV} m⁻² in the morning (sunrise, increasing temperature) and 3 W_{UV} m⁻² in the afternoon (sunset, decreasing temperature). The photocatalytic paint film promoted up to 45 % of n-decane conversion under 48 W_{UV} m⁻² in both periods of the day. The excess of photons reaching the photocatalytic bed favours the direct reaction pathway of CO₂ production. The PCO of n-decane enhanced 29 % resulting in 100 % of conversion using PC500 film instead of P25 film, under artificial UVA radiation while over PCP film no more than 25 % of n-decane was converted. Results indicate that combining both radiation sources, a 24 h continuous PCO process towards the removal of n-decane can be accomplished.

This chapter is based on the research article “Monteiro, R.A.R., Lopes, F.V.S., Rodrigues-Silva, C., Miranda, S.M., Faria, J.L., Ângelo, J., Mendes, A.M., Boaventura, R.A.R., Silva, A.M.T., Vilar, V.J.P., Evaluation of a solar/UV pilot scale annular photoreactor for 24 h continuous air purification”, under preparation.

8.1. Introduction

Photocatalytic oxidation processes (PCO) have been proven to be very promising for the purification of air from trace amounts of volatile organic compounds (VOCs) when compared to conventional techniques (*e.g.*, adsorption or air stripping processes) [1-6]. It provides three significant advantages: low operation temperature, chemical additives-free, and oxidation into innocuous or easily neutralized by-products (usually CO₂, H₂O, and mineral acids) [1-6]. In 1997, the Air Pollution Prevention and Control Division of the National Risk Management Research Laboratory of the U. S. Environmental Protection Agency (EPA) reported the cost effectiveness of PCO as an air cleaner technology [7]. The above-mentioned analysis reported that gas-phase PCO technology is more competitive than granular activated carbon technology at higher VOC concentrations representative of industrial applications. However, it estimated that PCO technology costs significantly more than granular activated carbon technology due to the ultraviolet (UV) light intensity required to degrade VOCs [7]. Two years before, Jacoby *et al.* [8] had already identified the use of artificial illumination as the most expensive component in the operation of a photoreactor. Thus, and since the solar energy is an important resource in many countries, the combination of sunlight and a photocatalyst is a promising option to make PCO technologies for air detoxification systems more economically attractive.

Although there is already a wide range of research studies related to the possibility of using sunlight on the gas-phase degradation of VOCs, almost all are meant for the photodegradation assessment of pure-targeted VOCs in small lab-scale devices [3-5]. Furthermore, the little experimentation performed in pilot plants has up to now been one of the main reasons for the absence of real applications in this field. Nonetheless, from the 1990s, solar photoreactors have been employed on gas-phase photodegradation of chemical air pollutants by National Renewable Energy Laboratory (NREL) [9], Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT) [10-15], Plataforma Solar de Almeria (PSA) [11, 13-15], Institute of Catalysis and Petrochemistry of the Spanish Council for Scientific Research (ICP-CSIC) [15], Chemistry Institute of the University of São Paulo (IQ-USP) [13], Center of Sciences and Technologies of the Darcy Ribeiro State University of Northern of Rio de Janeiro (CCT-UENF) [14, 15], and the University of Hong Kong (HKU) [16].

In 2002, Malato *et al.* [17] reviewed the use of sunlight in PCO of VOCs and detailed the experimental systems necessary for performing solar pilot scale PCO experiments. Within that work, the authors outlined: (i) pilot scale basic components; (ii) fundamental parameters associated to solar photocatalytic reactions; (iii) research carried out at PSA; (iv) brief description of its significance on wastewater treatment technologies [17]. In 2007 Imoberdorf *et al.* [18] have

proposed a design procedure for commercial pilot scale facilities based only on the information obtained in a lab-scale photoreactor used for air remediation. Despite not using solar radiation in their lab- and further pilot scale units, their study with UV continuous multi-annular photocatalytic reactors has shown that it is possible to design large-scale apparatus directly from laboratory experiments once we know: (a) a fairly complete reaction scheme of the chemical process; (b) a comprehensive representation of the effects of the different variables independently of the shape and configuration of the lab-scale photoreactor; (c) how to apply fundamentals of chemical reaction engineering and radiation transport [18]. Lately, Portela *et al.* [14] proposed a novel and versatile annular photoreactor able to operate 24 h a day using both solar and/or artificial radiation and different types of suspended or immobilized photocatalysts. The proposed photocatalytic reactor was employed in the H₂S photocatalytic oxidation and it is composed by: (a) a vertical, south-oriented, borosilicate glass annular reactor; (b) a CPC-type collector; (c) an inner UV lamp [14].

Taking into consideration the above-mentioned research studies as well as the lab-scale fix-bed experimental data, modelling simulations, and predictions of PCO of pure-targeted VOCs reported in the previous chapters, a pilot-scale, single-pass, continuous-flow fixed-bed annular photoreactor was designed and manufactured. This detoxification pilot unit is based on an optimized compound parabolic collector (CPC) to capture both direct and diffuse UV natural solar radiation and, simultaneously, on UVA-lamps, in order to examine the possibility of working continuously day and night. Therefore, it was employed in photooxidation experiments of pure-targeted VOCs over TiO₂-based photocatalytic films coated on cellulose acetate monolithic structures under solar or artificial radiation. Employing the same catalytic bed configuration, TiO₂-based photocatalytic films were dip-coated onto the cellulose acetate supporting substrates using two different titania sources: TiO₂ suspension (P25 and PC500); photocatalytic paint (PCP). Within this chapter, *n*-decane was selected as organic air pollutant model. The main reason for that is the high concentration of this pollutant (up to 0.05 ppm) that have been found in the indoor air of a wastewater treatment plant (WWTP) with closed facilities at different sampling sites and campaigns [19]. Additionally, photochemical and photocatalytic oxidation of *n*-decane was evaluated as a function of the radiation source: sunlight or UVA lamps illumination. The CO₂ production was also monitored and measured during the experiments in order to assess the extension of the *n*-decane conversion into CO₂ and water.

8.2. Experimental

8.2.1. Photocatalytic films preparation

Cellulose acetate monoliths (TIMax CA50-9/S – $L = 8$ cm, $d_{ch}^2 = 0.9$ cm $\times$ 0.9 cm, $e_{w, ch} = 0.1$ mm; Wacotech GmbH & Co. KG.) were used as supporting substrate of photocatalytic films by dip-coating method [20]. The photocatalytic films were prepared with: (a) P25 (Evonik®) suspension; (b) PC500 (Cristal®) suspensions; (c) a modified vinyl paint with PC500 (PCP) [21]. As already described in previous chapters the supporting substrate samples were soaked during 1 h with distilled water containing an anionic detergent (Extran®, Merck S.A.) and subsequently washed exhaustively with deionized water (Milli-Q, 18.2 MΩ cm) before coating; finally, samples were heated up to 323 K to dryness. The materials and chemicals employed on the photocatalytic films, the detailed experimental procedure, as well as the catalyst characterization (film surface morphology, chemical composition, crystallographic phase identification, and crystallite size determination) were reported in the previous chapters of this dissertation. In Table 8.1 are listed the dimensions of the photoreactor and characteristics of the photocatalytic films used in this chapter.

Table 8.1. Photoreactor dimensions and photocatalytic thin-films characteristics employed in the gas-phase PCO of VOCs under solar and UV radiation.

Photoreactor		
Outer tube (Pyrex-glass tube)	L_{ot} [cm]	150
	$d_{ot,e}$ [cm]	7.00
	$d_{ot,i}$ [cm]	6.56
Inner tube (Soda-lime glass tube)	L_{in} [cm]	150
	$d_{in,e}$ [cm]	2.30
	$d_{in,i}$ [cm]	1.94
In-between tubes	V_R [cm ³]	4.3×10^3
Cellulose acetate monolithic substrate, C	L_C [cm]	144
	A_C [m ²]*	1.400 ± 0.002
	m_C [g]*	55.4 ± 0.8
	ρ_C [g cm ⁻³]	1.30
	d_{ch} [cm]	0.9
Photocatalytic films		
P25	m_{P25} [g]	1.404
	$\rho_{A,P25}$ [g m ⁻²]	1.003
PC500	m_{PC500} [g]	0.744
	$\rho_{A,PC500}$ [g m ⁻²]	0.532
PCP	m_{PCP} [g]	5.13
	$\rho_{A,PCP}$ [g m ⁻²]	3.665

* mean values ($n = 18$) and corresponding standard deviation, where n is the number of cellulose acetate pieces used in each photocatalytic film deposition.

8.2.2. Solar/UV pilot-scale experimental unit

A pilot scale prototype was designed and manufactured for the study of air detoxification systems (see Figure 8.1). It is based on an optimized compound parabolic collector (CPC) that uses solar radiation or on ultraviolet light lamps (UVA-Lamps) placed inside the photoreactor to study the possibility of working continuously day and night. This facility contains three main sections: (i) feed generator of humid air streams contaminated with VOCs; (ii) a 1.5 m long continuous-flow annular photoreactor placed at the top of a parabolic reflective surface (named CPC); (iii) integrated analysis system for both *in situ* monitoring and sampling of the photoreactor feed and exit streams. These sections are described in the following general description and schematically represented in Figure 8.1a to 8.1c.

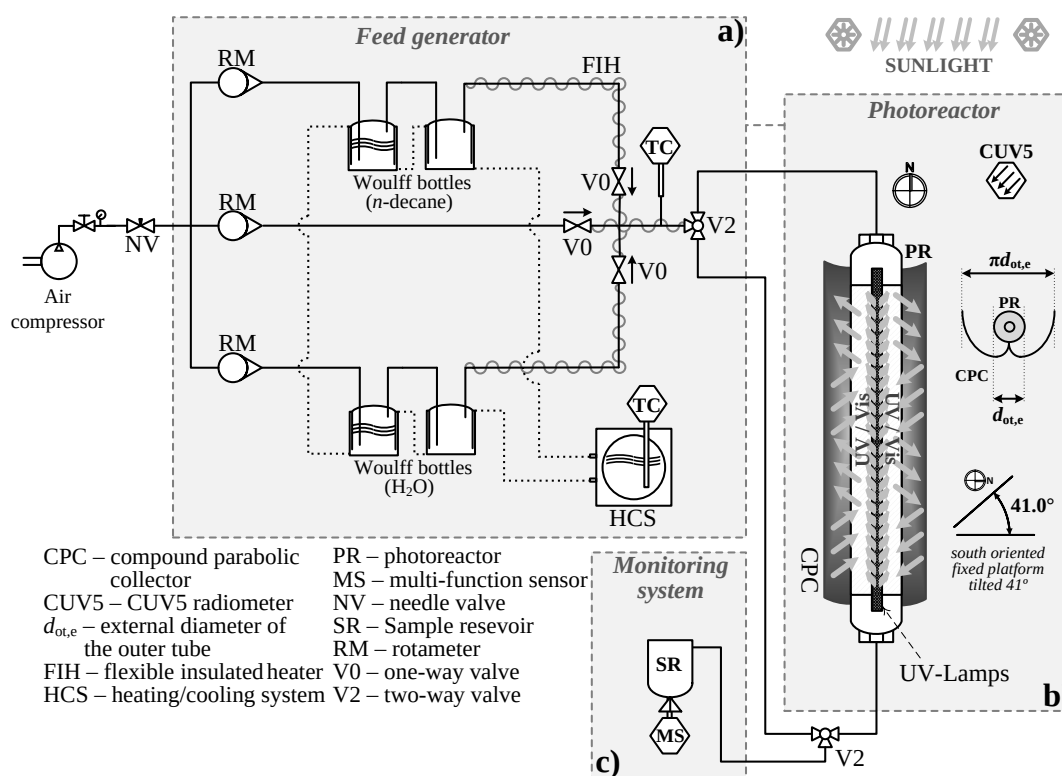


Figure 8.1. Schematic representation of the pilot unit: a) feed generator of air streams containing *n*-decane and water vapour; b) pilot scale continuous-flow annular photoreactor placed at the top of a CPC (at local latitude of 41° facing south); c) monitoring system used for the analysis of the photoreactor feed and exit streams.

