Selection of commercial photocatalytic materials based on their air-purifying ability

M. Palacios [(1)], L. Núñez [(1)], S. Suárez [(1)], B. Sánchez [(1)], M. Pujadas [(1)], J. Fernández-Pampillón [(2)]

[(1)] *CIEMAT (Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas).*
+34- 91 346 65 41, e-mail: magdalena.palacios@ciemat.es

[(2)] *UNED (Universidad Nacional de Educación a Distancia).*

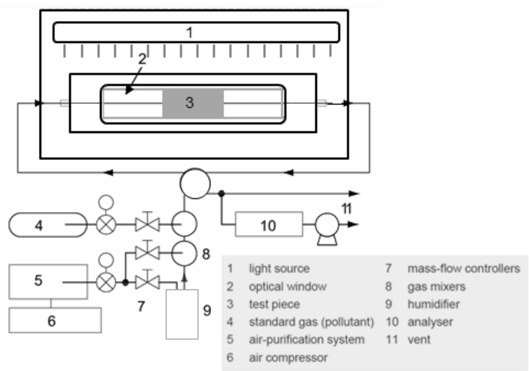
1. Introduction – Air pollution caused by road traffic is one of the major problems in highly populated areas. In particular, despite the increased control requirements and the installation of emission reduction systems, air pollution by nitrogen oxides (NO_x) from diesel engines remains a serious concern in inner-city areas [1]. Current environmental legislations [2] establish increasingly limiting values for NO_2 that promote the research and the development and tuning of control strategies that could help to alleviate the atmospheric impact of emission sources.

One complementary emerging strategy that could help to mitigate air pollution at urban areas is the use of photocatalytic products which can be implemented on a vast variety of urban infrastructures. Applying TiO_2-modified coatings or cementitious materials onto the external covering of buildings or roads might be a supplement to conventional technologies, such as catalytic converters fitted on the vehicles, for mitigating air pollution. These TiO_2-based products are activated in the presence of sunlight and can remove, more specifically, nitrogen oxides (NO_x) from the ambient air via heterogeneous photocatalysis [3]. This option could be especially interesting for different European urban agglomerations, exceeding the limit values for NO_2 (Directive 2008/50/EC), like the case of Madrid city and the close municipalities.

In the framework of the European project LIFE MINO$_x$-STREET, co-financed by the EU, a variety of commercial photocatalytic materials has been tested under controlled conditions and the results used to compare the potential usefulness of them to act as NO_x sink and select, among them, the most promising solutions to be implemented on urban surfaces at real conditions. Additionally, in order to assess which could be the environmental effect on pollution levels if photocatalytic materials were applied in one street of a particular city or, furthermore, modelling the foreseen effects if such materials were implemented in the whole city, NO_x deposition velocities need to be estimated. Here, a simple numerical approach for estimating NO_x deposition velocities is described and the estimates compared.

2. Experimental – Assessing the role that the use of commercial photocatalytic materials designed to air purification could play in combination with other strategies for air quality management make imperative to provide evidences from rigorous essays and tests on their physical-chemical properties and expected efficiency, not only under controlled laboratory conditions but also in real atmosphere.

Image 1. Scheme of the ISO 22197-1:2007 test equipment.



Since the variety of different commercial photoactive materials offered by the European market is very wide, a rigorous selection of the materials and conditions of use is needed.

In the framework of the European project just mentioned above, a strict essay protocol has been developed to test and compare the potential usefulness of a variety of commercial photocatalytic materials to act as NO_x sink when are implemented on urban surfaces at real conditions. On the one hand, their mechanical and physical properties, operation-induced changes and durability, involving both laboratory essays and large scale experiments, have been tested. On the other hand, their photoactivation and air-purifying capacity, chemical and structural properties and changes induced by ageing and regeneration processes, both under controlled as ambient conditions, have been investigated and documented. Finally, the selection, among them, of the most promising photoactive materials to be applied and tested at large scale under real ambient conditions has been done. In this work, we just present the essays and experiments carried out in order to characterize the air-purifying ability of several selected materials and estimate NO_x deposition velocities that are needed for modellers to evaluate the potential impact of their use at real urban scale.

