In-situ evaluation of the NO_x removal efficiency of photocatalytic pavements: statistical analysis of the relevance of exposure time and environmental variables

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Abstract

In the recent past, the NO_x removal efficiency of photocatalytic materials has been subject of many studies with promising results. However, many of these studies involve laboratory tests carried out under standardized climatic exposure conditions, often not representative of the real world environment. With the aim to bridge this gap, selected photocatalytic materials have been applied to different substrates in outdoor demonstrator platforms at pilot scale as part of the project LIFE-PHOTOSCALING. The paper presents the results of in situ measurements of NO_x removal efficiency of the materials, performed during 17 months. Statistical models accounting for the influence of exposure time and relevant environmental variables are derived. They suggest that photocatalytic emulsions on the tested asphalt experience a significant loss of activity over time irrespective of climatic conditions. The efficiency of photocatalytic slurries on asphalt and of concrete tiles, with the photocatalyst applied on surface or in bulk, mainly depends on substrate humidity.

Keywords: NO_x; photocatalysis; pavements; efficiency; in situ; outdoor test; pilot scale; environmental variables

1. Introduction

Even though NO_x has harmful effects on human health, agricultural crops and ecosystems, ceilings for NO_x are systematically exceeded in most of big European cities (EEA 2016). In this context, the development of photocatalytic construction materials represents a promising technology for the efficient removal of chemical contaminants. These materials incorporate a semiconductor, mainly TiO₂, in bulk or as surface coating and are activated by the UVA region of the solar spectrum.

In particular, for abatement of NO_x pollution from motor vehicle emission, the photocatalytic pavements are promising substrates due to their large surface area, closeness to the emission focus, and its relatively flat configuration that favours the interaction between the solar light irradiation and the photocatalyst.

In recent decades, a wide number of laboratory-scale tests have been performed in order to evaluate the NO_x depolluting properties of TiO₂ photocatalytic materials (Ballari et al. 2010, Bengtsson & Castellote 2010, Chen & Poon 2009, Folli et al. 2012, Jimenez-Relinque & Castellote 2015, Jimenez-Relinque et al. 2015). However, the experimental conditions of lab-scale tests usually are not representative of the environmental conditions and thus, the corresponding results may lack the required information for prediction of the behaviour of a material exposed to real outdoor climates. In order to bridge this gap, some attempts have been made (Suarez et al. 2014), (Caillol 2011), (Mo et al. 2009) and (Chen et al. 2007). Other real scale studies in streets or pilot street canyons are reported in (Boonen & Beeldens 2014), (Maggos et al. 2008) and (Ballari & Brouwers 2013). However, the results reported in these tests are quite different, as they have been determined by very different procedures. Model simulations and statistics are alternative approaches (Dylla et al. 2013), but they need a significant number of parameters subject to high uncertainties (i.e. meteorological conditions, air pollutants variety, street configuration etc.), what hinders a straightforward assessment of the validity and reliability of the results.

Within this context, the Life project LIFE-PHOTOSCALING (<http://www.life-photoscaling.eu/>) intends to scale up the photocatalytic technology in urban agglomerations from laboratory measurements to application in cities. In particular, the project aims at developing a decision support tool to assess the sustainability of a particular material in a particular environment based on the evaluation of its behavior according to three types of indicators (photocatalytic efficiency, durability and possible side effects). As one of the project actions, the NO_x removal efficiency of different materials has been evaluated by in-situ measurements at pilot scale. The tests have been carried out from February 2017 to June 2018, on slabs located in the city of Madrid.

The in-house developed experimental device PHOTONSITE (PCT/ES2016/070808 (Castellote 2016)) was used for the tests, as described in section 2. The results are presented in section 3, together with those of the laboratory analysis of cores extracted from the slabs at initial time. Subsequently, the relevance of exposure time and the effect of environmental parameters (temperature, humidity, and daylight hours) on the in-situ measurements is discussed on the basis of a statistical analysis (section 4).

2. Experimental

2.1. PHOTONSITE device

PHOTONSITE allows evaluating the photocatalytic activity in situ without altering the photocatalytic, mechanical and surface properties of the tested material. The sealing joints confine an area of 176.71 cm² (Figure 1). The device is adaptable to all types of materials and infrastructures under use of gas bottles (single configuration) or outdoor air incorporating a double chamber as reference (double configuration). PHOTONSITE enables the evaluation of photocatalytic efficiency for different contaminants incorporating the corresponding analytic tool. Integrated devices allow for temperature (T_{int}) and humidity (RH_{int}) monitoring inside the chamber. It is equipped with a system of irradiation (UV or visible light). Beside this, sunlight irradiation can be used by replacing the chamber cover for a transparent window cover. Two mass flow controllers are used to prepare the gas mixture supplying a specific flow rate. A fan homogenizes the NO_x concentration (C) inside the reactor. The raw results are transferred to a data acquisition system as depicted in Figure 1.