8.2.2.1. Feed generation

The experimental set-up (Figure 8.1a) used for generation of humid air streams containing a selected VOC mainly comprises an air compressor (Air Compressor CEVIK PRO 50 VX, 3 HP, Cevik S.A.), rotameters (FL-2010-SS and FL-2010-SS; Omega Engineering Ltd, UK), and Woulff bottles (supplied by Normax, Lda) filled with liquid VOC and H₂O, respectively, and

placed in a temperature controlling system (thermostatic bath GD100 R2, Grant Instruments). The selected VOC and humidity contents were fixed as a result of controlling the flow rate of each air stream, and its temperature and pressure. All 1/4" stainless steel tubing, fittings, connectors, adapters, and valves are Swagelok products (Swagelok, USA). For the generation of VOC-containing humid air streams *n*-decane (dec; $\geq 94\%$, Merck S.A.) without further purification, ultrapure water and deionized water were used.

8.2.2.2. Pilot-scale photoreactor

The 1.5 m long continuous-flow annular photocatalytic reactor (see Figure 8.1b) is composed by an outer Pyrex-glass tube (Duran borosilicate glass 3.3, Schott-Rorhglas GmbH) and, centred in the axial position along the bed, a concentric inner quartz tube (Quarzglas-Rohr, Quarzglasstechnik, GmbH & Co KG); these tubes allow the penetration of solar/UV radiation through their structures. The void between these tubes was packed with photocatalyst-coated cellulose acetate monolithic structures. The photocatalytic bed dimensions and characteristics are shown in Table 8.1.

8.2.2.3. Compound parabolic collector (CPC) and radiation sources

The photoreactor is placed at the top of a CPC of $0.220 \times 1.50 \text{ m}^2$ (0.330 m^2 of static collectors made of stainless steel, showing high reflectivity in the UV range) mounted on a south oriented fixed platform tilted 41° (local latitude). This involute reflective surface around the photoreactor enables almost all the UV radiation (both direct and diffuse) to be collected for processing, without the need for solar tracking [22]; the reflected light is distributed around the photoreactors maximizing the exposure area and making the irradiance on the catalytic bed uniform. The intensity of the incident solar radiation (only the UV fraction of the incident solar light) is measured within a spectral range of 280 – 400 nm with a broadband UV radiometer (CUV 5, Kipp & Zonen B.V.), mounted on the pilot plant at the same angle as the CPC; a handheld display unit (Meteon, Kipp & Zonen B.V.) is used to produce readings in terms of incident irradiance ($\text{W}_{\text{UV}} \text{ m}^{-2}$). Three 8 W UVA ($29 \text{ W}_{\text{UV}} \text{ m}^{-2}$) blacklight lamps (spectral peak centred at 365 nm) are placed inside the inner tube, centred in the axial position along the bed. Therefore, as soon as the sunlight intensity drops below a threshold value (in cloudy days or during the night), UVA-Lamps can illuminate the photocatalytic bed allowing the continuous operation of the pilot scale unit with low power consumption. The intensity of the incident UVA-Lamps radiation was measured with the broadband UV radiometer placed on the outside of the inner tube and in contact with it.

8.2.2.4. Photoreactor feed and exit streams analysis

The photoreactor feed and exit streams are monitored online through an automatic portable VelociCalc® multifunction 9565-P ventilation meter equipped with 986 VOCs probe (TSI® incorporated) (see Figure 8.1c). The TSI probe uses a photoionization detector (PID) to measure total VOCs; it is also used to monitor the temperature, relative humidity and the CO₂ concentration of the feed / exit gas stream of the photoreactor throughout the experimental time.

8.2.3. Photocatalytic experiments

First, the continuous-flow annular photoreactor was assembled with uncoated cellulose acetate samples in order to study the *n*-decane photochemical oxidation under solar or UVA radiation. Then, after packing the reactor with the coated supporting substrates, the performances of the TiO₂-based films toward *n*-decane photocatalytic conversion were compared in similar operational conditions. All experimental conditions are reported in Table 8.2. Prior to the solar photochemical and photocatalytic experiments and in the total absence of radiation (photoreactor initially covered by a blackout filter or the inner UVA lamp turned off), the photoreactor was continuously fed with the polluted air stream overnight, to ensure a constant volatilization of *n*-decane and, consequently, a constant feed composition (operating conditions reported in Table 8.2). Therefore, several samples (one sample after each five minutes) of the exit stream were analysed to confirm a constant feed composition.

The efficiency of the PCO process was expressed in terms of *n*-decane conversion and mineralization yield, calculated as follow:

$$\text{Conversion (\%)} = \left(1 - \frac{C_{\text{dec, exit}}}{C_{\text{dec, feed}}} \right) \times 100 \quad 8.1$$

$$\text{Mineralization (\%)} = \left(\frac{C_{\text{CO}_2, \text{exit}}}{C_{\text{dec, feed}}} \times \frac{1}{10} \right) \times 100 \quad 8.2$$

where $C_{\text{dec, feed}}$ and $C_{\text{dec, exit}}$ are the *n*-decane concentrations on the feed and exit streams, respectively and $C_{\text{CO}_2, \text{exit}}$ is the CO₂ exit stream concentration. All concentrations are expressed in ppm. For the solar PCO experiments, the time evolution of the incident irradiance (measured within 280 – 400 nm) was measured. Relative humidity and temperature of the photoreactor exit stream were also measured for the solar and artificial UVA PCO experiments.

Note that, before any PCO experiment, activation and degassing of the photocatalytic bed was carried out in the absence of radiation and using a water-containing air stream at a total flow

rate of 0.500 L min^{-1} (measured at 1 bar and 298 K).

Solar PCO of *n*-decane experiments were carried out during a full week period. Then, for each photocatalytic film, only artificial UVA radiation was employed to explore the behaviour of the photoreactor without the uncertainty of the solar radiation variability. The UVA PCO of *n*-decane experiments were performed during 8 h.

Table 8.2. Experimental conditions employed in gas-phase PCO of *n*-decane carried under solar or artificial UVA radiation.

Film	Q_{feed}^* [L min ⁻¹] (τ [s])	$C_{\text{dec, feed}}$ [ppm]	RH^* [%]	T_{feed} [°C]	Radiation source	$I^\#$ [W _{UV} m ⁻²]
None	2 (44)	10 ± 1	16.3 – 31.3	21.9 – 33.3	Sunlight	0.0 – 57.6
		11 ± 1	14.0 – 26.4	23.6 – 38.6	UVA	29 ± 5
P25		10 ± 1	12.5 – 34.1	17.5 – 31.0	Sunlight	0.0 – 57.2
		11 ± 1	15.2 – 65.3	26.7 – 32.0	UVA	29 ± 5
PC500		10 ± 1	9.1 – 39.1	12.6 – 40.9	Sunlight	0.0 – 58.9
		11 ± 1	13.2 – 36.5	27.0 – 37.3	UVA	29 ± 5
PCP		10 ± 1	12.4 – 31.7	20.1 – 35.7	Sunlight	0.0 – 64.1
		11 ± 1	16.6 – 58.8	23.4 – 33.3	UVA	29 ± 5
$P = 1 \text{ bar}$						

* measured at 298 K and 1 bar.

measured within 280 – 400 nm.

8.3. Results and discussion

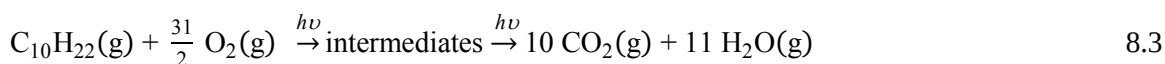
8.3.1. Solar/artificial UVA photolysis of *n*-decane

Control tests (photoreactor packed with uncoated cellulose acetate supporting substrates) were performed in order to establish the effect of the radiation on the conversion and mineralization of *n*-decane. This pollutant in contaminated air streams is able to absorb light over a wide range of wavelengths (absorption is often stronger at shorter wavelengths) [17]. Thus, if a Pyrex-glass outer tube is used as outer tube of the photoreactor, it will absorb most of the shorter wavelengths of the solar radiation (for $\lambda < 285 \text{ nm}$). For this reason, direct photolysis of *n*-decane with sunlight do not yield measurable ionization of *n*-decane (*i.e.* no conversion of *n*-decane is observed). Under artificial UVA radiation, no measurable *n*-decane conversion or mineralization was observed. Although the inner tube is made of quartz UVA radiation (peak centred at $\lambda = 365 \text{ nm}$) is not energetic enough to ionize *n*-decane molecules. Considering the negligible effect of the radiation (solar and artificial UVA) the evolution over time of conversion and mineralization of *n*-decane was not plotted.

8.3.2. Solar/artificial UVA PCO of *n*-decane

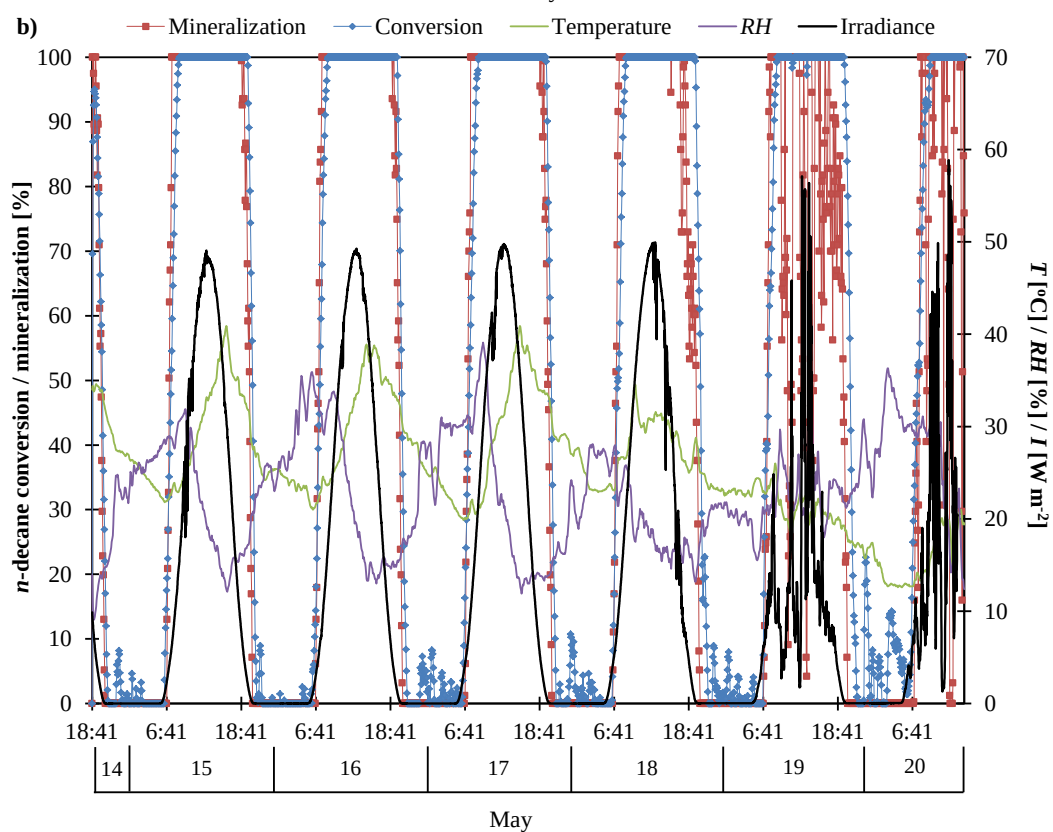
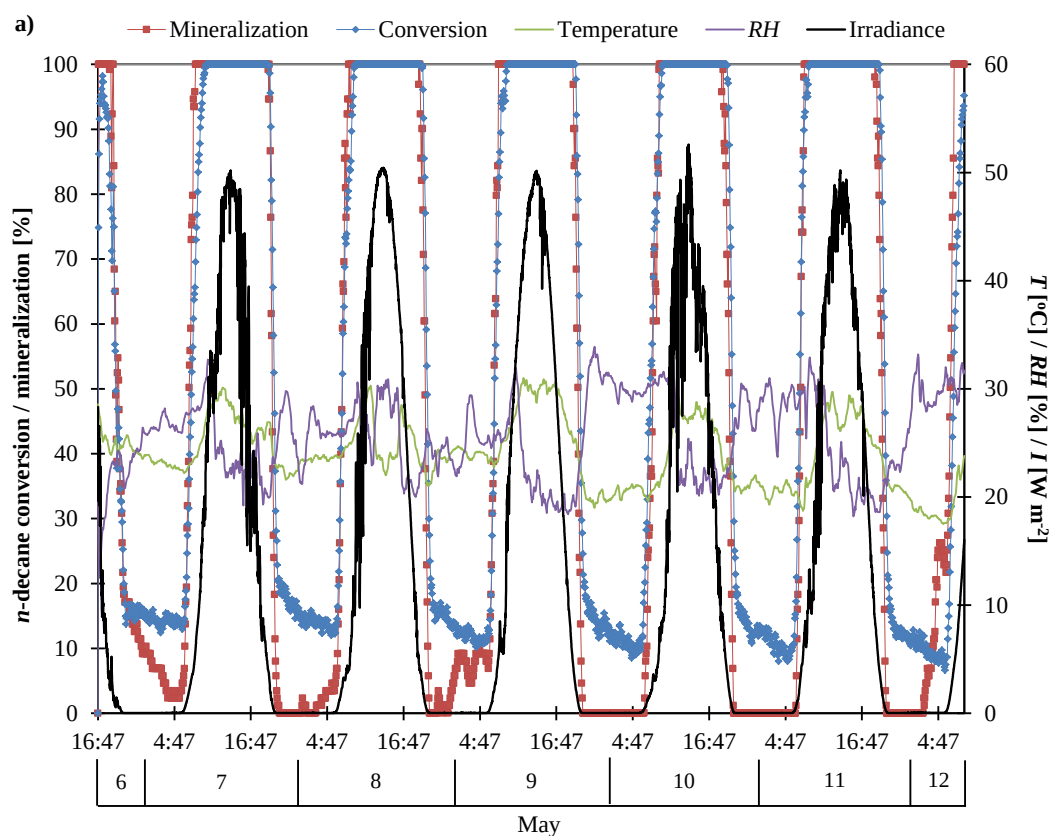
In Figure 8.2 is illustrated the PCO of *n*-decane over P25 (Figure 8.2a), PC500 (Figure 8.2b) and PCP (Figure 8.2c) photocatalytic films under solar radiation. In all cases is clearly shown the dependence of the conversion and mineralization on the irradiance. Photocatalytic activity was observed between 7:00 and 20:00 approximately reaching complete *n*-decane conversion over P25 and PC500 films and 45 % of conversion over PCP film at around 9:00 (15 W_{UV} m⁻² of irradiance) and 14:00 (48 W_{UV} m⁻²), respectively; remarkably, over P25 film, the recorded values of $C_{\text{dec, exit}}$ at night were below the $C_{\text{dec, feed}}$ (Figure 8.2a) revealing some adsorption capacity of P25. On the contrary, over PC500 and PCP films, the values of $C_{\text{dec, exit}}$ during the night were the same which means that both photocatalytic films presented low adsorption capacity. Then, with the sunrise, the photocatalytic activity of the films was resumed and the same cyclic behaviour was observed in each day of experiment.

