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Photocatalytic degradation of gaseous perchloroethylene in continuous flow reactors: Rate enhancement by chlorine radicals

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Abstract

The degradation of perchloroethylene (PCE) by UV/TiO_2 photocatalysis in gas phase was studied. The degradation efficiency has been compared in different continuous flow reactors: a photocatalytic tangential reactor (PTR) where the air flows tangentially over the catalytic medium and two photocatalytic filtering reactors (PFR) where the air flows through the porous catalytic medium. The degradation rate shows a linear dependence with the concentration of pollutants (up to 350 mg PCE/N m^3) for the PTR, but the degradation was negligible for the PFR. The degradation rate was enhanced by accelerating the chlorine radicals' formation (by adding HCl in catalytic quantity in the air flow or by PCE over-heating). In these conditions, the oxidation rate constant of PCE in the PFR was about five times higher than that in the PTR, although the mass of catalyst involved in the PFR was about 10 times lower and the contact time was about a 1000 times shorter than that of the PTR. Thus, the catalyst is globally more efficiently used in the PFR, as the mass transfer is not limiting. As a result, a degradation mechanism of PCE, involving the generation of free chlorine radicals, as the first limiting step, has been confirmed.

Keywords: Chlorine radicals; PCE; Photocatalysis; TiO_2; Rate enhancement

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1. Introduction

Both industrial and domestic activities are responsible for the emission of the volatile organic compounds (VOC) [1]. VOC are harmful and the most significant problem related to the emission of these pollutants is the possible production of photochemical oxidants, such as ozone [2]. Several chlorinated VOC, such as perchloroethylene (PCE–C_2Cl_4) are widely used as solvents at industrial scale in dry cleaning or metal degreasing facilities. PCE consumption raised up to 100,000 tonnes in Europe for the 2001 year, of which 90% have been used in dry cleaner's. The European directive 1999/13/CE sets the maximum emission level to 20 g PCE/kg clothing, which corresponds to the current average emission level. This solvent is toxic and considered as carcinogenic and extremely persistent in the environment [3]. Unfortunately, existing alternative solutions also have their drawbacks. Therefore, there is currently a great deal of interest in developing processes which can degrade this compound, such as photocatalytic oxidation in gas phase.

Heterogeneous photocatalysis for environmental cleanup operates at ambient temperature and the by-products are generally CO_2, H_2O and mineral acids. Nevertheless, the state-of-the-art mentioned some catalyst deactivation cases, due to some by-products (such as sulphurous compounds) which stay adsorbed on its surface. Moreover, the use of TiO_2 photocatalysts has been of great interest since TiO_2 is stable, harmless and inexpensive. Electron–hole pairs with a band gap potential of 3.2 eV are formed on anatase titanium dioxide surfaces irradiated by photons with wavelength shorter than 388 nm [4]. The electron–hole pairs then interact with adsorbed species facilitating oxidation–reduction reactions and the formation of highly reactive radical species [5–7]. It has been often postulated that the photogenerated holes react with adsorbed water molecules to form OH radicals which oxidize organic compounds. Direct oxidation of adsorbed

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VOC by photogenerated holes is also well described in literatures [5–7].

Photocatalytic degradation of gaseous PCE by TiO_2/UV is a widely described in international literature. Several by-products formation mechanisms are proposed, depending on operating conditions [8–11]. Two main mechanisms are suggested: $OH^•$ degradation pathway and $Cl^•$ degradation pathway.

Although photocatalytic oxidation has proven effective [12], continuous flow photocatalytic reactors for gas phase pollutants are usually not optimized for industrial applications. The reactor dimensions have to be reduced or the efficiency has to be increased. The use of photocatalytic filtering reactors will reduce significantly mass transfer problems. On the other hand, the contact time will be reduced. As a result, techniques are needed to increase the degradation kinetics of PCE. One way involves the introduction of the second, more reactive contaminant into the gas stream. A photocatalytic rate enhancement for the conversion of many pollutants was reported when co-fed with chloro-olefins, such as trichloroethylene (TCE) or PCE [13–15]. The mechanism of this enhancement is not established, but appears likely to be associated with the Cl radicals produced during the faster conversion of chloro-olefins [16,17]. A surface chain-reaction mechanism involving $Cl^•$ in the propagation sequence has been previously suggested for TCE in air conversions [18,19]. A chain-transfer reaction mechanism was proposed [20], in which surface chlorine radicals, generated by the TCE degradation, react with a second adsorbed reactant.