Figure 1. PHOTONSITE in single configuration.

The NO_x removal ability of PHOTONSITE was validated by comparison with the standard ISO 22197:1-2007. Five photocatalytic materials (paint –M1, aqueous emulsions–M2, M3, and pre-cast concretes–M4, M5) were tested at the lab in both chambers (ISO reactor and PHOTONSITE) using the same samples in the same conditions.

Two mass flow controllers were used to prepare the mixture supplying a flow rate of 3 ± 0.15 L/min. The gas supply was adjusted until reaching an initial concentration of 1000 ± 50 ppb of NO at a temperature of $25 \pm 2.5^\circ\text{C}$ and a relative humidity of $50 \pm 5\%$. The test gas was allowed to flow into both reactors without irradiation for 30 min. After 30 min, the sample was irradiated during 5 h at 10 W/m^2 . Subsequently, the light irradiation was stopped and clean air was allowed to enter into the reactors for a further 30 min. NO_x concentration of the gas was monitored using a chemiluminescence analyzer (AC-32M, Environment S.A.).

2.2. In-situ outdoor tests

The NO_x removal performance of photocatalytic materials in outdoor conditions was assessed by means of the PHOTONSITE device (section 2.1). The materials were implemented at pilot plant scale between October and November 2016 in two platforms located in Madrid, Spain. These platforms consist of different banks of proofs, constituted by 1×1 or $2 \times 2 \text{ m}^2$ sized slabs.

Nine different materials (“material” refers here to a specific commercial photocatalytic product applied to a specific type of substrate, asphalt (A)^a or tile (T), are analysed in the present paper). These nine materials can be distinguished into three types as follows:

1. Two cementitious slurries applied on asphalt (S/A-1 and S/A-2)
2. Three emulsions applied on asphalt (E/A-1, E/A-2, E/A-3)
3. Four concrete tiles with the photocatalyst applied on the surface or in bulk (T-1, T-2, T-3, T-4).

^aair voids UNE-EN 12697-08:2008 = 24.6 (%)

The operational conditions of the PHOTONSITE in situ tests have been: 450 ± 50 ppb_v of NO gas in air at a flow of 3 L min^{-1} with a relative humidity RH_{int} inside the chamber of around 25%. The irradiance inside the chamber was 10 Wm^{-2} (LEDs 365 nm) for 15 minutes. Prior and after irradiation, the gas flow passed through the PHOTONSITE chamber until stabilization of the conditions. The NO_x concentration of the gas was monitored using a chemiluminescence analyzer (AC-32 M, Environment S.A.). The pavement was not modified or preconditioned at all.

The percentage NO_x removal, R_{NO_x} , was determined 7 times (February, May, July, September and November 2017, and February and June 2018). A weather station located on the platform continuously monitored the outdoor relative humidity (RH_{air}) and temperature (T_{air}).

2.3. Laboratory tests

To evaluate the time-dependent durability loss of the NO_x removal ability of the materials under constant climatic exposure, laboratory measurements according to the standard ISO 22197-1:2007 were performed on specimens extracted from the slabs of the platforms at the time of implementation (t=0): at t = 6 and t = 19 months. In between these measurements, the specimens were stored in laboratory environment in plastic bags.

3. Results

3.1. PHOTONSITE test validation

The results of the PHOTONSITE test validation are shown in Figure 2, which plots the NO_x removal (R_{NOx}) [%] in the PHOTONSITE chamber against R_{NOx} measured in the ISO 22197:1-2007 chamber. The resulting data indicates that the PHOTONSITE chamber provides reliable and comparable measures of the NO_x removal rate obtained using the laboratory chamber according to ISO standard 22197:1-2007. This result validates the suitability of PHOTONSITE for the determination of the photocatalytic activity of construction materials.

Figure 2. Percentage NO_x removal, R_{NOx} (%), obtained for samples M1-M5 using PHOTONSITE vs ISO 22197:1-2007 chambers.