The CO₂ concentration was also measured during the experiments in order to assess the mineralization yield which is described by the following equation:



As expected, the mineralization of *n*-decane also increased with the solar irradiance being such trend observed for all three experiments. Generally, all the *n*-decane converted is mineralized into CO₂ and water over P25 and PC500 films. In opposition, under low irradiance conditions (but enough to attain 100 % of *n*-decane conversion), the mineralization is reduced: for example, on the 6th and 7th days of *n*-decane PCO over PC500 film (Figure 8.2b) 100 % of *n*-decane was converted however not all into CO₂ and water. This means that the excess of photons (in high irradiance conditions) favours the direct reaction pathway to produce CO₂ and water. The same behaviour was observed over PCP film (Figure 8.2c) for the first three days and the last day of experiment. By-products such as those already mentioned in Chapter 5 are, most likely, being formed and released to the atmosphere as final products of *n*-decane PCO as no formation of CO₂ was observed. During the 4th and the 5th days of experiment over PCP film around 40 % of *n*-decane was mineralized into CO₂ and water. Once again, high irradiance conditions favour the direct production of CO₂. In opposition, low irradiance conditions (sunrise and sunset) impair the mineralization as it drops to 0 %.

It is also worth noting that the PCO of *n*-decane over the three photocatalytic films did not evidence any catalyst deactivation during the experiments.



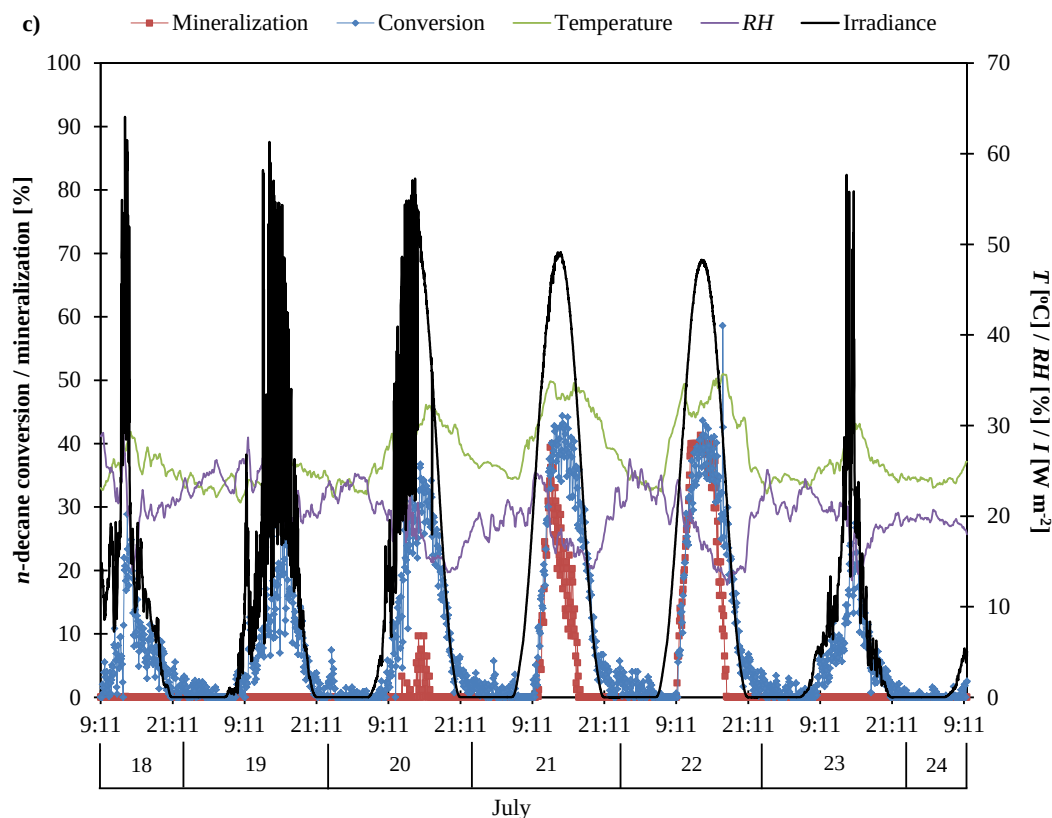


Figure 8.2. Time evolution of *n*-decane PCO over P25 (a), PC500 (b) and PCP (c) films under solar radiation (irradiance measured within 280 - 400 nm). Solar radiation collected with a CPC and UV irradiance measured on the outer tube of the photoreactor. Operating conditions: $C_{\text{dec, feed}} = 10 \text{ ppm}$; $Q_{\text{feed}} = 2 \text{ L min}^{-1}$ ($\tau = 44 \text{ s}$) as reported in Table 8.2.

In Figure 8.3 the conversion and the mineralization obtained during the fourth day of operation are plotted as a function of irradiance respectively for P25 (Figure 8.3a), PC500 (Figure 8.3b) and PCP (Figure 8.3c).

During the morning and due to the raising temperatures, 100 % of *n*-decane conversion was attained at around $15 \text{ W}_{\text{UV}} \text{ m}^{-2}$ whereas in the afternoon the total conversion was maintained up to $3 \text{ W}_{\text{UV}} \text{ m}^{-2}$. This hysteresis which was already described by Sánchez group [13, 14] repeated in every experimental day is a result of the difference in adsorption-desorption phenomena between morning and afternoon. When the sun rises, the temperature at the photocatalytic film surface increases and the readjustment of the adsorption equilibrium results in enhanced *n*-decane desorption; this way the conversion of the pollutant is reduced in comparison to that when the sun goes down, where the opposite effect is observed (*i.e.*, when the temperature decreases). Over PCP film the conversion of *n*-decane started after $20 \text{ W}_{\text{UV}} \text{ m}^{-2}$ of irradiance was reached and the topmost value of *n*-decane conversion was 45 % under $48 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (around 14:00). On the other hand, during the afternoon period the photocatalytic activity started to decrease below $48 \text{ W}_{\text{UV}} \text{ m}^{-2}$ until the sunset. In this case, the threshold to PCP photocatalytic film initiate activity is around

$20 \text{ W}_{\text{UV}} \text{ m}^{-2}$. It is worth noting that according to Figure 8.3b no mineralization of *n*-decane over PC500 film is observed up to $3 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (in the morning) despite the increasing conversion. This is probably due to the fact that at night the PC500 photocatalytic film saturates in *n*-decane while CO_2 is being desorbed. The higher adsorption of CO_2 is responsible for the delay in CO_2 appearance in the morning as well as for the high mineralization values observed at the sunset. A similar behaviour is also observed in Figure 8.3c: although the *n*-decane conversion started after $20 \text{ W}_{\text{UV}} \text{ m}^{-2}$ of irradiance the mineralization was only observed at around $30 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (in the morning period); in the afternoon, mineralization was kept until *n*-decane conversion was no longer observed.

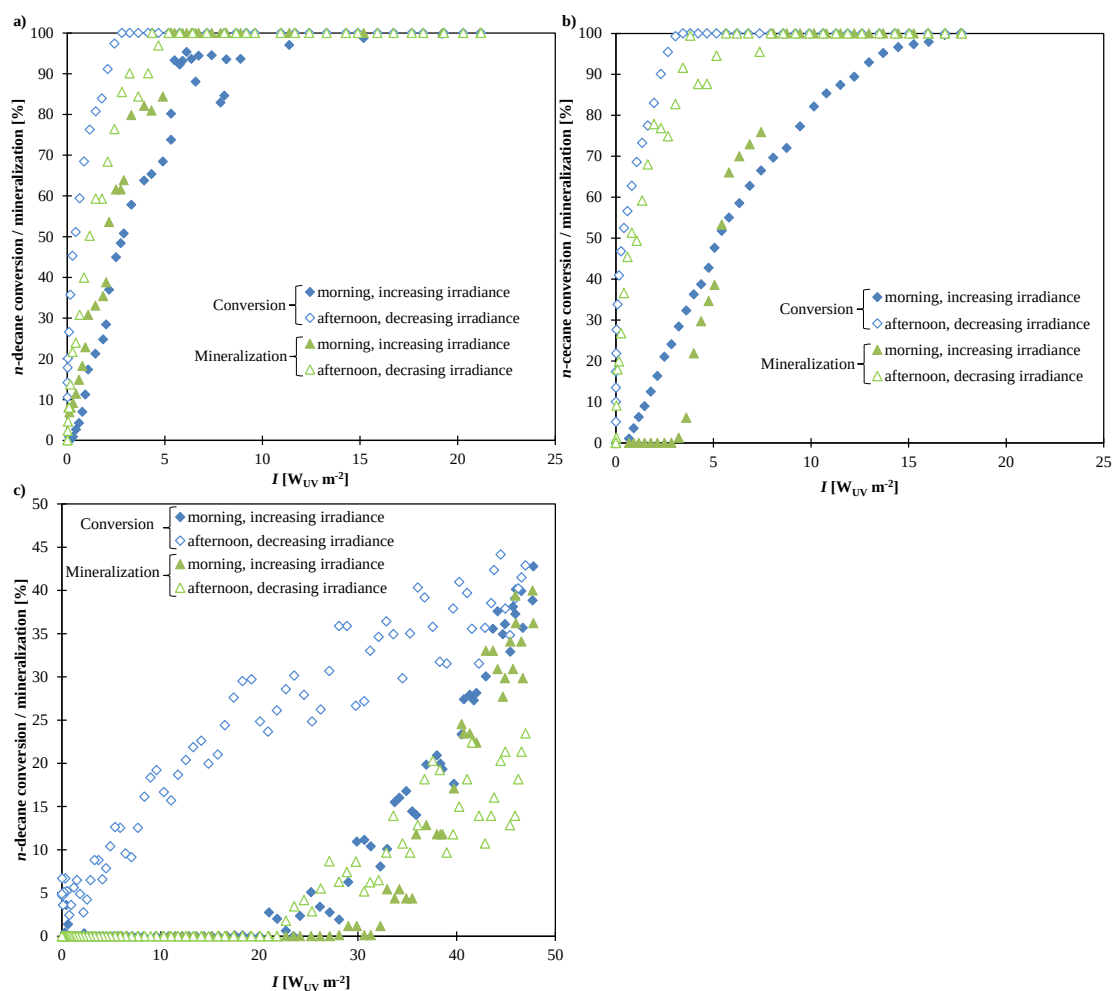


Figure 8.3. *n*-Decane conversion ($\blacklozenge$ morning, increasing irradiance; $\blue{lozenge}$ afternoon, decreasing irradiance) and mineralization ($\blacktriangle$ morning, increasing irradiance; $\green{triangle}$ afternoon, decreasing irradiance) over P25 (a) PC500 (b) and PCP (c) films under solar radiation during the fourth day of experiment. UV irradiance measured within 280 - 400 nm. Operating conditions: $C_{\text{dec, feed}} = 10 \text{ ppm}$; $Q_{\text{feed}} = 2 \text{ L min}^{-1}$ ($\tau = 44 \text{ s}$) as reported in Table 8.2.

