PHOTOCATALYTIC OXIDATION OF GASEOUS PERCHLOROETHYLENE OVER TiO_2-BASED PAINTS

R.A.R. Monteiro[1], A.M.T. Silva[2], J.R.M. Ângelo[3], A. M. Mendes[3], R.A.R. Boaventura[1], V.J.P. Vilar[1,*]

[1]LSRE - Laboratory of Separation and Reaction Engineering
[2]LCM - Laboratory of Catalysis and Materials, Associate Laboratory LSRE/LCM
[3]LEPAE - Laboratory for Process, Environmental and Energy Engineering
Faculdade de Engenharia, Universidade do Porto
Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[*] *Corresponding authors: vilar@fe.up.pt*

ABSTRACT – Tetrachloroethylene (PCE) is a volatile chlorinated compound persistently present in indoor air of several industrial closed facilities. Due to its environmental and human health impact, efforts have been directed in the last decades towards the degradation of this kind of air pollutants. Photooxidation of PCE study was conducted in an annular photoreactor under simulated solar radiation employing a plastic structure coated with TiO_2-based paint. The influence of coat thickness, structure configuration, PCE feed flow rate and concentration, relative humidity, and UV irradiance on the PCE degradation efficiencies was evaluated. Depending on the experimental conditions, up to 60 % of the initial PCE was converted.

1. INTRODUCTION

Heterogeneous photocatalytic oxidation (PCO) has attracted attention every year as an option for air and water depollution (Bahnemann 2004, Hoffmann *et al.* 1995). Operating at room temperature, using atmospheric air as the source of oxidant and exploiting solar radiation for photonic activation of the photocatalyst (usually TiO_2), the photocatalytic process is able to degrade/mineralize a wide range of organic pollutants into harmless or easily neutralized final products (CO_2, H_2O and mineral acids) (Linsebigler *et al.* 1995). A great deal of attention has been paid to the development of methods to support/immobilize the catalyst onto substrate materials without impairing its performance.

TiO_2 has been incorporated into construction materials such as cement mortar and tiles (Demeestere *et al.* 2008), paving blocks (Poon and Cheung 2007), glass (Langridge *et al.* 2009) and paints (Águia *et al.* 2010, Maggos *et al.* 2007), towards the improvement of air quality, self-cleaning and self-disinfecting agents. Paints, among all construction materials, are especially attractive as support for photocatalytic active TiO_2 materials mainly due to the fact that almost all surfaces can be painted. Promising results concerning photodegradation of air pollutants (Águia *et al.* 2010, Maggos *et al.* 2007) and photoinactivation of microorganisms (Sousa *et al.* 2013) using TiO_2-based paints have been achieved, however a lot of work has still to be done to fully understand the phenomena behind their photoactivity and subsequently to improve the paints performance.

Herein is presented a study on PCO of perchloroethylene (PCE) over a TiO_2-based paint, using a lab-scale continuous-flow annular photoreactor with a compound parabolic collector – CPC. Two configurations based on a honeycomb structure of cellulose acetate were used 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 honeycomb reactors (Hayes *et al.* 1992) 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 (Lim 2004). At the best of our knowledge, this is the first time that the performance of TiO_2-based paints and their applicability on gas-phase photooxidation processes for PCE abatement is evaluated. The photocatalytic oxidation of PCE was studied for different operating conditions, such as feed flow rate, PCE concentration, relative humidity, and UV incident irradiance.

2. EXPERIMENTAL

2.1. Photocatalytic films preparation and characterization

Based on the work of Águia *et al.* (2011), the TiO_2 photocatalyst PC500 (Millennium) was selected to modify a vinyl paint. The TiO_2 PC500 catalyst and exterior water-based vinyl paint properties are summarized in Table 1. 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 cm^3 of paint without 50% of pigmentary TiO_2 and mixing for 30 min at 300 rpm in a 100 cm^3 stainless steel vessel), as reported by Águia *et al.* (2010). The final TiO_2 PC500 and pigmentary TiO_2 content was 9 wt.% in wet basis (*ca.* 18 wt.% in dry basis).

