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Photocatalytic treatment of VOC industrial emissions: IPA removal using a sensor-instrumented reactor

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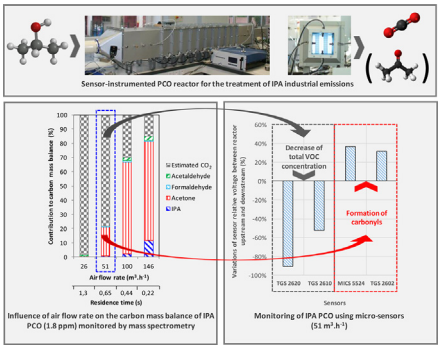
HIGHLIGHTS

- Sensor instrumentation of a semi-industrial photocatalytic reactor.
- Mapping of the influence of the main process parameters on isopropanol removal.
- Determination of the process carbon mass balance.
- Experimental evidences of the advantages and limitations of the sensors to monitor the process.

GRAPHICAL ABSTRACT



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ABSTRACT

This work aims at evaluating the applicability of photocatalytic oxidation (PCO) for industrial emission treatment. A dedicated single-pass semi-industrial PCO reactor is designed and the PCO removal of isopropanol (IPA) is investigated under industrial conditions: (i) high IPA concentrations ranging from 1.8 to 14.6 ppm and (ii) high air flow rates ranging from 26 to 146 $m^3.h^{-1}$. The concentrations of upstream and downstream IPA and by-products are monitored, not only using analytical instruments (mass spectrometry), but also gas micro-sensors. This approach aims at assessing the aptitude of commercially available micro-sensors to monitor a semi-industrial PCO reactor, and estimating their ability to automate such a process for industry. First, the influence of the main process parameters has been addressed: (i) IPA concentration, (ii) total air flow rate, (iii) number of PCO stages and (iv) number of PCO media. Irrespectively of the process condition, IPA PCO does not lead to deactivation of the media; whereas IPA mineralization and side-products formation are directly impacted by the process parameters. The increase of IPA concentration and air flow rate inhibits IPA mineralization, while the increase of number of stages and media promotes IPA mineralization. It is evidenced that selected gas micro-sensors can provide a semi-quantitative monitoring of the process performances. The main limitations of sensors are (i) their resolution regarding the detection of concentration variations and (ii) their cross-sensitivity to various classes of VOCs. Nevertheless, some sensors could be relevant for the automation and control of the PCO process once a preliminary metrological validation with relevant analytical devices is performed.

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1. Introduction

Emissions of Volatile Organic Compounds (VOC) from industrial processes show significant contributions to ambient air pollution, leading to negative impacts on human health and environment. In France, industrial processes account as the largest anthropogenic VOC sources [1] corresponding in 2002 to 27% of the total anthropogenic VOC emissions [2]. Depending on the country, industrial emissions may be submitted to different regulations such as the *directive 2010/75/EU* in Europe [3] or the *French decree of 02/02/1998* [4]. This *decree* limits the Total emitted VOC (TVOC) concentrations to 110 $mg.m^{-3}$ and, for some specific VOCs such as acetaldehyde, to 20 $mg.m^{-3}$. Two approaches can be considered to limit VOC emissions: (i) upstream source reduction and (ii) downstream VOC treatment. Regarding emission treatments, various techniques can be used [5–7], among them adsorption of VOCs onto sorbents [8], thermal oxidation [9], catalytic oxidation [10], non-thermal plasma (NTP) [11], plasma-catalysis [12], physical and chemical scrubbing [13], biological treatment [14], photocatalytic oxidation (PCO) [15] or various combinations of these techniques [16–21]. Among above-mentioned techniques, PCO is a low energy consumption [22] and easy to deploy oxidation process. Moreover, it possibly converts VOCs till mineralization into CO_2 and H_2O. PCO has been widely explored and applied for various applications such as antibiotics treatment in water [23], NO removal from off-gas combustion [24] or from ambient air [25], or indoor air treatment issues [26–28]. In order to enhance PCO efficiency or to activate photocatalysts with visible-light, novel catalytic materials are regularly developed, such as heterojunction catalysts [23,25] or composite catalysts composed of carbon nanomaterials [24,29]. Photocatalytic materials have been commercialized for several years. For instance, indoor air purifier prototypes based on PCO were formerly evaluated [30,31] and several devices are already commercialized [22].