3.2. In situ tests

The percentage NO_x removal, R_{NO_x} , measured in situ by means of the validated PHOTONSITE device at different points in time t (n° of months between implementation of the materials in the platforms and the NO_x measurement) is illustrated in Figure 3 (black, square-shaped dots). It can be seen that the behaviour is strongly material dependant; however, similar trends can be noticed in function of the type of material. Slurries on asphalts (S/A) show a relatively constant NO_x removal activity with minor fluctuations over time, indicating some dependency on the climatic exposure conditions. On the contrary, emulsions on asphalts (E/A) exhibit an almost steady decrease of the NO_x removal rate with increasing time of exposure. Finally, the materials belonging to the tiles group (T) show a behaviour characterized by significant fluctuations of R_{NO_x} over time, suggesting a significant influence of the environmental exposure conditions. A more detailed analysis of these influences on the NO_x removal ability of the different materials is given in section 4.

Figure 3. Observed and predicted R_{NO_x} [%] versus time parameter t [months].

3.3. Laboratory tests

The percentage loss of NO_x removal activity over time (LR_{NO_x}) with respect to the initial R_{NO_x} , obtained in the laboratory tests according to the standard ISO 22197-1:2007 is given in Figure 4. It can be seen that all tested materials show a certain loss of activity over time, except material T-3, which maintained its efficiency over time. These results confirm that both the type of the product and the substrate strongly affect the photo-activity lifetime of the materials. Emulsions on asphalts (E/A) seem to be affected most importantly by the time-dependant loss of NO_x removal capacity, whereas materials of the type S/A or T, with the exception of T-2, show a comparatively more stable behaviour over time. The results are in agreement with in situ measurement (section 3.2),

Figure 4. Logarithmic adjustment to percentage loss of NO_x removal, LR_{NO_x} , of photocatalytic pavement specimens kept at the laboratory.

4. Discussion

4.1. Modelling approach

The experimental results presented in section 3 suggest that the NO_x removal ability is influenced by both the exposure time and the environmental exposure conditions. The laboratory experiments for the specimens stored in indoor conditions showed that the percentage of NO_x removal (R_{NO_x}) by almost all analysed materials

steadily vanishes with increasing exposure time t (Figure 4), with significant differences depending on the type of material. The dashed line in Figure 5 is a schematic representation of this performance loss. However, the in-situ measurements realised on materials exposed to outdoor environmental conditions (square-shaped dots in Figure 3), showed that the steady, time-dependant durability loss might be significantly altered. It was observed that due to the continuously varying climatic influences like irradiation, temperature or relative humidity, the actual NO_x removal ability of specific materials might be subjected to significant fluctuations over time, as represented in a schematic manner in Figure 5.

Figure 5. Schematic representation of NO_x removal, R_{NO_x} , as a function of time t under exposure to, respectively, constant and real, variable climatic conditions

In order to quantify the two principal influences on the NO_x removal ability, i.e. the steady, time-dependent loss and the environmental influences, a statistical analysis has been performed. Least squares regression yields the relationship between the percentage of NO_x removal (R_{NO_x}), as measured in the in-situ tests carried out between February 2017 and June 2018 (section 3.2), a time parameter and different environmental influence variables, acquired by means of the weather station. The general expression of the proposed model is given by equation (1). Based on the observations on the laboratory experiments (Figure 4), the steady, time-dependant loss of R_{NO_x} is assumed as a logarithmic function of time parameter t that represents the number of months between the implementation of the photocatalytic materials and the date of evaluation. The potential environmental influence parameters on R_{NO_x} that are analysed in the present study are the outdoor air temperature at the time of the R_{NO_x} evaluation (T_{air}), the mean value of the relative air humidity over the last X days before this evaluation ($\text{RH}_{\text{air},X}$) and the number of daylight hours corresponding to the evaluation day (DLH). Further explanations on the choice of the T_{air} and $\text{RH}_{\text{air},X}$ is given below.

$$R_{\text{NO}_x} = a + b_1 \cdot \ln(t) + b_2 \cdot T_{\text{air}} + b_3 \cdot \text{RH}_{\text{air},X} + b_4 \cdot \text{DLH} \quad (1)$$

Where:

R_{NOx} :	Percentage removal of NO _x [%]
t :	Time parameter [n° of months between implementation of the materials and the NO _x measurement]
T_{air} :	Air temperature at time of NO _x measurement [°C]
$RH_{air,X}$:	Mean value of relative air humidity temperature over the last m days before the NO _x measurement [%]
DLH:	Daylight hours (hours between sunrise and sunset) [h]
a :	Intercept
b_i :	Parameter estimates