Table 1 –TiO_2 PC500 and paint properties (Águia *et al.* 2011)

TiO_2 PC500			
Manufacturer	PC500 (Millennium)	Surface area [m^2 g^{-1}]	345
Crystal structure	>99% anatase	Agglomerate size [μm]	1.2-1.7
Crystal size [nm]	5-10	Shape	Agglomerates
Exterior water-based vinyl paint (wet basis)			
Pigmentary TiO_2	18 wt.%	Polymer extender slurry	8 wt.%
Water	30 wt.%	Binder slurry	20 wt.%
$CaCO_3$ and silicates	18 wt.%	Additives	6 wt.%

Cellulose acetate honeycomb structures were coated with a thin film of the photocatalytic paint using the dip-coating method. Prior to dip-coating, the honeycomb structures were immersed for 1 h in distilled water and alkaline detergent, subsequently rinsed exhaustively with Milli-Q water, and finally, dried at 323 K. Afterwards, layers of photocatalytic paint were dip-coated at a withdrawal rate of 0.8 mm s^{-1} until a thin and uniform film with different thicknesses was formed on each support surface (these samples were dried at 323 K for 1 h between each layer deposition). The photocatalytic paint supported (P) on cellulose acetate honeycomb structures (C) was labelled as xPCy where x refers to the number of layers coated and y is represented by 1 for configuration 1 and 2 for configuration 2.

Sets of xPC1 were prepared in order to evaluate the influence of the coat thickness (n_{layers}) upon the photocatalytic activity. It must be pointed out that, honeycomb 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 (see Figure 1b). After assessing the optimum coat thickness, a set of xPC2 coated with the same photocatalytic paint having a comparable paint superficial density, ρ_A, was prepared in order to clarify the influence of the configuration on the photocatalytic activity. The study of PCE PCO was carried out using a set of xPC2. Table 2 summarizes the catalytic bed properties of all xPCy used and in Figure 1b can be found a schematic representation of both configurations.

Table 2 – Properties and configurations of the catalytic bed

Catalyst (P)	Pigmentary / PC500		9 wt.% / 9 wt.% (wet basis)	
	ρ_P [mg cm^{-3}]		2.61	
Support (C)	ρ_C [mg cm^{-3}]		1.30	
	l_{ch} [cm]		0.9	
Configuration 1 (xPC1)	A_{C1} [cm^2]	806.4	m_P [mg]	103.2 – 1237.4
	n_{layers}	1 – 12	$\bar{m}_{C1}$ [mg]	3.2219
Configuration 2 (xPC2)	A_{C2} [cm^2]	576.0	m_P [mg]	503.6
	n_{layers}	5	m_{C2} [mg]	2.0657

ρ_{Cx}, ρ_P – respectively support and photocatalytic paint (dry basis) density; l_{ch} –length of the honeycomb channel; A_{C1}, A_{C2} – respectively, support surface area under configuration 1 and configuration 2; n_{layers} – number of layers; m_p – paint coat mass; $\bar{m}_{C1}$ – mean support mass under configuration 1; m_{C2} –support mass under configuration 2; m_p – catalyst mass.

2.2. Experimental setup

A full description of the whole experimental setup apparatus is given elsewhere (Lopes *et al.* 2012). Briefly, the humid air stream contaminated with PCE was generated by flowing air through different Woulff bottles, one containing PCE and another filled with deionized water being the flows controlled by three mass flow controllers. The photocatalytic system consists of: i) a solar radiation simulator; ii) annular photoreactor; iii) an UVA light lamp (peak at 365 nm) for catalyst degassing and activation purposes, placed inside the inner tube; iv) a compound parabolic collector (CPC) placed below the photoreactor. Figure 1 schematically represents the photoreactor from a side and frontal point of view. PCE concentration histories were monitored using a GC with a FID.

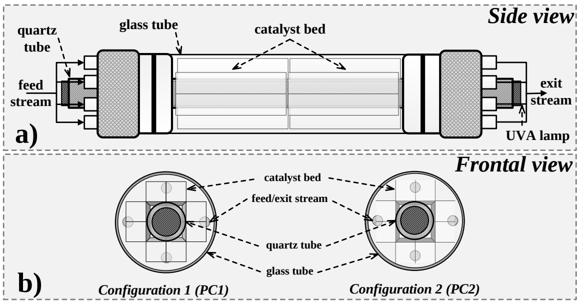

Figure 1 –Photoreactor schematic representation: a) side view; b) frontal view of the two configurations used.