In order to use the chlorine promotion effect, the pre-treatment of titanium dioxide catalysts with hydrochloric acid solutions was examined as an alternative approach. The chloride anion, introduced into the titanium dioxide surface structure, could be converted under photocatalytic conditions into chlorine radicals, which then react with adsorbed species (potentially producing rate enhancements). This pre-treatment has only a temporary positive effect [21–23].

We present below our initial study of the photocatalytic degradation of PCE with single pass continuous reactors using industrial titanium dioxide coated non-woven papers. In order to make the most of the “chlorine promotion” effect, we studied the rate enhancement for PCE when co-fed with a catalytic amount of hydrochloric acid.

2. Methods

The experimental units included four major elements: the gas mixture generation system, the catalyst medium, the photocatalytic reactor and the analytical system.

2.1. Polluted flow generation

Concentrated PCE gas stream was prepared from stripping of the compound by bubbling or evaporation. The temperature of the bubbler was maintained constant (according to the desired pollutant concentration) using a thermostatic bath. The reactor influent gas stream was prepared by mixing concentrated PCE vapour (100 L/h) with a main gas flow generated by a compressor. Temperature and humidity were, respectively, ranging from 16 to 19 °C and from 45 to 55% RH.

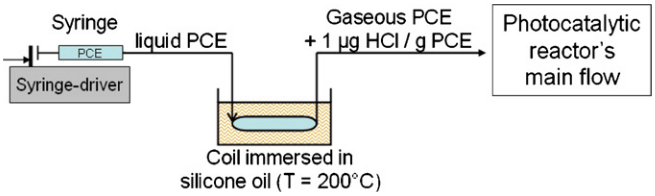

Fig. 1. Polluted flow generation with HCl co-feeding.

The hydrochloric acid co-feeding was made by direct injection of an HCl 5N solution in the air flow (0.1–0.5 mL/min). Another technique was used: PCE was heated to a temperature above its boiling point by means of a coil immersed in silicone oil. The vapour produced was then injected into the air flow and the liquid PCE flow rate was provided by a syringe/syringe-driver combination (Fig. 1). This technique provided a constant catalytic quantity of hydrochloric acid which came from the over-heated PCE, i.e. about 1 µg HCl/g PCE.

2.2. The catalyst medium

The photocatalytic medium (Fig. 2), used in all three reactors, was industrial titanium dioxide coated non-woven papers, produced by Ahlström. The catalyst used was Millenium® PC500, characterized by the manufacturer as having a surface higher than 300 m^2/g and a pure anatase crystal structure. TiO_2 is binded to cellulosic fibers with SiO_2

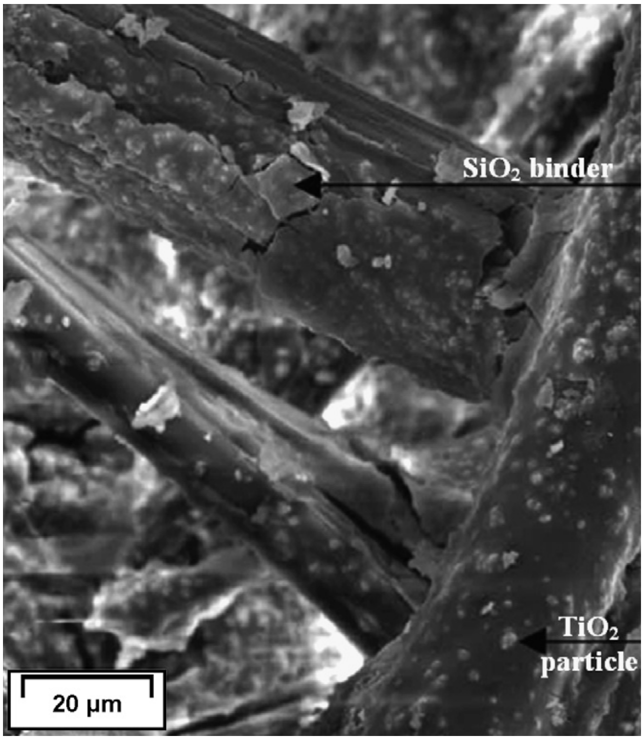

Fig. 2. SEM picture of photocatalytic medium fibers [24].