Figure 8.4 illustrates the reaction rate obtained as a function of irradiance over P25, PC500 and PCP photocatalytic films also for the fourth day of each experiment. Over P25 and

PC500 films at low radiation levels ($< 5 \text{ W}_{\text{UV}} \text{ m}^{-2}$ in the morning) the reaction rate increases linearly while between 5 and around $15 \text{ W}_{\text{UV}} \text{ m}^{-2}$ a power mode trend of the reaction rate is observed. Above $15 \text{ W}_{\text{UV}} \text{ m}^{-2}$ in the morning or $3 \text{ W}_{\text{UV}} \text{ m}^{-2}$ in the afternoon the reaction rate was controlled by transport phenomena and independent of the irradiance. The same behaviour was observed over PCP film above $45 \text{ W}_{\text{UV}} \text{ m}^{-2}$. Between around $20 \text{ W}_{\text{UV}} \text{ m}^{-2}$ and $45 \text{ W}_{\text{UV}} \text{ m}^{-2}$, in the morning period, the reaction rate over PCP film seems to follow a linear trend. The higher reaction rate attained in the afternoon for the three cases are related to the adsorption effect on conversion and mineralization values previously described.

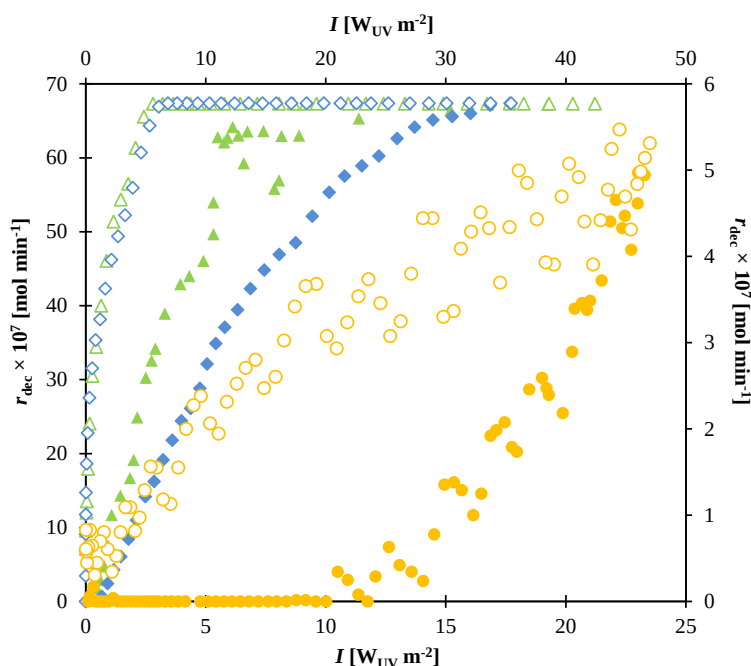


Figure 8.4. *n*-Decane PCO reaction rate (◆, ▲, ● morning, increasing irradiance; ◇, △, ○ afternoon, decreasing irradiance) over P25 (◆, ◇) PC500 (▲, △) and PCP (●, ○) films under solar radiation during the fourth day of experiment. UV irradiance measured within 280 - 400 nm. Operating conditions: $C_{\text{dec, feed}} = 10 \text{ ppm}$; $Q_{\text{feed}} = 2 \text{ L min}^{-1}$ ($\tau = 44 \text{ s}$) as reported in Table 8.2.

The same experiments were repeated using artificial UVA radiation instead of using solar radiation in order to explore the behaviour of the reactor without the uncertainty of the solar radiation variability, as illustrated in Figure 8.5.

Over P25 film, around 71 % of *n*-decane ($C_{\text{dec, feed}} = 10 \text{ ppm}$) was converted 15 min after turning on the UVA lamps ($29 \text{ W}_{\text{UV}} \text{ m}^{-2}$). The photocatalytic activity was kept until the end of the experiment with no catalyst deactivation nor formation of by-products as all the converted *n*-decane was mineralized into CO_2 and water. Regarding the PC500 photocatalytic film, similar behaviour under the same operational conditions can be found in Figure 8.5b. However, in this case, 100 % of the initial *n*-decane was converted into CO_2 and water which represents an

improvement of 29 % in conversion in comparison to that of P25 photocatalytic film. Finally, over PCP film only around 25 % of the initial *n*-decane was converted. This result is in accordance to that obtained under solar radiation: under approximately $29 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (in the morning) around 10 % is converted while *ca.* 25 % is converted in the afternoon under the same irradiance. Besides, the up most value of mineralization was around 52 % which means that 13 % is being converted in by-products while 75 % of *n*-decane remained unreacted. However, according to the mineralization profile, after 3.5 h of experiment this value starts to decrease which may suggest that photons are no longer in excess impairing the direct reaction pathway to produce CO_2 and water.

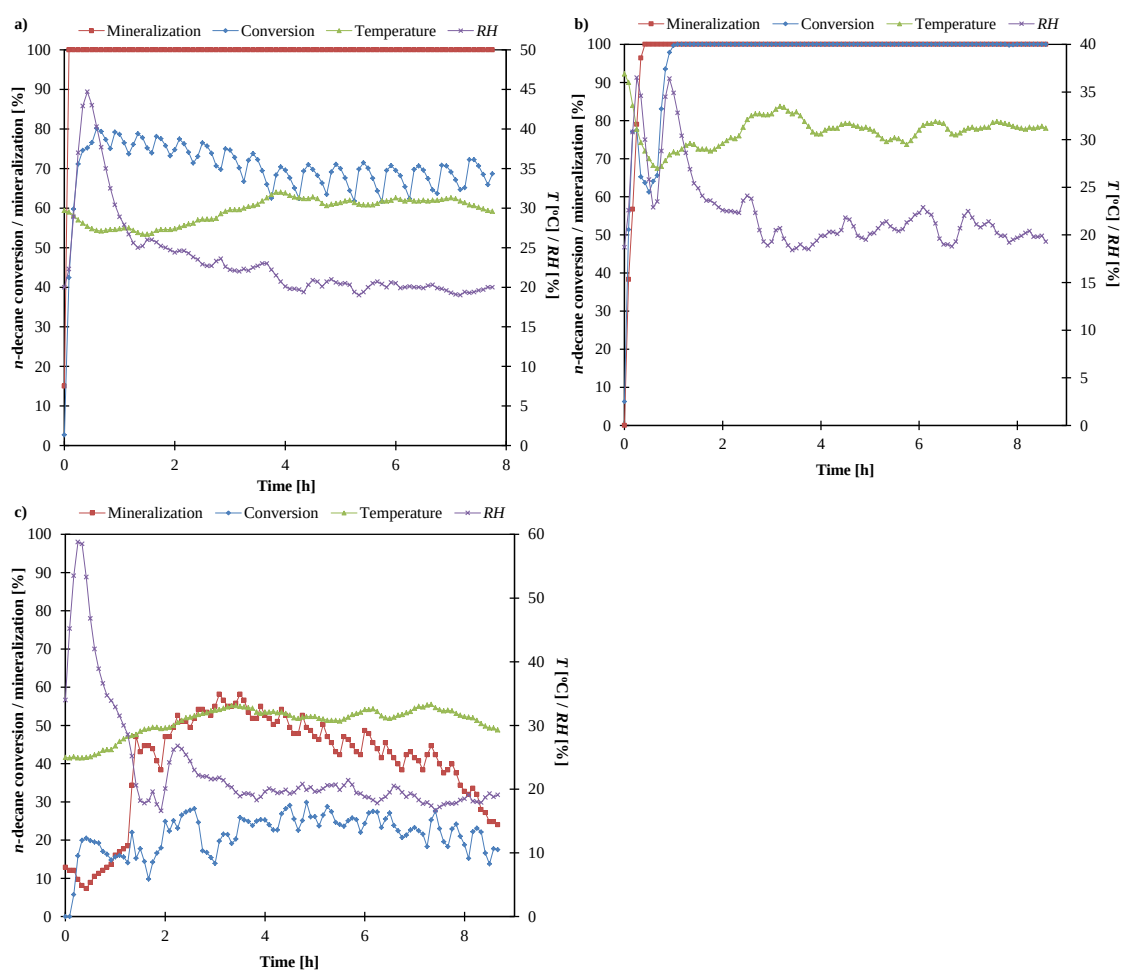


Figure 8.5. Time evolution of *n*-decane PCO over P25 (a), PC500 (b) and PCP (c) films under artificial UVA radiation. UV irradiance measured within 280 - 400 nm and facing the inner quartz tube of the photoreactor. Operating conditions: $C_{\text{dec, feed}} = 10 \text{ ppm}$; $Q_{\text{feed}} = 2 \text{ L min}^{-1}$ ($\tau = 44 \text{ s}$) as reported in Table 8.2.

The results obtained in this chapter are in line with those obtained in chapter 3 and chapter 5 regarding the efficiency of the photocatalytic films towards the conversion of *n*-decane by PCO process. In this sense, PC500 photocatalytic film presented the highest conversion of *n*-decane even considering the lower mass of photocatalytic film which may be ascribed to the

larger specific surface area of PC500 [23] and even considering that the smaller crystal size of PC500 may foresee higher density in surface defects [24-26] reducing the electron-hole recombination time, which ultimately results in lower photocatalytic efficiencies. Another approach is related to a faulty contact between the two P25 phases (anatase and rutile) in gas-phase photocatalytic reactions, resulting in poor charge-carrier separation and, subsequently, in a loss of photocatalytic efficiency. In the absence of any synergistic effect between the anatase and rutile mixed TiO₂ phases, it is accepted that anatase phase is much more active than rutile in the PCO of organic compounds in water and air [23]. Regarding the lower conversion values obtained for PCP photocatalytic films, several studies indicate that paint components can impair the photoactivity of paint films [27-35]. For example, Allen *et al.* [28] studied the effect of different paint components on the paints photoactivity. The results showed that the porosity, which is related to the particulated paint components (pigments and extenders) concentration, has a positive effect on photoactivity. However, higher content in CaCO₃ and high porosity makes paints prone to self-degradation. In the same line, Mendes and co-workers [36-38] developed a vinyl exterior paint modified with several TiO₂ photocatalysts: P25 (Evonik[®]), PC50 (Cristal[®]), PC105 (Cristal[®]), PC500 (Cristal[®]), ANX type PA (Kemira[®]), UV100 (Sachtleben[®]), AMT100 (Tayca[®]), UVLP7500 (Kronos[®]), VLP7000 (Kronos[®]), and VLP7101 (Kronos[®]); the authors stated that paint pigmentary TiO₂ is the most critical component affecting the photocatalytic activity for NO_x abatement due to its competitive absorption of the UV radiation [36-38].

It must also be pointed out that, although no experiments combining both radiation sources were conducted, *n*-decane PCO over P25 or PC500 films (in the operational conditions employed in this study) starts with the first morning solar rays completely removing *n*-decane under 15 W_{UV} m⁻². 24 W_{UV} m⁻² is the irradiance threshold when using PCP film. Considering that the UV irradiance of the UVA lamps is around 29 W_{UV} m⁻² it seems clear that under low or none solar irradiance conditions, such as at night, turning on the UVA lamps will enable the continuous PCO of *n*-decane.

8.4. Conclusions

A vertical and south-oriented pilot-scale, single-pass continuous-flow photocatalytic reactor featuring a CPC and inner UVA lamps is proposed for air depollution purposes. This reactor may operate 24 h a day by using both types of radiation, solar and artificial.

The photolysis under solar and artificial UVA radiation is rather inefficient since it leads to a negligible *n*-decane conversion.