2.3. Photocatalytic experiments

Firstly, the photoreactor was assembled without the catalytic bed to evaluate the photolytic oxidation of PCE. Afterwards, sets of xPC1 were prepared and assemble into the photoreactor to evaluate the influence of the coat thickness on the photocatalytic activity. Then, a new set of xPC2 was prepared by dipping a pre-establish number of layers considering the results attained with xPC1. The efficiency of the destruction process is expressed in terms of PCE conversion (equation 1) where $C_{\mathrm{PCE,\ feed}}$ and $C_{\mathrm{PCE,\ exit}}$ in ppm are the pollutant feed and exit streams concentrations, respectively

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

Several experimental conditions were employed, at steady-state, aiming the study of PCO of PCE: feed flow rate (75–300 $\mathrm{cm^3\ min^{-1}}$), PCE concentration (600-2200 ppm), feed relative humidity (0-40 %), and incident irradiance (18.9-38.4 $\mathrm{W_{UV}\ m^{-2}}$, measured for the spectral range between 280-400 nm). Before turning on the solar simulator, the catalytic bed was continuously fed and, by means of outlet stream sampling analysis, the feed composition steadiness was checked.

3. RESULTS AND DISCUSSION

3.1. PCO of PCE

A blank test consisting in an experiment without photocatalyst was performed, showing no measurable PCE concentration decrease (data not shown).

Influence of number of photocatalytic paint coating layers and support configuration

Sets of xPC1 from 1 to 12 layers were prepared by dip-coating resulting in a corresponding weight from 103.2 mg to 1237.4 mg of photocatalytic paint P (Table 2). Figure 2a) shows that conversion increases as the number of coating layers (n_{layers}) increases, reaching its maximum when seven layers (708.10 mg) of photocatalytic paint were coated on the cellulose acetate structure (*ca.* 38 % for an incident irradiance of 38.4 $\mathrm{W_{UV}\ m^{-2}}$). As foreseen, increasing the number of TiO_2 particles more photogenerated electron-hole pairs are expected at the surface of TiO_2 and, consequently, more molecules of PCE can be oxidized.

By contrast, above seven layers is found that photocatalytic activity gradually decreases as the number of layers increases. This contradictory effect was already described in earlier works (Chang *et al.* 2000) and explained by the blockage of the radiation propagation through the photocatalytic bed. As summarized in Table 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 1b). In order to have a comparable surface density, ρ_A, on 7PC1 and xPC2, 5 layers of photocatalytic paint were dip-coated on xPC2 – 5PC2.

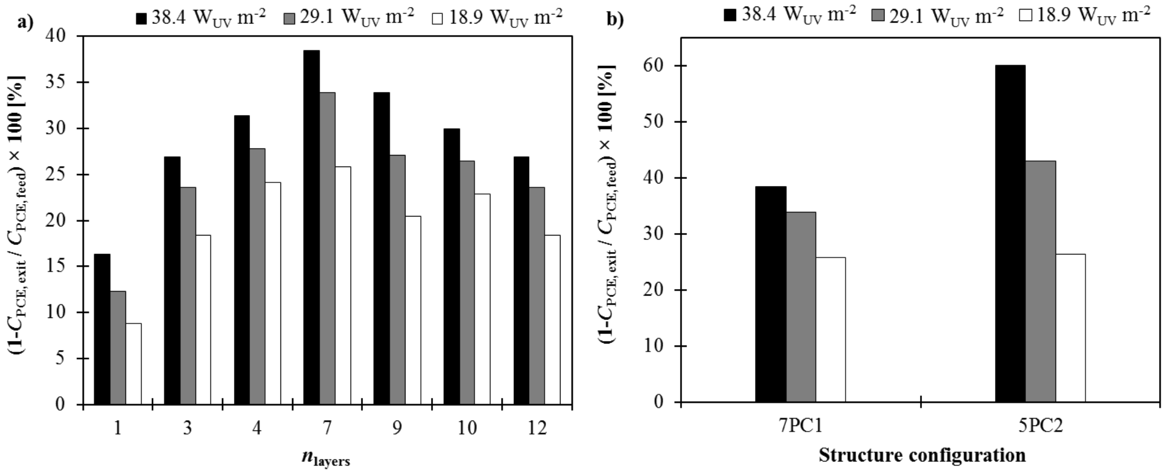

Figure 2 – Effect on PCE conversion of: a) number of layers of; b) structure configuration; $C_{PCE,\ Feed}$ = 1100 ppm, Q_{Feed} = 75 cm^3 min^{-1}, and RH_{Feed} = 40 %.