The photocatalytic activity of several photocatalytic materials (bituminous concrete pavements –BCP–, sidewalk concrete pavements –SCP– and coatings applied to facades –CF–) has been essayed under ISO 22197-1:2007 [4]. In bed flow photo-reactor experiments, like the one presented here, a test gas mixture flow (NO, air, H_2O) (50% relative humidity) is passed over the flat rectangular sample of typically 5 cm x 10 cm and is irradiated by UV-A light (10 W m^{-2} irradiance) through a UV transparent window with a distance to the sample of 5 mm. Under the conditions applied, a laminar-plugged flow is assumed and very short reaction times of only a few seconds are obtained. This set-up is comparable to a classical flow tube approach often used in heterogeneous chemistry [3]. However, in contrast to a classical first-order kinetic analysis of the uptake data, only the numbers of NO_x molecules (μmol) are quantified for a defined concentration, gas flow rate, reaction time and geometry of the reactor are used then for the ranking of the activity of the material.

It has been demonstrated that oxides such as NO, NO_2 at low concentration levels can be treated by TiO_2 under UV irradiation [5]. The mechanism of pollution decomposition is described elsewhere [6].

The amount of NO removed from the test gas can be calculated following the formula given by the ISO 22197-1:2007:

$$n_{NO} = (f/22{,}4) \int \left(\emptyset_{NO_{in}} - \emptyset_{NO_{out}} \right) dt \tag{1}$$

where n_{NO} is the amount of NO removed by the test piece (μmol), f is the air-flow rate converted into that at the standard state (0°C, 101.3 kPa, and dry gas basis) (l min^{-1}), $\emptyset_{NO_{in}}$ is the supply volume fraction of nitric oxide (μl l^{-1}) and $\emptyset_{NO_{out}}$ is the nitric oxide volume fraction at the reactor exit (μl l^{-1}).

Another way to express the photocatalytic efficiency is the conversion, χ. This is a dimensionless measure of the NO abatement and it is a function of the initial and final concentrations of the pollutant. The NO conversion, χ ,is defined as:

$$\chi = \left(\frac{\emptyset_{NO_{in}} - \emptyset_{NO_{out}}}{\emptyset_{NO_{in}}} \right) \cdot 100 \tag{2}$$

3. Results and Discussion – The nitric oxide (NO) removal efficiency for the different photocatalytic materials essayed (bituminous concrete pavements –BCP–, sidewalk concrete pavements –SCP– and coatings applied to facades –CF–), tested under ISO essay, showed a great variability from near non-active to highly active materials. This wide range of air-purification performance depends not only on the material or product itself but also on the substrate on which the products are applied (Images 2, 3 and 4). More specifically, the NO conversion χ obtained for BCP was in the 3 to 46, for SCP 3 to 65 and for CF 0.5 to 38 ranges, respectively.

Image 2. Nitric oxide (NO) removal efficiency for tested photocatalytic sidewalk concrete pavements.

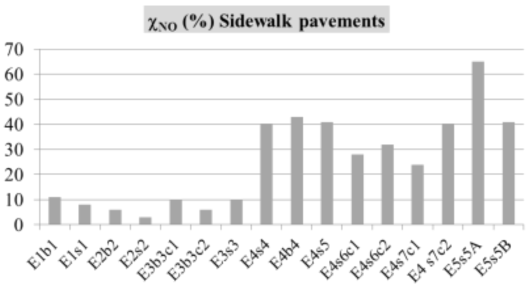


Image 3. Nitric oxide (NO) removal efficiency for tested photocatalytic bituminous pavements.

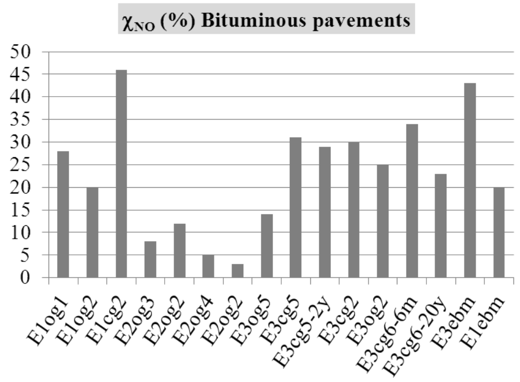
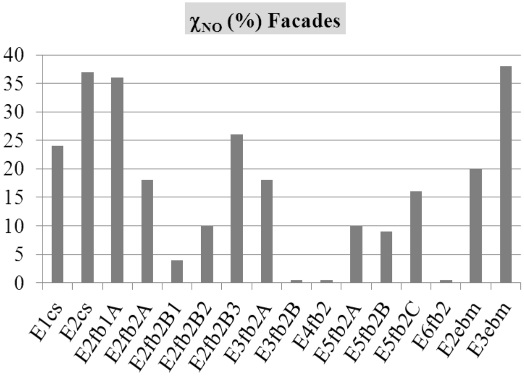


Image 4. Nitric oxide (NO) removal efficiency for tested photocatalytic coatings.