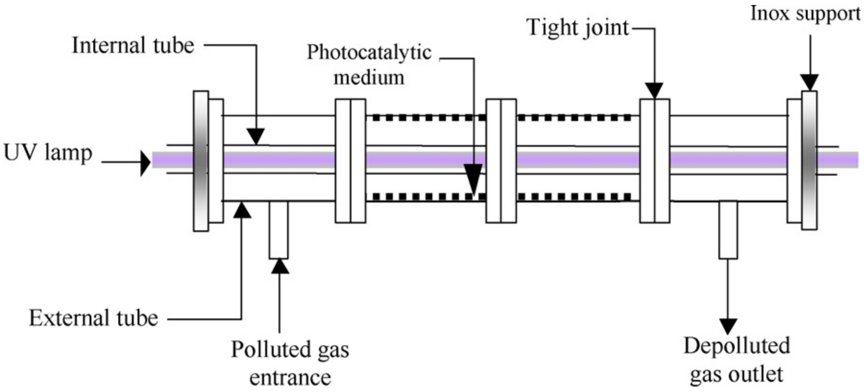

Fig. 3. PTR functional diagram.

[24] (manufacturer data: 1:1 ratio – 25 g TiO_2/m^2, 25 g SiO_2/m^2 – thickness of 250 μm).

2.3. *Continuous flow reactors*

2.3.1. *The photocatalytic tangential reactor (PTR)*

The photocatalytic tangential reactor used is presented in Fig. 3. The PTR consists of two concentric Pyrex glass tubes with inner diameter of 76 mm and outer diameter of 67 mm. Another internal tube with o.d. of 58 mm was available. The catalyst medium is fixed on the inside wall of the outer glass tube of the reactor. The length of the photocatalyst is 80 cm. The air flows tangentially over the catalyst medium with a flow rates varying from 2 to 10 m^3/h which correspond to gas residence times inside the photocatalytic section ranging from 0.29 to 1.45 s. A Philips UV A lamp (Cleo performance 80W/10 model) with a tube length of 150 cm was placed inside the inner tube. The emission spectrum of this lamp has a maximum at the wavelength of 365 nm. The UV power reaching the photocatalyst surface was measured with a radiometric probe at 365 nm (VLX-3W/CX 365). It was 24 ± 1 W m^{-2}.

2.3.2. *The photocatalytic filtering reactors (PFR)*

Fig. 4 illustrates the P50 PFR, comprising a compressor providing a flow rate up to 50 m^3/h for a 400 mbar available static pressure. The continuous reactor consists of three stainless steel mountable test boxes with a square cross-section (0.01 m^2) and a total volume of approximately 3 L. The first part is used for the main air flow inlet, pollutant injection, gas flow homogenisation using a perforated stainless steel plate and sampling for analysis before handling. The second part contained two photocatalytic media in filtering arrangement and a Philips UV A lamp (PLS 9W/10 model). The emission spectrum of this lamp has a maximum at the wavelength of 365 nm. The UV power reaching the photocatalyst surface was measured with a radiometric probe at 365 nm (VLX-3W/CX 365). It was between 15 and 35 W m^{-2} according to the distance to the lamp. The final part is used for sampling and the air flow outlet. The air flow rate generated by the compressor in the P50 PFR was measured with a float flow meter calibrated using a mass flow meter. The temperature of the incoming air flow is measured with a PT100 probe and the relative humidity with a ‘‘Testo 625’’ probe.

P5000 PFR (Fig. 5) is an air handling unit produced by CIAT (‘‘Compagnie Industrielle d’Applications Thermiques’’, French company specialized in thermal exchanges, air handling, refrigeration and air conditioning), with a flow rate capacity up to 5000 m^3/h. It is designed according to the ‘‘clean concept’’ principle with a 316 L stainless steel interior to be able to withstand corrosion induced by the most corrosive