Figure 2b) illustrates the difference between both configurations in terms of photocatalytic conversion. For the highest irradiance used (38.4 W$_{UV}$ m^{-2}) 5PC2 promoted a conversion of *ca.* 60 % of PCE against the *ca.* 38 % attained using 7PC1. Decreasing the irradiance from 38.4 W$_{UV}$ m^{-2} to 29.1 W$_{UV}$ m^{-2} the difference in conversion between 5PC2 and 7PC1 configurations diminished 36 % and 21 %, respectively, and when the irradiance was decreased to 18.9 W$_{UV}$ m^{-2} PCE conversion decreased only 2 %. These preliminary results show that for lower irradiances the configuration of the structure would not affect the photocatalytic activity; instead, using PC2 the higher irradiance employed higher the conversion attained. 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. Moreover, the uncoated configurations 1 and 2, are transparent to radiation in the range $300 < \lambda < 800$ 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 (data not shown).

Effect of feed flow rate and PCE feed concentration on PCE conversion

Lower values of Q_{feed} mean higher residence times and lower loads of pollutant per unit of time, resulting in a higher contact period between the pollutant molecules and the catalyst surface. Figure 3a) shows increasing four times the feed flow rate (from 75 cm^3 min^{-1} to 300 cm^3 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 converted PCE load per unit of time was observed that the highest value was attained using Q_{feed} = 150 cm^3 min^{-1}.

In Figure 3b) is evidenced the effect of $C_{\text{PCE, feed}}$ on photocatalytic conversion. Decreasing the number of input PCE molecules to the reactor, more $^{\bullet}$OH and $^{\bullet}$Cl radicals become available to oxidize the PCE molecules. In fact, decreasing from 2200 ppm to 600 ppm the $C_{\text{PCE, feed}}$, *ca.* 1.8 times higher PCE conversions were attained for the employed incident irradiances. In terms of converted pollutant amount the results show an almost linear correlation between that amount and the PCE feed concentration under I = 38.4 W_{UV} m^{-2}. Decreasing I, the linear dependence is not verified most likely due an insufficient generation of photons upon an increasing number of PCE molecules in the reactor.

