Applied Catalysis B: Environmental 232 (2018) 194–204

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Evaluation of self-cleaning photocatalytic paints: Are they effective under actual indoor lighting systems?

A. Galenda[a,*], F. Visentin[b], R. Gerbasi[a], M. Favaro[a], A. Bernardi[c], N. El Habra[a]

[a] CNR-ICMATE Institute of Condensed Matter Chemistry and Technologies for Energy, Italian National Research Council, Corso Stati Uniti, 4, 35127 Padova, Italy
[b] Department of Industrial Engineering, University of Padova, Via Gradenigo, 6/a, 35131 Padova, Italy
[c] CNR-ISAC Institute of Atmospheric Sciences and Climate, National Research Council, c/o Corso Stati Uniti, 4, 35127 Padova, Italy

ARTICLE INFO

Keywords:
Photocatalysis
Titanium dioxide
Self-cleanings
Indoor paints
Visible light

ABSTRACT

The aim of the paper is to assess the photocatalytic performance of self-cleaning paints – available in the market – designed for applications in indoor environment. Three self-cleaning photocatalytic paints were deeply characterised by means of complementary analytical techniques (X-Ray Diffraction, Thermogravimetry, Fourier Transform Infrared Spectroscopy in reflection mode and Absorption UV–vis Spectroscopy). In addition, the photocatalytic properties of the paints were tested accordingly to ISO 10,678 and ISO 2197-1 standards and in ad-hoc planned tests to evaluate their ability in methyl red and methylene blue bleaching under UVC, Xenon (with and without UV-400 filter), fluorescent and LED lamps exposure. To the best of our knowledge, this is the first paper dealing with the photocatalytic activity tests of indoor commercial self-cleaning paints under actual indoor light. Although restricted to the three investigated paints, the outcomes suggest that all samples are scarcely active under visible light and the pollutant probes are selectively bleached thanks to their sensitising effect. Consequently, the pollutants ability in injecting electrons in the TiO_2 conduction band deeply affects their removal. The paper highlights the requirement for an improved photocatalytic paint formulation with visible light active photocatalysts as well as the need of adequate ISO standards for visible light driven activity tests.

1. Introduction

The awareness of a healthy living environment is increasing in recent years and it concerns either outdoor or indoor locations. Recently, buildings and indoor living spaces have often been objects of dedicated studies aiming to optimise the energy demand in relation to heating and ventilating systems, as well as Indoor Air Quality (IAQ) management [1,2]. Designers and architects tend to limit the air mass exchanges with outdoor environment in order to minimise the energy demand for air conditioning, thus preferring the recycling of indoor air [3]. This involves the gradual increase in indoor pollutants and the decay in IAQ. The pollutants content in indoor spaces often reaches concentration higher than outdoor, thus requiring the introduction of adequate control and remediation systems in order to maintain a suitable air quality [4]. The main indoor air pollutants are usually particulate matters (PM), nitrogen oxides (NO_x), carbon monoxide (CO) and volatile organic compounds (VOCs) [5–7] that are produced by different sources like the adhesives and building materials' emission, the combustion processes as well as the use of household products, furniture, electric and electronic devices [8]. Skin and mucous membranes easily adsorb VOCs, which eventually induce damages to organs and metabolic systems or asthma and cardiovascular illnesses and are renowned for being linked to the Sick Building Syndrome (SBS) [4]. Finally yet importantly, the indoor VOC limits are not yet unambiguously set due to the wide number of chemicals involved, and the relevant guidelines differ from country to country [8]. The European Scientific Committee on Occupational Exposure Limits (SCOEL) [9] establishes the limits for several VOCs and hazardous chemicals in the workplaces but no clear indications can be easily found regarding domestic environments. To the best of our knowledge, some non-official reports indicate that a Total VOC (T-VOC) content lower than 200 $\mu g/m^3$ can be assumed as a good limit for preventing irritations or discomfort symptoms. 200–3000 $\mu g/m^3$ can lead to irritation and/or discomfort; in 3000–25,000 $\mu g/m^3$ range discomfort and headache are possible, while over 25,000 $\mu g/m^3$ the toxic range is reached. However, these limits are often not useful, since the effect of specific chemicals can be evident at very different concentrations (as an example, the 8-h TLV-TWA (threshold limit value – time weighted average) limit by SCOEL is 369 $\mu g/m^3$ for formaldehyde) and an ad-hoc study should be carried out for each specific compound.