Rather than the outdoor air temperature T_{air} , the temperature inside the PHOTONSITE reactor used for the tests (T_{int}) directly influences the photocatalytic process and hence R_{NOx} . However, it should be noted that T_{air} and T_{int} are strongly intercorrelated. A least squares regression over the 63 observations of, respectively, T_{air} and T_{int} , gathered during the seven R_{NOx} measurements corresponding to each of the nine photocatalytic materials, yields the relationship expressed by equation (2). The associated coefficient of correlation R amounts to about 0.93. Bearing this relationship in mind, the outdoor air temperature T_{air} is introduced instead of T_{int} as a potential explanatory variable in the regression analysis.

$$T_{int} \cong 4.2 + 0.85 \cdot T_{air} \quad T_{air} \text{ and } T_{int} \text{ in } [^{\circ}\text{C}] \quad (2)$$

As a measure for the humidity of the substrates to which the photocatalytic agents are applied, the mean values of the relative outdoor air humidity over the last $X = 1, 3, 7, 14$ or 28 days, respectively, before the R_{NOx} measurement ($RH_{air,X}$) are considered as potential explanatory variables in the analysis. Previous tentative trials suggested that the relative air humidity at the specific time of the NO_x measurements does not adequately represent the humidity of the substrates. This is attributable to the inertia of the materials associated with the adsorption and desorption of water, which is believed to depend primarily on the pore size and distribution (Andrade & Castillo 2003). Corresponding measurements are in progress and will be evaluated in future studies. It should also be kept in mind that the relative humidity inside the PHOTONSITE reactor during the R_{NOx} measurements, imposed by the test conditions (Section 3.2), is an almost constant value ($RH_{int} \approx 25\%$) that is not related to the outdoor relative humidity.

4.2. Statistical analysis

A stepwise analysis method known as “backward elimination” is applied (IBM 2012). This procedure consists in initially including all the potential explanatory variables X_i and in each subsequent step eliminating the least significant one, as determined by the t-test, based on the t-distribution by Student. The regression procedure

ends when the p-value for all the variables remaining in the model is less or equal than the specified threshold value of 0.1.

The evaluation and comparison of the goodness-of-fit of models with different numbers of explanatory variables X_i is based on the adjusted coefficient of determination $\bar{R}^2$ which takes into account the number of degrees of freedom, in turn depending on the number of observations ($n=7$) and the number of X_i included in the model (Smith 1988).

The results of the described regression analysis are summarised in Table 1. The presented findings include the coefficient of determination R^2 , the adjusted R^2 , $\bar{R}^2$, the model intercept a , as well as the parameter estimates b_i and associated p-values of the statistically significant explanatory variables X_i .

Table 1. Results of the multiple linear regression analysis

Substrate	Photocat. product	Material	R^2	$\bar{R}^2$	Intercept		Explanatory variables		
					a	p	X_i	b_i	p
A	S	S/A-1	0.91	0.81	6.85	0.068	T_{air}	-0.40	0.014
							DLH	0.85	0.018
							$RH_{air,28}$	-0.10	0.035
	E	S/A-2	0.89	0.86	4.11	0.000	$RH_{air,28}$	-0.05	0.002
		E/A-1	0.74	0.69	10.51	0.006	$\ln(t)$	-3.64	0.013
		E/A-2	0.74	0.69	9.71	0.004	$\ln(t)$	-3.11	0.013
T	E or B	E/A-3	0.89	0.87	12.72	0.001	$\ln(t)$	-4.53	0.001
		T-1	0.58	0.50	10.48	0.011	$RH_{air,3}$	-0.14	0.046
		T-2	0.96	0.92	40.03	0.007	$\ln(t)$	-4.05	0.008
							$RH_{air,3}$	-0.41	0.008
							T_{air}	-0.41	0.024
		T-3	0.80	0.76	18.22	0.000	$RH_{air,3}$	-0.19	0.007
		T-4	0.82	0.79	8.90	0.001	$RH_{air,3}$	-0.12	0.005

A: Asphalt; T = Tiles; S = Slurry; E = Emulsion coating; B = Bulk

For the two materials of type S/A (slurries on asphalt), S/A-1 and S/A-2, the analysis yields fairly well fitted models to the available data, as expressed by R^2 values of around of 0.9. In spite the laboratory tests of these materials performed under constant climatic conditions yielded a loss of R_{NOx} after $t \approx 19$ months, of respectively 33 and 48% (Figure 4), time parameter t is not identified as a statistically significant explanatory variable. The climatic influences alone are able to explain large part of the variance of the NO_x removal (R_{NOx}). A common finding for both S/A type materials is that the mean values of the relative outdoor air humidity over the last 28 days before the NO_x removal measurement ($RH_{air,28}$) has a statistically significant effect on R_{NOx} ,