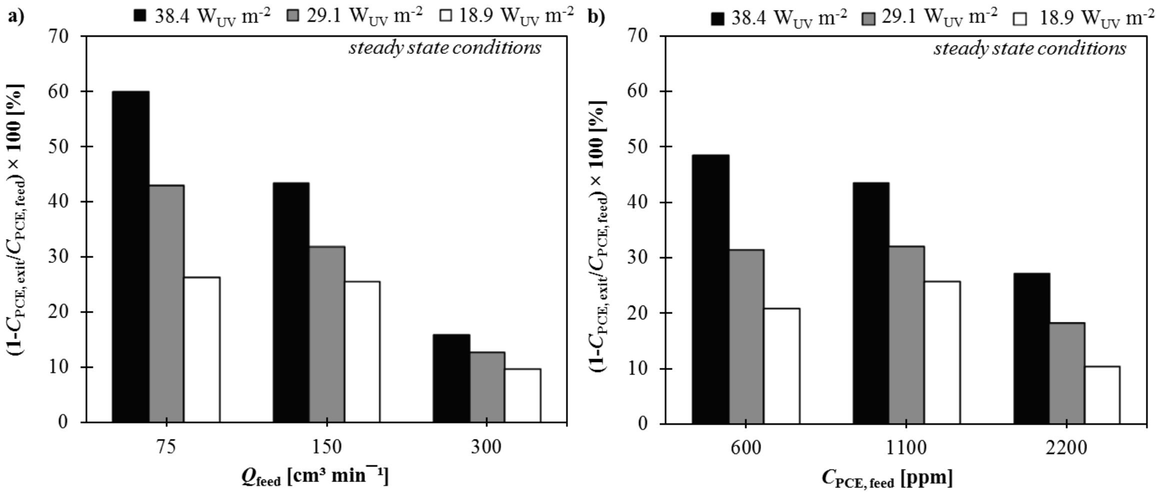

Figure 3 –Effect on PCE conversion of: a) feed flow rate ($C_{\text{PCE, feed}}$ = 1100 ppm) and b) PCE feed concentration (Q_{feed} = 150 cm^3 min^{-1}); RH_{feed} = 40 %.

Effect of water content

Figure 4 shows a similar reduction on the PCE conversion (*ca.* 31 %) as the RH decreases from 40 % to 0 % for the three irradiances employed.

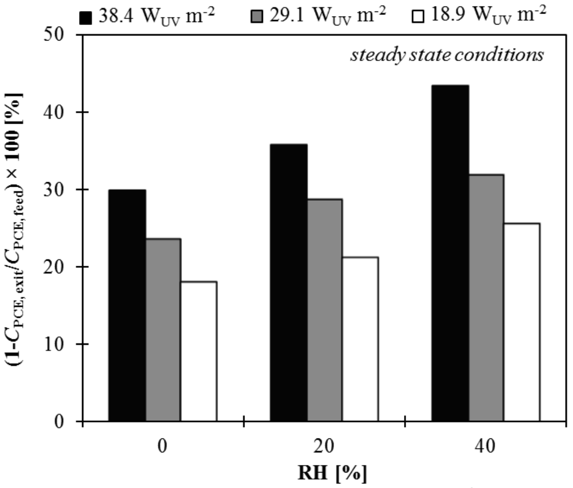

Figure 4 – Effect of HR on PCE conversion; Q_{Feed}^{*} = 150 cm^3 min^{-1} and $C_{\text{PCE, Feed}}$ = 1100 ppm.

The results suggest that $^{\bullet}OH$ radicals have an important role in the photocatalytic oxidation of PCE when operating in a range of 0–40 % of RH. Notwithstanding, differing effects of water content on the performance of TiO_2-based catalysts have been widely reported (Jo and Park 2004, Yamazaki *et al.* 2001): on one hand, the absence of water vapour seriously retards the PCO of several chemicals and the mineralization becomes incomplete; on the other hand, excessive water vapour inhibits the degradation by competitive adsorption to the photocatalyst surface. It must be pointed out that, the residual concentration of water present in the synthetic air stream ($\leq$ 3 ppm) used to accomplish 0 % of relative humidity experiments may justify the photoactivity observed for such experimental conditions.

4. CONCLUSIONS

The annular reactor employed in this study for the photodegradation of PCE over a TiO_2-based paint showed good effectiveness under simulated solar light radiation. Cellulose acetate structures as support for the photocatalytic paint can gather the operating advantages of an annular reactor (simple geometry and better radiation distribution) and of an monolithic reactors (low pressure and high catalytic surface area per unit of reactor volume). The comparison between the two tested substrate configurations provided interesting results: by removing the outer walls of the substrate (configuration 2) enhanced up to 56% depending on I. Using such configuration, was observed that PCE conversion is greatly affected by the Q_{feed} of the inlet gas stream and $C_{\text{PCE, feed}}$: increasing the Q_{feed} from 75 to 300 $cm^3\ min^{-1}$, PCE conversion decreased from 60 % to 16 % at I = 38.4 $W_{UV}\ m^{-2}$ corresponding to a 73 % reduction; in terms of converted PCE load per unit of time it was observed that the highest value was attained using Q_{feed} = 150 $cm^3\ min^{-1}$; increasing the PCE feed concentration from 600 to 2200 ppm under 38.4 $W_{UV}\ m^{-2}$ the converted PCE load also increased although the PCE conversion showed a reduction of 43 %. As the RH decreases from 40 % to 0 % a 31 % reduction on the PCE conversion (for the three irradiances employed) was observed suggesting that the action of hydroxyl radicals should not be excluded from the photocatalytic mechanism.

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