The PCO of gas-phase *n*-decane yields conversions up to 100 %, when using P25 or PC500 photocatalytic films for a $Q_{\text{feed}} = 2 \text{ L min}^{-1}$ ($\tau = 44 \text{ s}$) and $C_{\text{dec, feed}} = 10 \text{ ppm}$, under solar irradiances of $15 \text{ W}_{\text{UV}} \text{ m}^{-2}$ in the morning and $3 \text{ W}_{\text{UV}} \text{ m}^{-2}$ in the afternoon. This behaviour is due to the differences in adsorption-desorption phenomena between both periods which are caused by the raising temperatures in the morning and decreasing temperatures in the afternoon. Regarding the film made by photocatalytic paint (PCP film), up to 45 % of the initial *n*-decane ($Q_{\text{feed}} = 2 \text{ L min}^{-1}$ and $C_{\text{dec, feed}} = 10 \text{ ppm}$) was converted under $48 \text{ W}_{\text{UV}} \text{ m}^{-2}$ in the morning, reducing from this point until the sunset. Measuring the CO_2 formation and subsequently the mineralization of *n*-decane, P25 and PC500 films enabled complete conversion into CO_2 and water in all irradiance range while over PCP film around 40 % of *n*-decane was mineralized under high irradiance conditions (above $45 \text{ W}_{\text{UV}} \text{ m}^{-2}$). An important effect of the UV radiation on the mineralization of *n*-decane was observed, suggesting that at high irradiance conditions the excess of photons favours the direct reaction pathway to the formation of CO_2 and water. Otherwise, a reduction in the mineralization yield is observed.

Under artificial UVA radiation, P25 film enabled 71 % conversion of the initial *n*-decane while 100 % was achieved over PC500 film. Over PCP film 52 % out of 25 % of the initial *n*-decane was mineralized into CO_2 and water. As expected, PC500 film promoted higher conversion of *n*-decane by PCO most likely due to the higher specific surface area in comparison to that of P25. On the other hand, *n*-decane PCO over PCP film resulted in the lowest conversion values obtained in this study. However, considering the wide range of paint applications, results can be seen as promising for air treatment. For this reason it is mandatory to keep improving the performance of photocatalytic paints as well as understand the phenomena behind their photoactivity.

8.5. References

- [1] D.-K. Lee, I.-C. Cho, *Microchem. J.* 68 (2001) 215-223.
- [2] N. Petit, A. Bouzaza, D. Wolbert, P. Petit, J. Dussaud, *Catal. Today* 124 (2007) 266-272.
- [3] J. Zhao, X. Yang, *Build. Environ.* 38 (2003) 645-654.
- [4] J. Mo, Y. Zhang, Q. Xu, J.J. Lamson, R. Zhao, *Atmos. Environ.* 43 (2009) 2229-2246.
- [5] C. Feiyan, S.O. Pehkonen, M.B. Ray, *Water Res.* 36 (2002) 4203-4214.
- [6] N. Fukami, M. Yosida, B.-D. Lee, K. Taku, M. Hosomi, *Chemosphere* 42 (2001) 345-350.
- [7] D.B. Henschel, Cost analysis of activated carbon vs photocatalytic oxidation for removing VOCs from indoor air, Engineering Solutions to Indoor Air Quality Problems, in Pollution Prevention and Control Division. National Risk Management Research Laboratory. Office of Research and Development. U.S. Environmental Protection Agency (EPA), North Carolina, USA, 1997.
- [8] W.A. Jacoby, D. Blake, R.D. Noble, C.A. Koval, *J. Catal.* 157 (1995) 87-96.
- [9] A.S. Watt, K.A. Magrini, L.E. Carlson, E.J. Wolfrum, S.A. Larson, C. Roth, G.C. Glatzmaier, *J. Air Waste Manag. Assoc.* 49 (1999) 1368-1373.
- [10] M. Romero, J. Blanco, B. Sánchez, A. Vidal, M. Sixto, A.I. Cardona, E. Garcia, *Sol. Energy* 66 (1999) 169-182.
- [11] J.M. Coronado, B. Sánchez, R. Portela, S. Suárez, *J. Sol. Energy Eng.* 130 (2008) 011016.
- [12] J.M. Coronado, B. Sánchez, F. Fresno, S. Suárez, R. Portela, *J. Sol. Energy Eng.* 130 (2008) 041012.
- [13] S. Suárez, T.L.R. Hewer, R. Portela, M.D. Hernández-Alonso, R.S. Freire, B. Sánchez, *Appl. Catal. B: Environ.* 101 (2011) 176-182.
- [14] R. Portela, S. Suárez, R.F. Tessinari, M.D. Hernández-Alonso, M.C. Canela, B. Sánchez, *Appl. Catal. B: Environ.* 105 (2011) 95-102.
- [15] R. Portela, R.F. Tessinari, S. Suárez, S.B. Rasmussen, M.D. Hernández-Alonso, M.C. Canela, P. Ávila, B. Sánchez, *Environ. Sci. Technol.* 46 (2012) 5040-5048.
- [16] W.H. Ching, M. Leung, D.Y.C. Leung, *Sol. Energy* 77 (2004) 129-135.
- [17] S. Malato, J. Blanco, A. Vidal, C. Richter, *Appl. Catal. B-Environ.* 37 (2002) 1-15.
- [18] G. Imoberdorf, H. Irazoqui, O. Alfano, A. Cassano, *Chem. Eng. Sci.* 62 (2007) 793-804.
- [19] J.V. Teixeira, S.M. Miranda, R.A.R. Monteiro, F.V.S. Lopes, J. Madureira, G.V. Silva, N. Pestana, E. Pinto, V.J.P. Vilar, R.A.R. Boaventura, *Environ. Monit. Assess.* 185 (2013) 59-72.
- [20] M.A. Anderson, L.W. Miller, M.I. Tejedor-Anderson, Waveguide, United States Patent, Wisconsin Alumni Research Foundation (Madison, WI, US), 2001.
- [21] R.A.R. Monteiro, F.V.S. Lopes, A.M.T. Silva, J. Ângelo, G.V. Silva, A.M. Mendes, R.A.R. Boaventura, V.J.P. Vilar, *Appl. Catal. B-Environ.* 147 (2014) 988-999.
- [22] J. Blanco, S. Malato, P. Fernández, A. Vidal, A. Morales, P. Trincado, J.C. Oliveira, C. Minero, M. Musci, C. Casalle, M. Brunotte, S. Tratzky, N. Dischinger, K.H. Funken, C. Sattler, M. Vincent, M. Collares-Pereira, J.F. Mendes, C.M. Rangel, *Sol. Energy* 67 (1999) 317-330.
- [23] V. Puddu, H. Choi, D.D. Dionysiou, G.L. Puma, *Appl. Catal. B: Environ.* 94 (2010) 211-218.
- [24] C. Colbeau-Justin, M. Kunst, D. Huguenin, *J. Mater. Sci.* 38 (2003) 2429-2437.
- [25] J. Taranto, D. Frochot, P. Pichat, *Ind. Eng. Chem. Res.* 48 (2009) 6229-6236.

- [26] O. Tahiri Alaoui, A. Herissan, C. Le Quoc, M.e.M. Zekri, S. Sorgues, H. Remita, C. Colbeau-Justin, *J. Photochem. Photobiol. A* 242 (2012) 34-43.
- [27] J. Auvinen, L. Wirtanen, *Atmos. Environ.* 42 (2008) 4101-4112.
- [28] N.S. Allen, M. Edge, G. Sandoval, J. Verran, J. Stratton, J. Maltby, *Photochem. Photobiol.* 81 (2005) 279-290.
- [29] T. Salthammer, F. Fuhrmann, *Environ. Sci. Technol.* 41 (2007) 6573-6578.
- [30] T. Maggos, J.G. Bartzis, M. Liakou, C. Gobin, J. Hazard. Mater. 146 (2007) 668-673.
- [31] J. Chen, C.-s. Poon, *Build. Environ.* 44 (2009) 1899-1906.
- [32] L. Hochmannova, J. Vytrasova, *Prog. Org. Coat.* 67 (2010) 1-5.
- [33] S. Laufs, G. Burgeth, W. Duttlinger, R. Kurtenbach, M. Maban, C. Thomas, P. Wiesen, J. Kleffmann, *Atmos. Environ.* 44 (2010) 2341-2349.
- [34] A. Costa, G.L. Chiarello, E. Selli, M. Guarino, *J. Environ. Manage.* 96 (2012) 86-90.
- [35] V.M. Sousa, C.M. Manaia, A. Mendes, O.C. Nunes, *J. Photochem. Photobiol. A* 251 (2013) 148-153.
- [36] C. Águia, J. Ângelo, L.M. Madeira, A. Mendes, *Catal. Today* 151 (2010) 77-83.
- [37] C. Águia, J. Angelo, L.M. Madeira, A. Mendes, *J. Environ. Manage.* 92 (2011) 1724-1732.
- [38] C. Águia, J. Ângelo, L.M. Madeira, A. Mendes, *Polym. Degrad. Stabil.* 96 (2011) 898-906.

9. Final remarks and suggestions for future work

This final chapter presents the most pertinent results and conclusions reported in the previous chapters. Some suggestions for future work are also proposed.

9.1. Final Remarks

The main objective of this thesis was to evaluate the efficiency of solar gas-phase heterogeneous photocatalysis towards the elimination of pollutants such as VOCs present mainly in indoor air atmospheres. The process was performed in lab- and pilot-scale experimental units equipped with single-pass, continuous-flow, annular photoreactor featuring Compound Parabolic Collectors (CPCs) and/or UV lamps. The results showed that the use of heterogeneous photocatalysis as an alternative technology for air treatment is an interesting and feasible option.

9.1.1. Photolysis

Gas-phase solar and UV photolytic experiments as well as aqueous-phase visible light-driven photolytic experiments were performed in order to assess the influence of incident radiation on the conversion/inactivation of the target pollutants/bacteria.

The UVC photolysis demonstrated that PCE conversion was negligible ($\sim 0\%$) or almost complete (98 %), depending on the material of the inner tube of the lab-scale annular photoreactor (glass or quartz, respectively). Product analysis by GC/MSD for PCE photolysis, under steady-state conditions and using the quartz inner tube, isolated the main following intermediates: methyl chloroformate; butanal; chloroform; carbon tetrachloride; methyl trichloroacetate.

PCE and *n*-decane solar photolytic experiments performed in the lab-scale annular photoreactor ($L_r = 16.0$ cm and $V_r = 220$ cm³) under three different incident irradiances, *i.e.*, 18.9, 29.1, and 38.4 W_{UV} m⁻² (sunlight UV fraction: 280 – 400 nm range) showed no measurable conversion of both pollutants ($C_{\text{PCE, feed}} = 1095$ ppm, $C_{\text{dec, feed}} = 71$ ppm, $Q_{\text{feed}} = 150$ cm³ min⁻¹, $\tau = 88$ s and $RH = 40\%$).

Diphenhydramine, DP (10 mg L⁻¹, adsorption at $\lambda < 280$ nm) showed to be a very recalcitrant pollutant in the absence of a photocatalyst, since the conversion observed was less than 3 % in 60 min under visible light ($\lambda > 430$ nm). Negligible *E. coli* inactivation was also observed in the experiments performed under UVA light radiation (25 W m⁻², spectral peak of 365 nm) without any photocatalyst.

MEK and H₂S UVA (45.3 W m⁻², spectral peak of 365 nm) and solar (0.7 W_{UV} m⁻²) photolytic experiments demonstrated that no reaction occurred in the absence of photocatalyst.

n-Decane photolytic experiments ($Q_{\text{feed}} = 2$ L min⁻¹, $\tau = 44$ s, and $C_{\text{dec, feed}} = 10$ ppm) carried out in pilot-scale photoreactor ($L_R = 144$ cm and $V_r = 4300$ cm³) under natural solar and

artificial UVA radiation (29 W m^{-2} , spectral peak of 365 nm) showed to be inefficient to convert this pollutant.