The treatment of VOCs in the gas phase by PCO is extensively studied but mostly for indoor air purposes, where conditions highly differ from industrial effluent ones. For instance, indoor total VOC concentrations are mostly lower than 100 ppb [32]. In the case of industrial effluent treatment, VOC concentrations range from few ppm to thousands of ppm. Moreover, industrial emissions are generally characterized by high flow rates, from hundreds to tens of thousands of $m^3.h^{-1}$ [14], and require high-dimension single-pass PCO reactors. These requirements can significantly impact PCO efficiency since the residence time of the pollutants to be treated within the photocatalyst vicinity can be limited by the treated air flow rate [33,34]. Thus, under industrial conditions, residence time is often lower than one second. Moreover, high VOC concentrations may induce side-product formation and their subsequent accumulation onto the photocatalyst may possibly lead to deactivation [35,36]. So far, only few studies were dedicated to the treatment of industrial emissions by PCO under realistic conditions. Nevertheless, former works evidenced that single-pass PCO reactors can lead to noteworthy VOC conversions with continuous flows of VOCs and ppm-level concentrations [37–41]. However, in these studies, experimental conditions differ from typical conditions of industrial emissions: (i) air flow rates did not exceed 5 $L.min^{-1}$, corresponding to 0.3 $m^3.h^{-1}$ and (ii) residence times of VOCs into the photocatalyst vicinity were in the range of seconds to minutes [33]. Ginestet et al. reproduced the closest industrial effluent treatment conditions, with single VOCs (toluene, acetone and ethanol), concentrations ranging from 7–12 ppm and continuous flow rates of 40 and 80 $m^3.h^{-1}$ [42]. However, reported single-pass VOC conversions were lower than 50% which questions the relevance of PCO for VOC industrial effluents. Thus, further studies are needed to evaluate if PCO is effective for continuous flow rates of tens of $m^3.h^{-1}$, inducing residence times of the VOCs in the photocatalyst vicinity lower than one second, and VOC concentrations higher than 1 ppm.

This study aims at evaluating photocatalytic oxidation process for the treatment of industrial emissions under realistic conditions. To that end, a 500 L semi-industrial single-pass PCO reactor is designed. Performances in terms of isopropanol (IPA) conversion and mineralization are evaluated under semi-industrial emission conditions, i.e. (i) continuous flow rates from 26 to 146 $m^3.h^{-1}$ and (ii) VOC concentrations ranging from 1.8 to 14.6 ppm. These flow rates and concentrations are in the lowest range of usual industrial emission conditions, i.e. VOC concentrations ranging from few ppm to thousands of ppm and flow rates from tens to tens of thousands of $m^3.h^{-1}$. However, these experimental conditions were defined from a realistic industrial issue. The designed reactor encompasses a variable number of treatment stages, from 1 to 10, and a variable total number of photocatalytic media, from 0 to 30, in order to modulate the PCO treatment capacity. Ultimately, in order to emphasize the impact of the structure of the initial VOC, the performances of the PCO reactor are evaluated regarding acetaldehyde mineralization.

IPA is selected as model VOC since it is a widespread VOC in industry [43,44]. IPA is extensively used as degreasing agent in the semiconductor industry for the cleaning of silicon wafer surfaces [43] and in precision machinery industry [45]. The photocatalytic oxidation of IPA was formerly studied [46–48], but far from any realistic industrial effluent consideration. Nevertheless, it can be noticed that authors reported the generation of reaction intermediates, particularly acetone. Complete carbon mass balances of IPA PCO were seldom addressed. Carbon mass balances are though crucial for the assessment of VOC conversion into inert compounds, namely CO_2.

Furthermore, considering that industrial treatment requires low cost, effective and responsive instruments to continuously assess the process performances, the designed reactor is instrumented with commercially available metal oxide based gas micro-sensor arrays, to evaluate their ability to monitor IPA real-time PCO efficiency. Indeed, micro-sensor arrays may appear as relevant alternatives to conventional sampling and analytical techniques [49], especially when used in network with adequate pattern recognition algorithms [50]. There is a huge interest for micro-sensor arrays in various research fields, such as food industry [51], breath monitoring [52], olfactometry [53], outdoor pollution [54] and indoor air quality monitoring [55]. However, no study focused on their ability to follow the dynamic performances of an industrial air treatment system so far.

This work is divided into three parts: (i) a preliminary overview of IPA treatment with a defined initial reactor configuration, (ii) the investigation of operating parameter influence, i.e. IPA initial concentration, air flow rate, number of treatment stages, number of photocatalytic media and nature of inlet VOC and (iii) an operation cost comparison with other emission treatment techniques. The relevance of micro-sensor arrays is assessed throughout the different steps of the study to provide a global overview of their performances and limitations regarding PCO monitoring.

2. Experimental

2.1. Semi-industrial sensor instrumented PCO reactor

Experiments are carried out with an especially designed 500 L semi-industrial reactor, schematised in Fig. 1. This reactor is composed of a stainless steel air duct with a 30 cm × 30 cm square section. It can be divided into 3 main parts: (i) IPA injection section, (ii) upstream and downstream measurement sections and (iii) PCO treatment section.

The first section of the reactor consists in the IPA injection section. Gaseous IPA is generated and mixed with the main air flow. IPA is produced by bubbling from 375 $mL.min^{-1}$ to 2.25 $L.min^{-1}$ of zero air through liquid IPA (Sigma-Aldrich, 99.9%) placed in a Ministat 230 temperature-regulated bath (Huber). The IPA bubbler temperature is varied from −20 °C to 10 °C to modulate IPA concentration at the outlet of the bubbler. Typically, a temperature of 10 °C leads to 22,000 ppm of IPA at the outlet flow of the bubbler. In order to avoid any condensation of gaseous IPA, outlet tubing is regulated in temperature between 35