A detailed discussion of the factors influencing the photocatalytic efficiency observed is out of the scope of this work. However, it is important to note that not only the substrate and photocatalytic products but also the way of application of those products (spraying, rolling) can have a huge influence in the efficiency observed. So, apart from the inter-sample variability that can be expected, the intra-sample variability can be non-negligible in some cases and should be taken into account and quantified. This factor could have a greater relevance at real scale where the conditions of application are not always so well controlled.

Taking the removed NO as starting point, it is possible to estimate an NO deposition velocity by using the NO mass removed. A surface deposition velocity, V_{surf}, can be approximated from the removed NO under the testing conditions as follows:

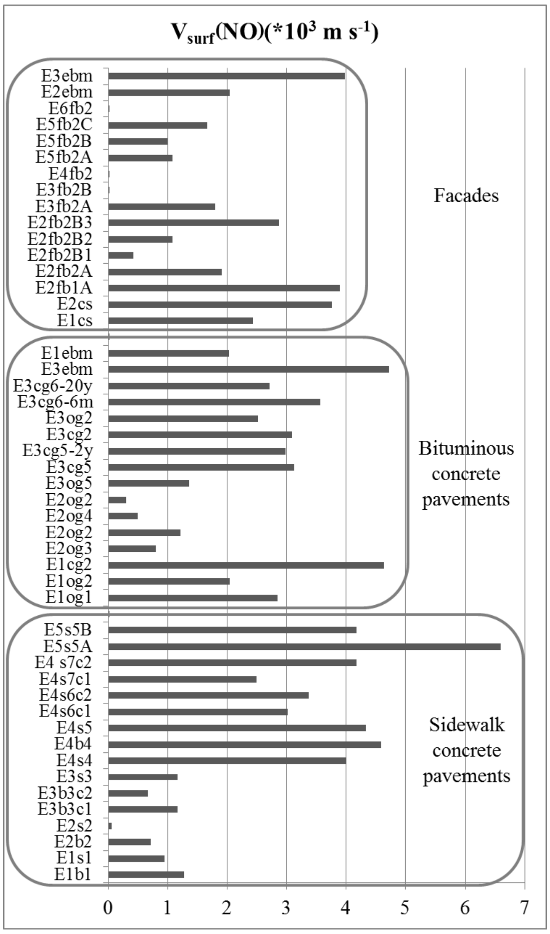
$$F_{surf} = \frac{f \cdot \left(\emptyset_{NO_{in}} - \emptyset_{NO_{out}}\right)/22{,}4}{W \cdot L} \cdot M_{NO} \qquad (3)$$

where W is the test piece width (m), L is the test piece length (m), M_{NO} is the molar mass of NO (g mol^{-1}) and F_{surf} is the NO flow at the surface (e.g. µg m^{-2} s^{-1}).

Then, an approximate surface deposition velocity can be estimated as follows:

$$V_{surf} = -\frac{F_{surf}}{C_{NO_{in}}} \qquad (4)$$

Image 5. NO surface deposition velocities approximated by NO mass balance.



where V_{surf} is the deposition velocity (ms^{-1}) and $C_{NO_{in}}$ is the NO mass concentration (µg m^{-3}) at the inlet.

Consequently, the surface deposition velocities, V_{surf}, computed by following a simple NO mass balance approximation, reflect the diverse purifying capabilities (Image 5).

The average estimated values of V_{surf} (m s^{-1}) for the types of photocatalytic materials tested were 0.0027±0.0019 (BCP), 0.0024±0.0013 (SCP) and 0.0017±0.0014 (CF), respectively.

4. Conclusions – A comparative study on photocatalytic materials, available in the European market, was carried out in order to assess their efficiency. NO degradation was found to vary notably under optimum laboratory conditions. Not all products tested under ISO essay have shown a significant photocatalytic activity. However, some of them have demonstrated a substantial capacity to remove NO, potentially enough to observe NO sink effects in ambient air. Nevertheless, a proper selection of air-purifying products for projected applications at real scale is mandatory.
Additionally, experimental results of the ISO test can be used to compute an approximate surface deposition rate of NO by using a simple mass balance. This deposition rate is dependent on both the geometry of the photo-reactor and the physical conditions in which the test is carried out. However, they can be useful to have an estimation close to the actual value of the NO deposition velocities magnitude we could expect for different photocatalytic materials and their potential effect in outdoor conditions.

5. References

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