9.1.2. Photocatalysis using a lab-scale photoreactor

PCE conversion by PCO over TiO_2 P25 under UVC radiation (0.8 W m^{-2} , spectral peak centred at 253.7 nm) and conducted in a lab-scale packed bed (glass spheres) annular photoreactor ($L_r = 20.0 \text{ cm}$ and $V_r = 275 \text{ cm}^3$) was evaluated upon different $C_{\text{PCE, feed}}$ and Q_{feed} : (1) for a 4.25 fold increase in PCE concentration feed (574 – 2442 ppm), a reduction of ~44% (from 63 to 35 %) on the PCE conversion was observed; (2) increasing the feed flow rate (from 59 to $300 \text{ cm}^3 \text{ min}^{-1}$), a ~5 fold reduction of the residence time was observed, leading to poor degrees of conversion (~33 %). On the other hand, in terms of PCE PCO reaction rate, i.e., organic load converted, the trend followed an opposite direction: (1) for the same 4.25 fold increase in PCE concentration feed (574 – 2442 ppm), an increase of 2.4 times (from 3.93×10^{-5} to $9.28 \times 10^{-5} \text{ mol min}^{-1}$) on the photocatalytic reaction rate was observed; (2) increasing the feed flow rate (from 59 to $300 \text{ cm}^3 \text{ min}^{-1}$), the PCO reaction rate achieved $8.69 \times 10^{-5} \text{ mol cm}^{-3}$. Under steady-state conditions, product analysis by GC/MSD for PCE photocatalytic reaction showed butanal, chloroform, and carbon tetrachloride as the main isolated intermediates. The photocatalytic approach led to a 51 % PCE conversion with complete mineralization

Different PCO reactions were carried out in another lab-scale annular photoreactor ($L_r = 16.0 \text{ cm}$ and $V_r = 220 \text{ cm}^3$) packed with a transparent cellulose acetate monolithic structure coated with TiO_2 -based films (by *dip-coating* technique). This reactor configuration in comparison to the previous one ensured a low pressure drop, high catalyst surface-area-to-volume ratio, much less amount of photocatalyst and minimized “shading effects”. This photoreactor featured a CPC in order to illuminate the whole reactor perimeter and catalytic bed. The results showed that films using the commercial TiO_2 photocatalyst PC500 provided higher conversion and mineralization values of PCE and *n*-decane than those with P25 film, under simulated solar radiation. Photocatalytic conversions close to 100 % were obtained for *n*-decane and PCE ($C_{\text{dec, feed}} = 71 \text{ ppm}$ and $C_{\text{PCE, feed}} = 1095 \text{ ppm}$, respectively) when $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$, $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$ ($\tau = 88 \text{ s}$), and $RH = 20 \%$. The mineralization of PCE ($C_{\text{PCE, feed}} = 1095 \text{ ppm}$) showed no differences between both photocatalytic films. Over PC500 film the complete mineralization of *n*-decane ($C_{\text{dec, feed}} = 71 \text{ ppm}$) was observed while over P25 film only 69 % was mineralized in the following conditions $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$ ($\tau = 88 \text{ s}$), $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ and $RH = 40 \%$. Although the smaller crystallite size suggests the possibility of higher density in surface defects impairing the charge carriers and, therefore the photocatalytic efficiency, the higher surface area of PC500 catalyst may justify superior performance of PC500

photocatalytic film towards the conversion of *n*-decane and PCE in comparison to the film prepared from P25 catalyst under steady state conditions. In terms of *n*-decane and PCE PCO reaction rates over PC500 photocatalytic film, the upmost values were attained when their conversion was maximized, *i.e.*, when the following sets of conditions were used: $C_{\text{dec, feed}} = 71 \text{ ppm}$, $C_{\text{PCE, feed}} = 1095 \text{ ppm}$ and $Q_{\text{feed}} = 300 \text{ cm}^3 \text{ min}^{-1}$ or $C_{\text{dec, feed}} = 284 \text{ ppm}$, $C_{\text{PCE, feed}} = 2738 \text{ ppm}$ and $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$; on the other hand, the lowest *n*-decane and PCE PCO reaction rates over PC500 photocatalytic film were attained when the following operational conditions $C_{\text{dec, feed}} = 71 \text{ ppm}$, $C_{\text{PCE, feed}} = 1095 \text{ ppm}$ and $Q_{\text{feed}} = 75 \text{ cm}^3 \text{ min}^{-1}$ or $C_{\text{dec, feed}} = 71 \text{ ppm}$, $C_{\text{PCE, feed}} = 548 \text{ ppm}$ and $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$ were used. It is worth noting that the highest conversions were attained using these conditions.

In all the above cases, it was demonstrated that increasing Q_{feed} and/or $C_{\text{VOC, feed}}$, the organic load entering the reactor will be increased enhancing the mass transfer between the pollutant molecules and the catalyst surface and, therefore, the PCO reaction rate increased. On the other, for high Q_{feed} or $C_{\text{VOC, feed}}$ conditions, a reduction in the conversion of both pollutants was observed. This was due to an insufficient residence time inside the reactor (higher Q_{feed}) or an excessive presence of pollutant molecules in comparison to the number of photons/hydroxyl radicals (higher $C_{\text{VOC, feed}}$) which impairs the photocatalytic conversion of the gas-phase pollutants.

The PCO of PCE over a TiO_2 -based paint using the same lab-scale annular photoreactor ($L_r = 16 \text{ cm}$ and $V_r = 220 \text{ cm}^3$) was studied under simulated solar radiation, using the CPC to increase the photonic efficiency and cellulose acetate monolithic structures as substrate for the photocatalytic paint. The influence of substrate configuration (one structure with closed channels and another with open channels) was demonstrated in PCE PCO experiments: removing the outer walls of the substrate (configuration with open channels), further exposing more surface area to radiation, the PCE conversion through PCO enhanced up to 58 %, depending on the incident irradiance ($C_{\text{PCE, feed}} = 1100 \text{ ppm}$, $Q_{\text{feed}} = 75 \text{ cm}^3 \text{ min}^{-1}$, $I = 18.9, 29.1 \text{ or } 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$). Using such configuration, it was observed that PCE conversion was greatly affected by the flow rate of the inlet gas stream and initial PCE concentration: increasing four times the feed flow rate (from 75 to $300 \text{ cm}^3 \text{ min}^{-1}$), PCE conversion decreased 73 % under $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ of irradiance; in terms of photocatalytic reaction rate it was observed that, the highest value was attained for $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$ ($C_{\text{PCE, feed}} = 1100 \text{ ppm}$ and $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$) and increasing Q_{feed} to $300 \text{ cm}^3 \text{ min}^{-1}$ the reaction rate of PCE decreased. Such behaviour was ascribed to a reduced mass transfer between the PCE molecules and the photocatalytic paint surface above $150 \text{ cm}^3 \text{ min}^{-1}$ impairing the reaction rate most likely due an insufficient residence time inside the photoreactor. For a 3.7-fold PCE feed concentration increase (from 600 to 2200 ppm) under $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ the

PCE reaction rate also increased although PCE conversion reduced 43 %. In this case, the mass transfer between the PCE molecules and the photocatalytic paint surface was increased as $C_{\text{PCE, feed}}$ increased for the range of $C_{\text{PCE, feed}}$ employed.

The PCO of *n*-decane over a TiO_2 -based paint coated on cellulose acetate monolithic structures (configuration with open channels) using the lab-scale annular photoreactor ($L_r = 16$ cm and $V_r = 220$ cm³) was also studied under simulated solar radiation. The gas-phase photocatalytic experiments showed that highest *n*-decane conversion (98 %) was attained at the lowest Q_{feed} (75 cm³ min⁻¹) and $C_{\text{dec, feed}}$ (41 ppm), and highest *RH* (40 %) and I (38.4 W_{UV} m⁻²). Feeding the photoreactor with the double flow rate, the *n*-decane conversion decreases from 96 to 62 %. Alternatively, when the *n*-decane concentration on the feed stream was doubled, the remaining unreacted *n*-decane fed increased from 4 to 46 %.

PCO efficiency is a result of the combination of pollutant concentration and *RH* depending on the relative adsorption affinity of the photocatalyst for the pollutant and water molecules and on the mechanism of the hydroxyl radical attack (which also depends on the pollutant). Despite the acceptance that water is essential for photocatalysis as it is responsible for the formation of HO[•] radicals, each case requires a specific study which can hardly be extrapolated. Therefore, within this dissertation the effect of *RH* on the *n*-decane and PCE PCO was studied individually as follows:

- The effect of *RH* on the PCE PCO over TiO_2 P25 under UVC radiation (0.8 W m⁻², spectral peak centred at 253.7 nm) and conducted in a lab-scale packed bed (glass spheres) annular photoreactor ($L_r = 20.0$ cm and $V_r = 275$ cm³) was evaluated in the range 12 – 40 %. The conversion of PCE increased *ca.* 16 % as *RH* increased ($C_{\text{PCE, feed}} = 1221$ ppm, $Q_{\text{feed}} = 150$ cm³ min⁻¹ and $I = 0.8$ W m⁻²);
- In the PCO reactions of *n*-decane and PCE carried out in the lab-scale annular photoreactor ($L_r = 16.0$ cm and $V_r = 220$ cm³) packed with a cellulose acetate monolithic structure coated with PC500 photocatalytic film, the effect of *RH* was assessed in the range 3 – 40 %. The results demonstrated that in the range 3 - 20 % of *RH* competitive adsorption between water and pollutant molecules is unlikely to occur since the pollutants conversion increases with *RH* (except for $C_{\text{dec, feed}} = 71$ ppm at $Q_{\text{feed}} = 150$ cm³ min⁻¹ and $C_{\text{PCE, feed}} = 1095$ ppm at $Q_{\text{feed}} = 150$ cm³ min⁻¹ where negligible effect of *RH* on *n*-decane or PCE was, respectively, observed). On the other hand, at 40 % of *RH* the pollutant conversion over of PC500 film decreases, which means competitive adsorption between the above-mentioned molecules (*n*-decane: $C_{\text{dec, feed}} = 142$ and 284 ppm, $Q_{\text{feed}} = 150$ cm³ min⁻¹ and $I = 38.4$ W_{UV} m⁻²; PCE: $C_{\text{PCE, feed}} = 1095$ ppm,

$Q_{\text{feed}} = 300 \text{ cm}^3 \text{ min}^{-1}$ and $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$). The results also showed that the effect of RH on the n -decane and PCE conversion is dependent on the organic load entering the reactor.

- In the PCO over a TiO_2 -based paint using the same lab-scale annular photoreactor ($L_r = 16 \text{ cm}$ and $V_r = 220 \text{ cm}^3$) it was observed that the conversion of PCE decreased *ca.* 31 % (from 43 to 30 % when $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$, $C_{\text{PCE, feed}} = 1100 \text{ ppm}$ and $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$) as RH decreased from 40 % to 3 % while n -decane conversion only decreased *ca.* 1 % (from 96 to 95 % when $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$, $C_{\text{dec, feed}} = 73 \text{ ppm}$ and $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$) when RH decreased in the same range.

The effect of irradiance was also assessed in the PCO experiments carried out in the lab-scale annular photoreactor towards the conversion of n -decane and PCE over photocatalytic films made by TiO_2 powders or by photocatalytic paint. The radiation source is responsible for providing enough energy to generate electron-hole pairs on the photocatalyst surface, leading to the PCO of pollutants. Higher irradiance values will produce higher amount of electron-hole pairs that will participate in the redox reaction steps during the process and thus increasing the conversion of the pollutants. Therefore and as expected, in all PCO experiments where irradiance was a variable operational condition (n -decane and PCE PCO conducted in the lab-scale annular photoreactor packed with cellulose acetate monolithic structures coated with PC500, P25 or TiO_2 -based paint photocatalytic films), increasing the irradiance from 18.9 W m^{-2} to 38.4 W m^{-2} the conversion of n -decane or PCE also increased.

Different kinetic rate expressions employed in the developed mathematical model for simulating the PCE kinetics through PCO over TiO_2 P25 under UVC radiation (0.8 W m^{-2} , spectral peak centred at 253.7 nm) and conducted in the lab-scale packed bed (glass spheres) annular photoreactor ($L_r = 20.0 \text{ cm}$ and $V_r = 275 \text{ cm}^3$) indicated that PCE and H_2O molecules may have to be considered in association with different specific active sites of the surface of the catalyst as the Langmuir-Hinshelwood bimolecular non-competitive two types of sites model (M-4) described better the experimental data. However, in the n -decane PCO over TiO_2 -based paint coated in cellulose acetate monolithic structure and using the same lab-scale annular photoreactor ($L_r = 16 \text{ cm}$ and $V_r = 220 \text{ cm}^3$) a Langmuir-Hinshelwood mechanism where both species (water and n -decane molecules) compete for adsorption within different specific active sites (type 1 and 2) of the photocatalytic paint surface was able to describe the PCO of n -decane

Regarding the effect of gas-phase molecular oxygen, the conversion of n -decane and PCE by PCO (PCO experiments conducted in the lab-scale annular photoreactor packed with cellulose acetate monolithic structure coated with PC500 photocatalytic film) was drastically impaired or

even not observable in the absence of such species indicating the key role of oxygen in photocatalysis ($Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$, $C_{\text{dec, feed}} = 71 \text{ ppm}$, $C_{\text{PCE, feed}} = 1100 \text{ ppm}$ and $I = 18.9 - 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$). In the PCO of PCE over TiO_2 -based paint coated on cellulose acetate monolithic structures (lab-scale photoreactor - $L_r = 16 \text{ cm}$ and $V_r = 220 \text{ cm}^3$) removing oxygen from the feed, only 15 % of PCE was converted corresponding to an up to 56 % reduction in the PCO efficiency depending on the incident irradiance ($Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$, $C_{\text{PCE, feed}} = 1095 \text{ ppm}$ and $I = 18.9 - 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$).