Several remediation systems are available and indoor pollutant

* Corresponding author.
E-mail address: alessandro.galenda@cnr.it (A. Galenda).

https://doi.org/10.1016/j.apcatb.2018.03.052
Received 13 December 2017; Received in revised form 16 March 2018; Accepted 17 March 2018
Available online 19 March 2018

removal takes currently advantage of various technologies. Air filtration through filtering and/or adsorbing cartridges is often used, nevertheless this simple procedure need a periodic cartridges replacement-regeneration (thus producing new wastes) and an ad-hoc ventilating system for the air circulation through the filters (i.e. the installation of the fan system and the energy consumption for the working operations) [8].

An alternative and low-cost VOCs remediation system is based on the Advanced Oxidation Processes (AOPs), thanks to the employment of suitable photocatalytic wall paints [10], which are usually also known as "self-cleaning"; thanks to their ability to self-remove organic dirty stains from their surface. A photocatalytic paint exploits the properties of a photocatalytic substance promoting the mineralisation of the volatile organic and inorganic pollutants compounds present in air or deposited on paint surface, thus obtaining carbon dioxide, water and inorganic inert salts as final products, improving the air quality and preserving the original aesthetic aspect. Briefly, in the photocatalytic process, a semiconductor is irradiated by photons with adequate energy, thus creating a couple of a photo-electrons (e^-) and photo-holes (h^+) which can react with electron acceptors (O_2 as an example) and donors molecules, and initiating the oxidation process. Four main parameters affect the oxidation process, in particular: the catalyst amount, the photon wavelength, the concentration of the reactants and the radiation flux. Temperature does not deeply influence the catalyst performance if it is maintained in a room temperature range [11].

Dedicated scientific papers have always taken into account the performance of the photocatalysts themselves, but rarely the photocatalytic paint formulations have been characterised nor their performance accurately assessed in real or simulated indoor conditions [12–14]. The paint components, indeed, can significantly affect and modify the performance of the active photocatalytic compounds.

The self-cleaning photocatalytic paints can be designed for specific applications such as outdoor or indoor environments. In the latter case, the paint formulation should consider different light sources with respect to the outdoor one (i.e. the sun), with very different energy content for the activation of the photocatalytic compounds. Nevertheless, in the technical sheets of the paints under investigation, they are reported to be "active under artificial lights" and "effective without UV light", while the specific lighting requirements for their activation are not reported.

The self-cleaning photocatalytic paint formulation, of course, is topic of industrial patents, but most of the indoor photocatalytic paint producers describe their products involving titanium dioxide, which is considered one of the most suitable photocatalysts because of its chemical stability, non-toxicity toward environmental and living species, low cost and wide availability [15]. Nevertheless, TiO_2 large band gap requires UV photons for the electrons-holes generation, while common and next future indoor artificial light sources emit low (energy saving fluorescent lamps) or almost no-UV radiations (LED lamps).

The aim of the present manuscript is to assess the performances in different conditions of three commercial indoor self-cleaning photocatalytic paints with respect to their photocatalytic performances in different conditions. The products have been analysed anonymously and the brand is intentionally not reported. The producers declare that the active paints are designed for indoor application and do not requiring UV radiation for their activation. The selected paints have been fully characterised and their photocatalytic performance has been investigated toward NO_x (i.e. for the indoor air quality improvement) and methylene blue removal (i.e. for self-cleaning action), according to the ISO standards 22197-1 [16] and 10678 [17] respectively. The ISO standards have been taken into account in order to provide an impartial evaluation of the paint performance, thus giving a benchmark for the comparison of the obtained results. Ad-hoc experiments were furthermore designed for testing their action in bleaching methyl red and methylene blue stains under different light sources (UVC, Xenon, fluorescent and LED lamps).