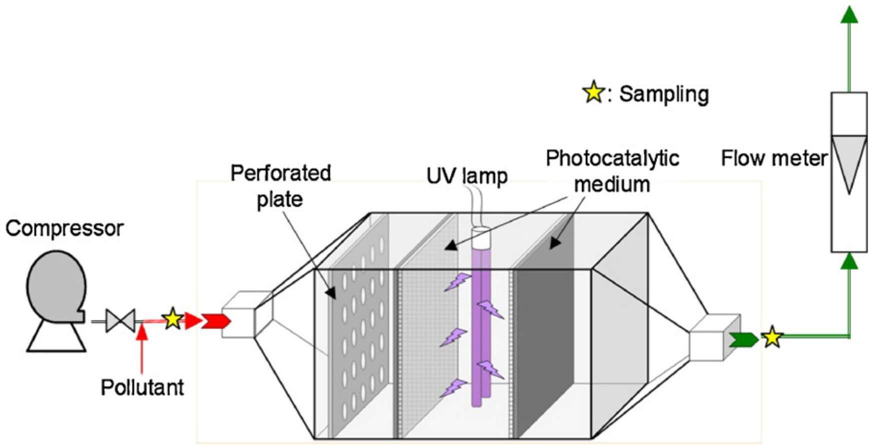

Fig. 4. P50 PFR functional diagram.

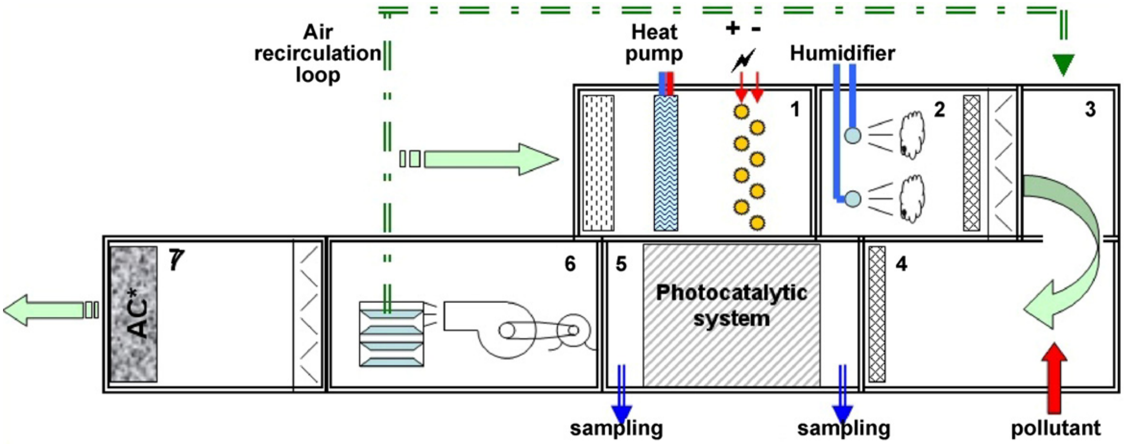

Fig. 5. P5000 PFR functional diagram.

chemical compounds. The unit comprises a pre-filtration box, a cooling bank, an electric heater (box no. 1), a vapour humidifier (box no. 2), a pollutant injection area (box no. 4), an upstream pollution measurement box, a photocatalytic treatment system, a downstream concentration measurement box (box no. 5), a fan (box no. 6) and a final activated carbon filtration (box no. 7). Pre-filtration is performed by G4 and F8 filters (standard EN 779:2002). A four-row cooling bank provides a maximum cooling capacity of 16.1 kW, depending on the temperature and humidity conditions. In addition, this bank can also be reversed to provide a maximum heating capacity of 34.1 kW. An electric heater with a 31.2 kW output completes the heating capacity. The humidifier makes it possible to generate a vapour mass flow rate of 25 kg_{water}/h. This humidity is controlled proportionally by an external regulator. The pollutant injection box is devised to enable distribution of the chemical contaminants over the entire section. The purification box has a cross-section of a filtration cell of 0.61 m × 0.61 m. It contains two photocatalytic pleated media offering a surface of 1 m^2 in filtering arrangement and eight Philips UV C lamps (TUV-PLL 55W model). The emission spectrum of this lamp has a maximum at the wavelength of 253.7 nm. The UV power reaching the photocatalyst surface was not measured. The ventilation box consists of a medium-pressure centrifugal fan. This scroll-free fan is coupled directly to a 3 kW motor. The assembly is driven by a frequency generator.

The instrumentation available for the experimental system is used to validate the parameters affecting efficiency. The air flow passing through the P5000 PFR was quantified via a pressure drop on either side of a diaphragm; in the event of an air flow fault, a pressure switch is used to secure the ancillary electrical components on the fan and filter clogging can be evaluated by measuring the upstream/downstream pressure differential. The P5000 loop is equipped with a Carel μAC humidity/temperature regulation system using a Carel IP40 probe and a Carel NTC sensor. The gas residence times for both PFR in photocatalytic media ranging from about 1 to 2 ms.