Based on the intermediate analysis by GC/MSD and on the experimental results three major reaction mechanisms may be implicit in PCE and *n*-decane PCO. One is the formation of reactive species from the adsorbed gas-phase molecular oxygen, which will oxidize the pollutants. The second involves the action of the oxygen from the lattice of TiO_2 . The third mechanism involves the classical hydroxyl radical formation on the TiO_2 surface which acts directly over the pollutant molecules or as a trap for holes delaying the charge recombination and therefore promoting the formation of other oxidant species. In the case of PCE, chlorine radicals, $\text{Cl}^\bullet$, chain propagation reactions are also involved in the PCO reaction mechanism. Through chain propagation reactions, $\text{Cl}^\bullet$ may be essential to maintain the process while the action of $\text{HO}^\bullet$ radicals is probably related to the initiation of the PCO process (necessary step to generate $\text{Cl}^\bullet$ radicals).

9.1.2.1. TiO_2 photocatalytic properties enhancement

Effective visible light active nitrogen modified TiO_2 P25 photocatalysts were synthesized by a simple and low-cost preparation method, well suited for scale-up mass production. XPS analyses showed that anion-like nitrogen (N^-) was present in the structure of TiO_2 , as O–Ti–N and Ti–O–N linkages.

The catalytic activity of N-modified TiO_2 materials for the degradation of an indoor air pollutant, PCE, under simulated solar radiation, and for the inactivation of *E. coli* bacteria in aqueous solution, under UVA radiation was found to depend on the amount of urea used in the preparation method. The calcination temperature also influences the catalytic activity as observed in the aqueous-phase degradation experiments of the pharmaceutical pollutant, diphenhydramine (DP), under visible light illumination.

Nitrogen-modification of TiO_2 P25 reduced the photocatalytic activity towards the degradation of gas-phase PCE under simulated solar radiation. While bare TiO_2 P25 presented the highest activity (67 % of PCE conversion) only 35 % of conversion was attained over

$N_{0.50}P25-380$ (material with a urea:TiO₂ weight ratio of 1:2 and calcined at 380 °C). Regarding the aqueous-phase experiments over the same materials, $N_{0.50}P25-380$ exhibited the highest photocatalytic efficiency for DP degradation and completely inactivated *E. coli* bacteria in 10 min; TiO₂ P25 needed almost 40 min to completely inactivate *E. coli* under the same experimental conditions. However, further tests are needed in order to clarify the overall photocatalytic mechanism of nitrogen modified TiO₂ samples towards the elimination of harmful organic molecules and microorganisms inactivation whether present in air or water media are still not fully understood.

N-modified TiO₂ nanotubes exhibiting visible-light photocatalytic properties were synthesized at low temperature by the hydrothermal treatment method owning significant absorbance in the visible-light range. Transmission electron microscopy evidenced the unidimensional nature of the TiO₂ materials; however, their structure seemed to be sensible to a high calcination temperature (400 °C). From BET surface area results, it was suggested that the closest to one was the TiNT/urea ratio, the higher the specific surface area of the nitrogen-modified TiNT. This fact suggests a commitment between the amount of doping and the treatment temperature in order to define the optimal doping conditions of the catalyst. X-ray photoelectron spectroscopy indicates that the chemical states of the nitrogen in TiO₂ nanotubes may coexist in the form of N-Ti-O and Ti-O-N. Although for higher N/Ti ratio nitrogen seems to be concentrated at surface being more easily sputtered through Ar⁺ ion bombardment. Synthesised materials poorly degraded MEK and its mineralization was not efficient, generating intermediates: probably ethane, ethylene, formic acid, and/or formaldehyde. These compounds remained at the surface of the photocatalyst promoting its strong deactivation. Nevertheless, it was found that nitrogen-modified TiNT material is active photocatalyst for H₂S degradation under UV radiation. A moderate photocatalytic activity was also observed under solar light. In both cases, SO₂ was generated (with low concentration under UV radiation) and should be kept as low as possible since it still is a hazardous gas.

9.1.3. Photocatalysis using a pilot-scale photoreactor

A vertical and south-oriented pilot-scale, single-pass continuous-flow photocatalytic reactor ($L_R = 144$ cm and $V_r = 4300$ cm³) featuring a CPC and inner UVA lamps was proposed for air depollution purposes. This innovative reactor may operate 24 h a day using both types of radiation, solar and artificial.

The PCO of gas-phase *n*-decane yields conversions up to 100 %, when using P25 or PC500 photocatalytic films for $Q_{\text{feed}} = 2$ L min⁻¹ ($\tau = 44$ s) and $C_{\text{dec, feed}} = 10$ ppm, under solar

irradiances of $15 \text{ W}_{\text{UV}} \text{ m}^{-2}$ in the morning and $3 \text{ W}_{\text{UV}} \text{ m}^{-2}$ in the afternoon. This behaviour was due the differences in adsorption-desorption phenomena between both periods which are caused by the raising temperatures in the morning and decreasing temperatures in the afternoon. Regarding the film made by photocatalytic paint (PCP film), up to 45 % of the initial *n*-decane ($Q_{\text{feed}} = 2 \text{ L min}^{-1}$, $\tau = 44 \text{ s}$ and $C_{\text{dec, feed}} = 10 \text{ ppm}$) was converted under $48 \text{ W}_{\text{UV}} \text{ m}^{-2}$ in the morning reducing from this point until the sunset. Measuring the CO_2 formation and subsequently the mineralization of *n*-decane, P25 and PC500 films enabled complete conversion into CO_2 and water in all irradiance range while over PCP film 40 % of *n*-decane was mineralized under high irradiance conditions (above $45 \text{ W}_{\text{UV}} \text{ m}^{-2}$). An important effect of the UV radiation on the mineralization at *n*-decane conversion was observed, suggesting that at high irradiance conditions the excess of photons favours the direct reaction pathway to the formation of CO_2 and water.

Under artificial UVA radiation, P25 film enabled 71 % conversion of the initial *n*-decane while 100 % was achieved over PC500 film. Over PCP film 52 % out of 25 % of the initial *n*-decane was mineralized into CO_2 and water. As expected, PC500 film promoted higher conversion of *n*-decane by PCO most likely due to the higher specific surface area in comparison to that of P25. On the other hand, *n*-decane PCO over PCP film resulted in the lowest conversion values within the operational conditions of this study. However, considering the wide range of paint applications, results can be seen as promising for air treatment. For this reason it is mandatory to keep improving the performance of photocatalytic paints as well as understand the phenomena behind their photoactivity.

9.2. Suggestions for future work

As suggestions for future work, it would be interesting to develop new photocatalysts with high activity in the visible light region beside those described in Chapters 6 and 7. Moreover, considering the possible (eco)toxicity of nanoscale catalysts ($< 100 \text{ nm}$) research focused in modifying the morphology of TiO_2 to nanorods, nanosheets or nano whiskers or even forcing irreversible agglomeration of TiO_2 nanoparticles would also greatly benefit gas-phase photocatalysis as a clean and safe technology. Finding new and long-lasting substrates to support the photocatalysts will also add value to such technology.

Regarding the photocatalytic reaction mechanisms it would be interesting coupling a mass spectrometer to the gas chromatographer used in this work which would enable the prompt identification of intermediates or by-products of pollutants. In this way, a deeper knowledge about photocatalysis mechanism of reaction would be acquired. This concept can also be applied to the paint used within this work: several authors claim that photocatalytic paints release VOCs, such

as acetaldehyde and formaldehyde and free radicals; therefore, more and deeper studies must be conducted focused on the influence of paints components, interfering pollutants, as NO_2 , on the photocatalytic reaction mechanisms.

The development of photocatalytic membrane reactors allows the immobilization of the photocatalyst in the form of a porous membrane being capable of not only selective permeation but also a photocatalytic reaction. In this way, the reactants are forced by convection to the TiO_2 membranes while the PCO occurs on the outer and inner surface of the porous TiO_2 membranes where high concentrations of $\text{HO}^\bullet$ radicals are expected.

Finally, the photocatalytic process can be enhanced by using Microreactors/Static mixers and through breakthrough optical system designs for the optimal transfer of light radiation (either natural/simulated sunlight or artificial) between the source and the reactor (non-imaging optics techniques). Computational fluid dynamics tool (CFD-tool) can also be employed providing data related to the hydrodynamic conditions inside the reactor as also to the reaction at the photocatalyst surface.

Appendix

A. Master gas chromatography (MGC)

A.1. MGC calibration curves

A master gas chromatographic analysis system (MGC Fast GC, Dani Instruments S.p.A.), with a coupled two-position valve for sampling storage, is used for pollutant concentration analysis of the reactor feed and exit streams, through a flame ionization detector. The MGC is able to analyse air samples containing several volatile organic compounds (VOCs) using a fused silica capillary column (Volcol – $L_{cc} = 20$ m; $d_{i,cc} = 0.18$ mm; $d_{f,cc} = 1.00$ μ m; Supelco, Sigma–Aldrich Co. LLC.). The MGC operates with constant fluxes of helium (carrier gas), hydrogen and air (flame), and nitrogen (make-up) of 2, 30, 280, and 15 cm³ min^{−1} (at 298 K and 1 atm), respectively. Two MGC oven temperature methods were employed: for perchloroethylene (PCE) the oven temperature initially starts at 343 K for 1.2 min, followed by a 2 K min^{−1} heating ramp to reach 351 K (fixed for 1.8 min); for *n*-decane, it initially starts at 343 K for 1.2 min, then reaches 351 K by a 2 K min^{−1} heating rate, followed by a heating ramp of 30 K min^{−1} until reaching 433 K.

For the calibration of the MGC method, pulse injections of PCE and *n*-decane were performed in the MGC carrier flow stream. The calibration curve is the graphical representation of the results obtained in terms of moles number of the pulse-injected VOC (n_{VOC} in mol) versus the corresponding area under the peak (A_{peak} in V s); A_{peak} [V s] can be determined by:

$$A_{peak} = \int \Delta U_{peak} \times dt \quad A.1.$$

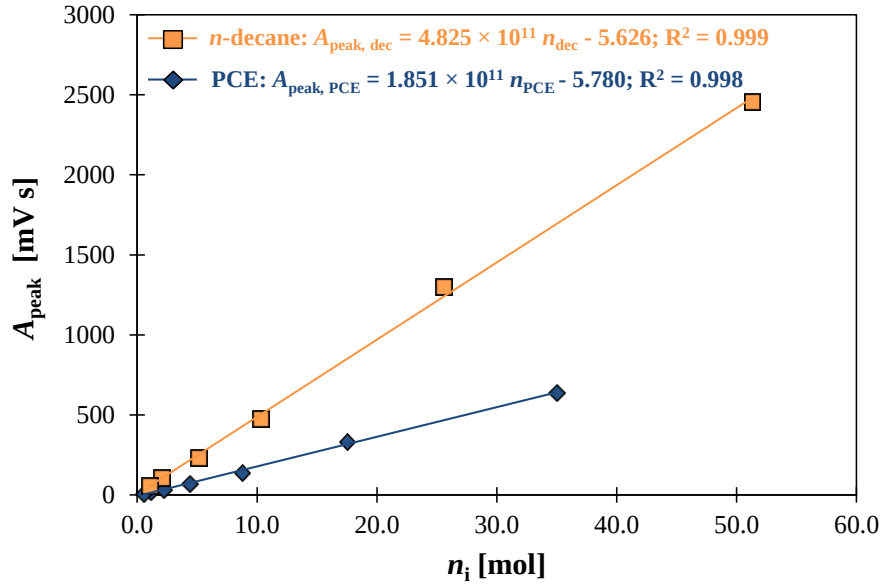
where ΔU_{peak} [V] is the electrical potential difference (also named as voltage), and t [s] is the time. Calibration plots like these may be called “linear” since the pulse area (generally) increases proportionately with the number of moles. In this way, a linear regression can be employed (frequently attaining squared correlation coefficients higher than 0.995), and the resulting linear equation allows the determination of any experimental VOC moles number within the range studied:

$$A_{peak} = m \times n_{VOC} + b \quad A.2$$

where m [mV s mol^{−1}] is the straight-line slope and b (V s) is the y-intercept. The calibration data obtained for the PCE and *n*-decane are reported in Table A.1 In Figure A.1 are represented the calibration curves obtained for PCE and *n*-decane.

