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Photocatalytic oxidation of gaseous perchloroethylene over TiO_2 based paint

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ABSTRACT

Perchloroethylene (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 toward the degradation of this kind of air pollutants. The photocatalytic oxidation (PCO) of PCE was studied in an annular photoreactor equipped with a compound parabolic collector (CPC) and employing two different configurations of a monolithic structure of cellulose acetate coated with an active TiO_2-based paint (9 wt.% of TiO_2 PC500) under solar radiation. The influence of the experimental conditions, namely feed flow rate (Q_{feed}), initial concentration ($C_{PCE,feed}$), relative humidity (RH) in the system, absence of oxygen and incident irradiance on the PCE conversion was evaluated. Under the best experimental conditions ($C_{PCE,feed}$ = 1100 ppm, Q_{feed} = 75 $cm^3\ min^{-1}$, RH = 40% and I = 38.4 $W_{UV}\ m^{-2}$ in the presence of oxygen) 60% of the initial PCE concentration was converted. The results showed that depending on the configuration of the structure, photocatalytic degradation of PCE can be enhanced by approximately 58%. Results obtained at low RH suggest that Cl radical chain propagation reactions may be included in the PCO mechanism of PCE. Also, in the absence of oxygen the photoreaction can still take place.

1. Introduction

Heterogeneous photocatalytic processes have been considered a good option for air and water decontamination, since they can operate at room temperature, uses atmospheric air as oxidant source, and solar radiation for the photonic activation of the photocatalyst (usually TiO_2 [1]), and are able to degrade/mineralize a wide range of recalcitrant organic pollutants into harmless or easily neutralized final products (CO_2, H_2O and mineral acids) [1–3]. 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 and make them resistant to mechanical abrasion and to environmental aging without impairing their performance. In this sense, a substrate for the deposition of active nanomaterial's for gas-phase photocatalysis should have the following requirements [3]: (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.

TiO_2 has been incorporated into a wide range of construction materials such as, tiles [4,5], paving blocks [6,7], wall papers [8,9] and paints [10–14], toward the improvement of air quality, self-cleaning and self-disinfecting agents. Among all construction materials, paints are especially attractive as support for photocatalytic active TiO_2 materials mainly due to the fact that almost all indoor and outdoor surfaces can be decorated with a thick and

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opaque film without impairing its photoactivity and obviously to esthetic applications. Bygott et al. [10] conducted a field trial painting 300 m^2 of walls with a silicate-based paint incorporating 7.5 wt.% of photocatalytic TiO_2. The authors reported a daily NO_x abatement of *ca.* 4.5 g in about 10,000 m^3 of air around school children playground [10]. Maggos et al. [12] stated a NO and NO_2 reduction of 19% and 20% respectively, using a white acrylic TiO_2-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 Fuhrmann [13] tested two different types of commercially available wall paints in a 1 m^3 test chamber with and without air exchange using artificial sunlight. The results showed that formaldehyde was photo-oxidized under static conditions. But, for typical VOCs under dynamic conditions, no significant photocatalytic activity was observed. In another real-outdoor conditions study, Ângelo et al. [14] determined the NO photo-abatement efficiency of photocatalytic paints when irradiated by sunlight. The paints were applied in a fiber cement board with $70 \times 20\,cm^2$ and a stable NO feed stream was fed to the photoreactor ($C_{NO} = 100 \pm 20$ ppbv). The best performing paint tested was formulated with PC500 and calcium carbonate yielding *ca.* 95% of NO conversion.

Although, the promising results and potential application concerning photodegradation of air pollutants using TiO_2-based paints, only few studies can be found in the literature regarding their use in the degradation of chlorinated VOCs. In addition, this paper presents a study on gas-phase PCO of PCE over TiO_2 (when incorporated in a paint), using a lab-scale continuous-flow single-pass annular photoreactor equipped with a compound parabolic collector—CPC (instead of studying the paint as common construction material). In our previous work [15] we reported a large concentration of PCE 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. Considering its high toxicity and volatility and since it is suspected to be carcinogenic to humans and extremely persistent in the environment, as well as to generate toxic reaction intermediates such as phosgene, chloroform and carbon tetrachloride, PCE present in water and/or air must be removed. 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 [16] as well as to profit from the fact that the whole reactor and the catalytic bed can be illuminated, enhancing the photonic efficiency [17]. Besides, the presence of an internal cylinder allows the use of a UVA or solar light lamp which may enable photocatalysis even at low or none natural irradiance conditions such as night and/or in indoor environments [18,19]. To the best of our knowledge, this is the first time that the performance of TiO_2-based paints and their applicability on gas-phase photo-oxidation 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.

2. Experimental

2.1. Materials and chemicals

TiO_2 photocatalyst PC500 (Cristal) was selected to modify a vinyl paint. This choice was based on Águia et al. [20] works where is reported a water-based vinyl paint loaded with TiO_2 photocatalyst PC500 (Cristal) that produced higher NO conversions among several other commercially available photocatalysts and, thus, it was selected for the studies shown in the present work. PC500 photocatalyst properties are detailed in Table 1.

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. For the generation of humidified air streams contaminated with PCE,

Table 1
TiO_2 PC500 and paint properties and photoreactor dimensions employed in the gas-phase PCO of PCE under simulated solar radiation.

Catalyst and paint [20]		
TiO_2	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
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.%
Photoreactor		
Outer tube (Pyrex-glass)	$d_{ot,e}$ [cm]	5.00
	$d_{ot,i}$ [cm]	4.64
Inner tube (Pyrex-glass)	$d_{in,e}$ [cm]	2.00
	$d_{in,i}$ [cm]	1.64
Photoreactor	L_R [cm]	16.0
	V_R [cm^3]	220