2.4. Analysis system

The PCE concentration was measured by a Perkin-Elmer Autosystem gas chromatograph (GC) using a flame ionisation detector (FID, 30 mL H_2/min and 200 mL O_2–N_2/min) and a Agilent DB-624 column (length = 30 m and internal diameter = 0.25 mm). Nitrogen was used as a carrier gas (20 psi). The temperature conditions for the oven, the injection chamber and the detector were, respectively, 100, 250 and 300 °C. The detection limit was 1 mg m^{-3}. The analysis was carried out by a direct sampling with a 250 μL syringe and injection into the GC. The calibration was performed by evaporation of different known quantities of PCE in closed flasks. The correlation of the pollutant GC-FID peak area as a function of its concentration was made.

By-product analysis was carried out by a Fisons Instruments GC 8000 Series using an Electron Capture Detector (ECD 800 model – carrier gas: Ar 90%/CH_4 10%) and a Hewlett Packard GC 5890 Series II Plus (carrier gas: He) using mass spectroscopy (MS – HP 5972 Series model). Both were equipped with DB-5MS columns and the temperature conditions were optimized. The analysis was carried out by a direct sampling with a 250 μL syringe and injection into the GC-ECD or by Carbotrap (Supelco 300 model) concentration and thermal desorption (Dynatherm Analytical Instrument, 890 model) into the GC–MS.

Ion-chromatography (Dionex DX-120 with an anion IonPac AS19 4 mm column model and a conductimetric detection – eluent: KOH 1 mL/min, 10–45 mmol/L) was used to detect formed Cl^- ions by bubbling a fraction of the exhaust gas flow through water.

3. Results and discussion

3.1. PFR/PTR comparison with a pure PCE gas stream (without HCl co-feeding)

The efficiency of the photocatalytic degradation of PCE during each experiment was calculated with the average concentrations of contaminant in the inlet and the outlet gas when steady-state values were reached (after 1–2 h). Gas samples were taken every 10–15 min and the steady-state was kept during 2 h at least. No deactivation was observed after a week period of operation.

Fig. 6 shows that the degradation rate of PCE depends linearly on the concentration of pollutant in the PTR (first order

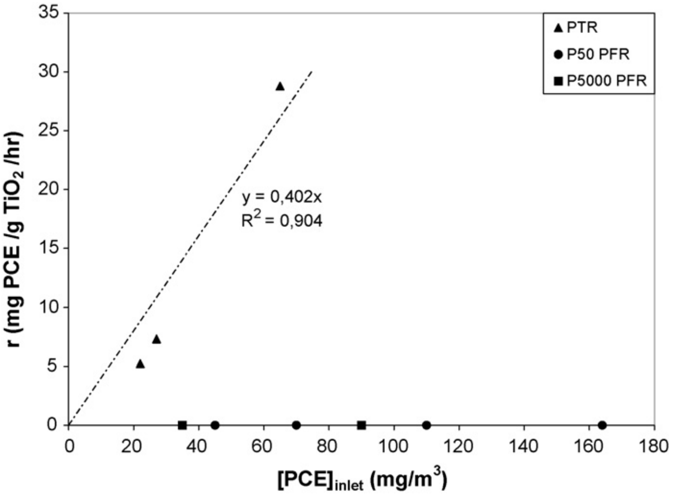

Fig. 6. PTR/P50 PFR degradation rates comparison without HCl promotion (residence time PTR: 0.58 s; PFR: 1.8 ms).

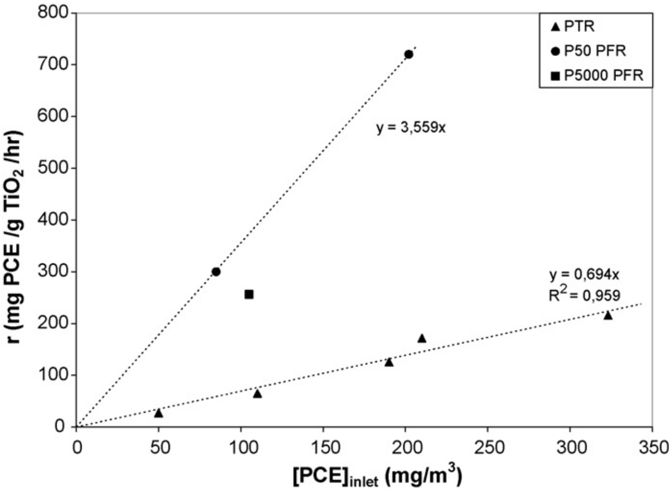

Fig. 8. PTR/P50 PFR degradation rates comparison with HCl influence (residence time PTR: 0.58 s; PFR: 1.8 ms).