The paint producers usually refer to the ISO standards for the certification of the photocatalytic properties and these protocols are generally planned under UVA light. This light source, however, is not used in the ordinary indoor conditions. Therefore, the paints were tested under prevalent indoor lights (fluorescent and LED lamps) in order to provide a valuable comparison with respect to more energetic sources. The recent ISO 19810:2017 standard [18] takes into account the use of visible light for testing the self-cleaning properties of photocatalytic materials. Nevertheless, this protocol prescribes the monitoring of the water contact angle (CA) as photocatalytic activity indicator. Unfortunately, the CA measurement cannot be performed on porous substrates (like the paints) that immediately absorb water.

2. Experimental

2.1. Materials

The three white (i.e. without any kind of colouring agent) commercial photocatalytic paints were kindly supplied by the manufactures and used without any further modification. They were named in general terms as Self-Cleaning Paint 1–3, shortly "SCP-1", "SCP-2" and "SCP-3".

2.2. Measurements

The photocatalytic paints were characterised by complementary analytical techniques. The crystallographic structure was determined by X-Ray Diffraction (XRD) performed by means of a Philips X'Pert PW 3710 powder diffractometer operating in Bragg–Brentano θ–2θ geometry mode, using Cu Kα radiation ($\lambda = 0.154$ nm, 40 kV and 30 mA). Standard 2002 ICDD database files supported the phase identification.

The IR spectra were collected by a FT-IR Thermo-Nicolet IS10 spectrophotometer accumulating 32 scans at a resolution of 4 cm^{-1}. The samples were directly analysed in ATR mode (paint on glass slide). Moreover, a small amount of each commercial paint was treated with chloroform and the extract analysed in reflection mode with micro-IR (Thermo-Nicolet IS10 spectrophotometer coupled with Nicolet Continuμm microscope) by FT-IR.

Thermogravimetric analyses (TG/DTA) were carried out under air atmosphere, with a heating rate of 5 °C/min from room temperature up to 1200 °C, using the Netzsch STA 449 TG/DTA analyser.

The optical characterisation of the samples was performed with the Unicam UV500 spectrophotometer.

Each paint was deposited on microscope glass slides (1 mm in thickness was pursued in order to avoid any contribution by the holder material and thus observing only the actual paint effect) and dried in air for 24 h at room temperature (the paint homogeneity (absence of significant cracks) was checked by optical microscope at increasing magnitudes). The slides were then stained with 20 μL of methyl red (MR) or methylene blue (MB) solutions (56 μmol/L), dried in air at RT in dark conditions for 24 h and then exposed for 10 h to: UVC lamp (low pressure Hg lamp, total power 25 W, 750 lx, 10.5 W/m^2 in 220–280 nm range, 0.55 W/m^2 in 280–315 nm range, 0.30 W/m^2 in 315–400 nm range, 2.5 W/m^2 in 400–1050 nm range), Xenon lamp (5000 lx, with UV-400 filter – 0.001 W/m^2 in 220–280 nm range, 0.0005 W/m^2 in 280–315 nm range, 0.072 W/m^2 in 315–400 nm range, 23.6 W/m^2 in 400–1050 nm range and without UV-400 filter 0.0013 W/m^2 in 220–280 nm range, 0.001 W/m^2 in 280–315 nm range, 0.135 W/m^2 in 315–400 nm range, 23.9 W/m^2 in 400–1050 nm range), LED (500 lx, 0.0007 W/m^2 in 220–280 nm range, 0.0003 W/m^2 in 280–315 nm range, 0.0002 W/m^2 in 315–400 nm range, 1.2 W/m^2 in 400–1050 nm range) and fluorescent lamps (500 lx 0.0009 W/m^2 in 220–280 nm range, 0.0004 W/m^2 in 280–315 nm range, 0.0033 W/m^2 in