Table A.1. VOC(*i*) data obtained for the calibration of the MGC method: PCE and *n*-decane.

VOC	$n_i \times 10^{10}$ [mol]	A_{peak} [mV·s]	$n_i \times 10^{10}$ [mol]	A_{peak} [mV·s]	$n_i \times 10^{10}$ [mol]	A_{peak} [mV·s]	$n_i \times 10^{10}$ [mol]	A_{peak} [mV·s]
PCE	35.02	661.4	17.51	308.9	4.380	69.89	1.095	17.72
	35.02	661.0	17.51	342.7	4.380	72.05	1.095	17.71
	35.02	606.3	8.760	147.9	4.380	68.99	1.095	17.72
	35.02	634.0	8.760	145.0	2.190	34.94	0.5475	8.624
	35.02	632.3	8.760	134.9	2.190	34.82	0.5475	8.756
	17.51	324.6	8.760	143.9	2.190	36.98	0.5475	8.381
	17.51	358.1	8.760	141.8	2.190	33.96	0.5475	8.431
	17.51	328.3	8.760	138.1	2.190	35.02	0.5475	9.950
	17.51	315.4	4.380	68.05	1.095	17.51	-	-
	17.51	358.2	4.380	71.56	1.095	17.25	-	-
<i>n</i> -decane	51.30	2384	25.60	1290	5.130	241.8	2.050	115.5
	51.30	2522	10.30	481.4	5.130	234.1	1.030	55.87
	51.30	2466	10.30	472.8	2.050	115.1	1.030	54.12
	25.60	1361	10.30	485.2	2.050	104.7	1.030	55.47
	25.60	1252	5.130	224.4	2.050	108.1	1.030	55.23

**Figure A.1.** GC calibration curves for PCE and *n*-decane.

The Limit of Quantification (LOQ) and Limit of Detection (LOD) values were calculated from the following calculations (adapted from Miller and Miller [1]):

$$\text{LOQ: } y_{\text{LOQ}} = m \times x_{\text{LOQ}} + b, \text{ where } y_{\text{LOQ}} = b + 10 \times s_b \quad \text{A.3}$$

$$\text{LOD: } y_{\text{LOD}} = m \times x_{\text{LOD}} + b, \text{ where } y_{\text{LOD}} = b + 3 \times s_b, \quad \text{A.4}$$

Table A.2 presents a summary of the analytical parameters of the calibration curves for each VOC.

Table A.2. Analytic parameters of PCE and *n*-decane calibration curves.

	<i>Regression equation parameters</i>				
	$(m \pm s_m)^a \times 10^{-9}$ [mV s mol ⁻¹]	$(b \pm s_b)^b$ [mV s]	R^{2c}	$SS_{res}^d \times 10^{-2}$ [V ² s ²]	s_m/m^e
PCE	185 ± 3	- 6 ± 5	0.998	5.14	1.78
<i>n</i> -decane	482 ± 8	6 ± 20	0.999	51.2	1.70
	y_{LOQ}^f [mV s]	y_{LOD}^g [mV s]	CV_h^h [%]	CV_m^i [%]	CV_l^j [%]
PCE	44.7	9.35	3.61	3.35	7.30
<i>n</i> -decane	201	64.4	2.82	3.73	1.36

^a *m* stands for slope and *s_m* for standard deviation of *m*; ^b *b* stands for y-intercept and *s_b* for standard deviation of *b*; ^c Correlation coefficient; ^d Residual sum of squares; ^e Sensitivity; ^{f, g} Limits of Quantification and Detection, respectively; ^{h, i, j} High, middle and low coefficient of variation, respectively.

A.2. MGC data treatment

The experimental VOC concentration of the photoreactor feed or exit stream ($C_{VOC, feed}$ and $C_{VOC, exit}$ in mol cm⁻³, respectively) can be determined by:

$$C_{VOC, feed/exit} = \frac{n_{VOC, feed/exit}}{V_{loop}} \times \frac{T_{loop}}{T_{feed/exit}} \times \frac{p_{feed/exit}}{p_{loop}} \quad A.5$$

where $n_{VOC, feed/exit}$ [mol] is the VOC moles number in the feed/exit stream (equal to the loop-sampled VOC moles number), V_{loop} [cm³] is the sampling loop volume, T_{loop} and $T_{feed/exit}$ [K], and p_{loop} and $p_{feed/exit}$ [atm] are the sampling loop and reactor feed/exit temperatures and pressures, respectively.

Both temperatures are monitored through different thermocouples installed in the lab-scale experimental unit, considering that T_{feed} and T_{exit} are equal to the temperature inside the photoreactor (T_R in K). It is assumed that $p_{feed} = p_R = p_{exit} = 1$ atm, where p_R [atm] is the pressure inside the photoreactor, and, based on the vacuum employed (affected by the pre-selected peristaltic pump rpm), p_{loop} varies from 0.19 up to 0.60 atm.

The theoretical VOCs concentrations in the feed stream for further comparison with the experimental results obtained through MGC analysis may be calculated as follows. Considering that the saturation temperature of component *i* (VOC or H₂O) is the temperature for a corresponding saturation pressure at which component *i* molecules boils into its vapour phase. However, if complete saturation is not achieved, the partial pressure of component *i* in the vapour phase (p_i in atm) can be determined by:

$$\varphi_i = \frac{p_i}{p_i^{\text{sat}}} \quad \text{A.6}$$

where p_i^{sat} [atm] is the saturation pressure of component i at saturation temperature (T_i^{sat} in °C), and φ_i is the relative vapour pressure. The relative vapour pressure depends on the flow rate that passes through the liquid solution (Q_i in $\text{cm}^3 \text{min}^{-1}$). The generation of contaminated air streams in the lab-scale unit has shown that both H_2O and VOCs relative vapour pressures vary with the flow rate (see Figure A.2):

$$\begin{aligned} \varphi_i &= -4.3 \times 10^{-5} \times Q_i^2 + 2.1 \times 10^{-3} \times Q_i + 0.93 \quad \forall \quad 5 \leq Q_i \leq 25 \text{ cm}^3 \text{min}^{-1} \\ \varphi_i &= 0.959 \quad \forall \quad Q_i > 25 \text{ cm}^3 \text{min}^{-1} \end{aligned} \quad \text{A.7}$$

for Q_i measured at 1 atm and 298 K.

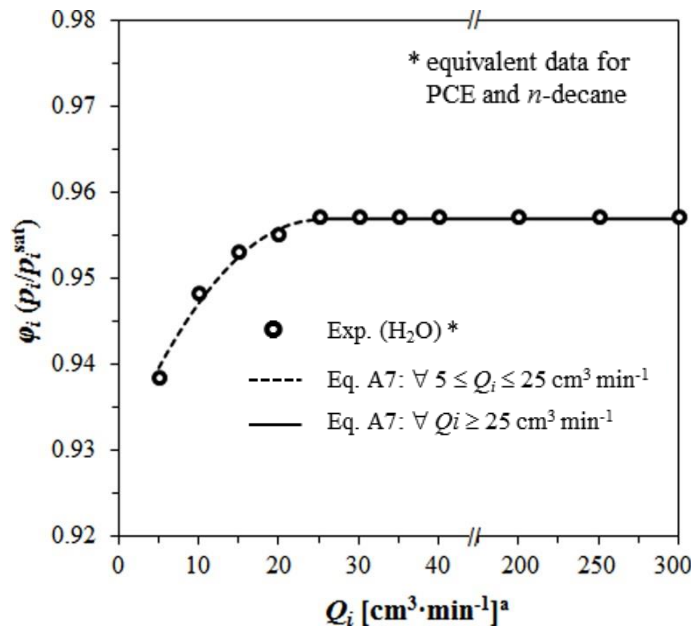


Figure A. 2. Effect on component (i)-relative vapour pressure ($\varphi_i = p_i/p_i^{\text{sat}}$) applying different air flow rates (Q_i): experimental data obtained for H_2O (points) determined at 281.15 K [$^{\text{a}}$ measured at 293.15 K and 1 atm]; lines for eq. A.7.

The saturation pressure (p_i^{sat} in mmHg) and temperature (T_i^{sat} in °C) are correlated through the Antoine equation:

$$\log(p_i^{\text{sat}}) = A_i - \frac{B_i}{C_i + T_i^{\text{sat}}} \quad \text{A.8}$$

where A_i , B_i , and C_i are the component(i)-specific Antoine coefficients (Table A.2).

Table A.3. Component(*i*)-specific Antoine coefficients: PCE, *n*-decane and water [2].

Component (<i>i</i>)	Specific Antoine coefficients [*]			Temp. range [°C] [#]	
	A_i	B_i	C_i	$T_{\min}$	$T_{\max}$
PCE	7.06832	1458.45	226.986	-22.35	346.85
<i>n</i> -decane	7.21745	1693.93	216.459	-29.66	345.30
water (H ₂ O)	8.05573	1723.64	233.076	0.01	373.98
Antoine equation: $\log p_i^{\text{sat}} = \frac{A_i - B_i}{C_i + T_i^{\text{sat}}}$, with p_i^{sat} in mmHg and T_i^{sat} in °C					

^{*} values based on regression of experimental data and researched estimates;

[#] $T_{\min}$ and $T_{\max}$ describe the temperature range for which the equation is valid.

Based on a derivation of the ideal gas equation of state, the generated component *i* molar flow rate (F_i in $\mu\text{mol}\cdot\text{min}^{-1}$) can be determined by:

$$p_i Q_i = F_i R_g T^{\text{MFC}} \quad \text{A.9}$$

where Q_i [$\text{cm}^3 \text{min}^{-1}$] is the flow rate that passes through the VOC/H₂O liquid solution, R_g is the gas constant ($\sim 8.206 \times 10^{-5} \text{ cm}^3 \text{ atm K}^{-1} \mu\text{mol}^{-1}$), and T^{MFC} [K] is the temperature at mass flow controlling time. This stream can be diluted so, the total molar flow rate (F_T in $\mu\text{mol}\cdot\text{min}^{-1}$) can be determined by

$$p_T Q_T = F_T R_g T^{\text{MFC}} \quad \text{A.10}$$

where p_T [atm] and Q_T [$\text{cm}^3 \text{min}^{-1}$] are the total pressure and total flow rate of the contaminated air stream, respectively. The flow rate depends on the temperature so, considering the flow rate exiting the mass flow controller (measured at 298 K and 1 atm), it should be used $T^{\text{MFC}} = 298 \text{ K}$. Moreover, since the contaminated air stream is at atmospheric pressure, its component(*i*)-vapour mole fraction (y_i) is given by:

$$y_i = \frac{F_i}{F_T} \quad \text{or} \quad y_i = \frac{n_i}{n_T} \quad \text{A.11}$$

Thus, with the ideal gas equation of state:

$$p_{\text{loop}} V_{\text{loop}} = n_T R_g T_{\text{loop}} \quad \text{A.12}$$

From eq. A.12 is now possible determine the loop-collected total moles numbers in the vapour phase (n_T in μmol), and then, the theoretical component(*i*)-moles number in the vapour phase (n_i in mol). Finally, the theoretical component(*i*)-concentration of the stream feeding the reactor ($C_{i, \text{feed}}$ in $\mu\text{mol cm}^{-3}$) can be calculated using eq. A.12, for $C_{\text{VOC, feed}} = C_{i, \text{feed}}$ and $n_{\text{VOC, feed}} = n_{i, \text{feed}}$.

A.3. References

- [1] J.C. Miller, J.N. Miller, *Statistics for Analytical Chemistry*, Wiley, New York, 1984.
- [2] C.L. Yaws, P.K. Narasimhan, C. Gabbula, *Yaws' handbook of Antoine coefficients for vapor pressure*, 2nd electronic ed., Knovel, 2009.