reaction), whereas the degradation was negligible for the PFR. The gas residence times inside the photocatalytic reactors were very different for the same gas flow rate: it was 1.8 ms in the PFR and 0.58 s in the PTR at 5 m^3/h. Even if the mass transfer is not a limitating step in filtering reactors compared to the tangential flow reactor, the contact time between the catalyst and the pollutant is not sufficient to ensure a significant degradation.

As surface chain-reaction mechanisms involving $Cl^\bullet$ in the propagation sequence have been previously suggested for chloro-olefins degradation acceleration [18,19], we have studied this way of rate enhancement. So, we tried to bring a continuous amount of HCl into the gas flow in order to extend this effect.

3.2. PFR/PTR comparison with a PCE gas stream co-fed with HCl

As the degradation was not significant, we first have shown that HCl solution injection into the gas flow leads to the PCE degradation in the P50 Photocatalytic Filtering Reactor (Fig. 7). But the amount of liquid injected HCl was difficult to control. Consequently, a second technique was used, as described before: the PCE over-heating. A constant amount of HCl (1 μg/g of vaporized PCE) was brought into the system. This had a positive influence on the photocatalytic tangential reactor and a striking effect on the photocatalytic filtering reactor (Fig. 8).

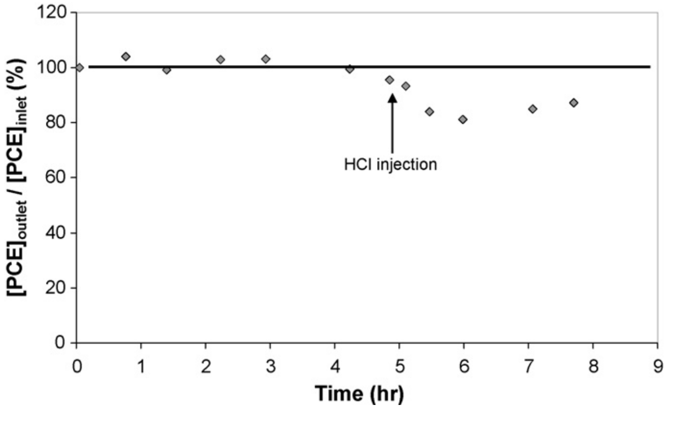

Fig. 7. HCl influence on PCE degradation in the P50 PFR—$[PCE]_{inlet}$ = 50 mg/m^3 at 5 m^3/h.

The degradation rate enhancement is linked to the radical species formation [16,17], i.e. if the first radical species formation is made easier, the degradation of adsorbed pollutants will start quicker and the residence time could be shorter. Although the PFR was ineffective with a pure PCE gas stream, its oxidation rates were about five times higher than that of the PTR with HCl co-feeding, regarding to the photocatalytic medium surfaces involved. In the PFR, as the air flows through the porous catalytic medium, the mass transfer is not limited. Thus, when the degradation occurred, the catalyst is globally more efficiently used in the PFR. Hydrochloric acid is more reactive than PCE toward photocatalysis. As a result, first chlorine radical formation occurs from co-fed HCl rather than PCE photo-oxidation. Once first $Cl^\bullet$ species are present onto the catalyst, fast radical degradation sequences can attack adsorbed PCE. The apparent rate constant increases from 0 without HCl to 3.56 m^3/g TiO_2/h with HCl promotion. So, HCl co-feeding brought initiating step acceleration. As the residence time was longer in the PTR, this acceleration was less pronounced (from 0.40 without HCl to 0.69 m^3/g TiO_2/h with HCl promotion for the apparent rate constant). In fact, chlorine radicals' formation occurred in the first part of the PTR, even without co-feeding. Moreover, the degradation is calculated for the entire reactor. That is why the impact of co-fed HCl is less visible in this case.

3.3. Industrial scale PFR efficiency

The photo-oxidation of PCE was carried out also at an industrial scale by means of P5000 PFR, with gas flow rate varying from 500 to 1500 m^3/h (transitory flow regime for both PFR). Results were similar than that of P50 PFR (Figs. 6 and 8). No significant degradation was observed without HCl co-feeding. With the chlorine promotion effect, degradation rates (regarding to the medium surface and the flow rate) were similar than that of P50 PFR (Fig. 8). The light differences with the P50 PFR are due to the use of a pleated medium and UV C irradiations in the P5000 PFR. Experiments were carried out up to 630 mg PCE/g TiO_2/h at 1500 m^3/h for a PCE inlet concentration of 80 mg/m^3.

3.4. Two major steps mechanism proposition

Many studies have shown that PCE photocatalytic degradation can take place by the mean of two initiation steps: $OH^\bullet$ and $Cl^\bullet$ pathways [11,25,26]. Comparison of available kinetic data for the PCE + $OH^\bullet$ reaction and for the PCE + $Cl^\bullet$ reaction suggests that this last is several hundred times faster [27]. As described in literature, $OH^\bullet$ degradation pathway of PCE leads to $Cl^\bullet$ formation [11]. As a consequence, $Cl^\bullet$ formation is the kinetic limitating step for PCE photocatalytic degradation without HCl co-feeding.

Several different mechanisms are described in the literature as many by-products are usually detected, such as $COCl_2$ or CCl_4. Although PCE percent degradation was significant during the experiments on the PTR and the PFR (up to 40% with a single pass), no significant amounts of intermediates, other than HCl resulting from 45 ± 5% PCE mineralization, could be detected by GC-ECD and GC–MS. Intermediates might stay adsorbed onto the photocatalyst medium until complete mineralization. So the degradation pathway of PCE can be described by several steps:

Initial radicals' formation:

$$TiO_2 + h\nu \leftrightarrow h^+ + e^-$$

$$h^+ + H_2O \rightarrow OH^\bullet + H^+$$

$$Ti^{4+} + e^- \rightarrow Ti^{3+}$$

$$Ti^{3+} + O_2 \rightarrow Ti^{4+} + O_2{}^-$$

Chlorine radical formation (kinetic limitative step):

$$\text{Fast}: HCl + OH^\bullet \rightarrow H_2O + Cl^\bullet$$

$$\text{Slow}: PCE + OH^\bullet \rightarrow HOCCl_2C^\bullet Cl_2 \rightarrow HOCClCCl_2 + Cl^\bullet \text{ [11]}$$

Main PCE degradation pathway:

$$\text{Fast}: PCE + Cl^\bullet + O_2 + H_2O \rightarrow \ldots \rightarrow CO_2 + HCl$$

Termination (example):

$$H_2O + Cl^\bullet \rightarrow HCl + OH^\bullet \text{ (presence of } H_2O)$$

$$2Cl^\bullet \rightarrow Cl_2 \text{ (absence of } H_2O)$$

4. Conclusions

The degradation of PCE by UV/TiO_2 photocatalysis in gas phase using industrial titanium dioxide coated non-woven papers was studied. The degradation efficiency has been compared in different continuous flow reactors: photocatalytic tangential reactor where the air flows tangentially over the catalytic medium and two photocatalytic filtering reactors where the air flows through the catalytic medium. The degradation rate of PCE shows a linear dependence with the concentration of pollutants for the PTR, but the degradation was negligible for the PFR. Regarding to the literature, we managed to enhance the degradation rate by accelerating the chlorine radicals' formation. To do this, a catalytic quantity of HCl was brought continuously in the air flow. In these conditions, the oxidation rate constant of PCE in the PFR was about five times higher than that in the PTR, although the contact time was about three hundred times shorter. Thus, the catalyst is globally more efficiently used in the PFR, as the mass transfer is not limited. As a result, a mechanism of degradation of PCE, involving the generation of chlorine free radicals as the first limiting step, has been confirmed.

During the experiments, no significant amounts of intermediates, other than HCl resulting from PCE mineralization could be detected. The efficiency of the laboratory-scaled PFR has been confirmed on an industrial-scaled PFR (up to 1500 m^3/h).

Considering dry cleaning issue, as PCE recycling takes place in situ and can produce small amount of HCl during the distillation process, the chlorine promotion conditions could be present yet.

This great efficiency of PFR under chlorine promotion is very interesting in order to make photocatalysis effective for industrial issues. Actually, the use of filtering configuration enables to shorten the photocatalytic system dimensions, which is essential for industrialization.

Further experiments will permit to find the optimal needed quantity of HCl and to test other potential radicals' initiators, such as H_2O_2 or O_3.

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