what seems to be relatable to the humidity of the substrate. In addition, the outdoor air temperature T_{air} and the daylight hours DLH are found to be significant in case of material S/A-1. However, a variance inflation factor (VIF) of 6.7 corresponding to T_{air} indicates a strong intercorrelation between T_{air} and, respectively, $RH_{\text{air},28}$ and DLH. However, taking account of this intercorrelation, a simplified model for the NO_x removal by means of material S/A-1 can be deduced, depending on two explanatory variables only, $RH_{\text{air},28}$ and DLH. The parameter estimates b_i corresponding to these variables, which can be considered as independent of each other, are $b_3 = b_{RH,28} = 0.01$ and $b_4 = b_{DLH} = 0.17$. The corresponding intercept is 1.61. Figure 3a compares the predicted R_{NO_x} by means of both models, the original and the simplified model, to the R_{NO_x} obtained the in-situ tests, plotted versus time parameter t . The prediction accuracy of the simplified model is not as high as in the original model, but on average still reasonable. The comparison for material S/A-2 is given in Figure 3b. In this case, the deduced model, depending on $RH_{\text{air},28}$ only, delivers very accurate predictions.

NO_x removal of the three materials belonging to type E/A (emulsions on asphalt) is neither significantly influenced by the relative humidity, nor by any other of the herein studied parameters. The regression analysis suggests that the NO_x removal ability exclusively depends on time parameter t . This is revealed by the obtained p values corresponding to explanatory variable $\ln(t)$, all significantly below the established threshold value of 0.1. The significant influence of time t on R_{NO_x} corroborates the results from the laboratory tests, where a comparatively high loss of NO_x removal after $t \approx 19$ months was detected for the E/A type materials, between $LR_{\text{NO}_x} = 57$ and 100% (Figure 4). The comparison between observed and predicted R_{NO_x} is provided in Figure 3c to 3e.

The NO_x removal of the four materials corresponding to type T (concrete tiles with the photocatalyst applied on the surface or in bulk) is found to be dependent on the relative air humidity. However, rather than the 28 days average, which is relevant to the performance of the S/A-type materials, the mean value over the last 3 days before the measurement ($RH_{\text{air},3}$) is identified as a statistically significant variable for all four T-type materials. The negative sign of the corresponding parameter estimates reveals that, as could be expected, the lower $RH_{\text{air},3}$ the higher is the predicted R_{NO_x} .

Other explanatory variables than $RH_{\text{air},3}$, namely the air temperature T_{air} and $\ln(t)$, are relevant for material T-2 only. As observed before for material E/A-1, relatively large VIF up to 10 are indicative of significant intercorrelations among the explanatory variables. In particular, air temperature T_{air} and relative humidity $RH_{\text{air},3}$ are strongly intercorrelated, whereas the intercorrelation between $\ln(t)$ and these environmental variables could, for sake of simplicity, be neglected. Taking account of the intercorrelations, a simplified model for R_{NO_x} might be derived, which depends on $\ln(t)$ and $RH_{\text{air},3}$ only. The associated parameter estimates are $b_1 = b_{\ln(t)} = -2.32$ and $b_3 = b_{RH,3} = -0.16$ and the intercept is $a = 16.13$. Figure 3g offers a comparison of the predicted R_{NO_x} by means of both models, the original and the simplified model, to the R_{NO_x} obtained the in-situ tests on material T-2.

The significant dependency of the NO_x removal of material T-2 on the exposure time was already anticipated in the laboratory tests, where a very significant loss of 68% with respect to the initial R_{NO_x} value was measured after t = 19 months (Figure 4). However, the R_{NO_x} models corresponding to the other T-type materials are not significantly influenced by exposure time t. For material T-3 that was indeed to be expected, since the laboratory tests under constant climate conditions revealed almost constant R_{NO_x}, independent of t. On the contrary, in case of material T-4, the laboratory measurements concluded with a loss of 44% after t = 19 months, a value of similar order as detected for material S/A-2 (48%). However, in both cases, T-4 and S/A-2, the influence of the time parameter t is not sufficiently high to be considered as statistically significant to the explanation of R_{NO_x}. In both cases, the relative humidity alone explains large part of the variance of R_{NO_x}, as indicated by correspondingly low p-values and high R² (R² = 0.82 for T-4). In general, the adjusted models predict the R_{NO_x} dependency on RH_{air,3} of the T-type materials with reasonable accuracy, as shown in Figure 3f to 3i.

As final remark, it must be stressed that the scope of the predictions by the herein derived models is necessarily limited to the specific PHOTONSITE test conditions. This refers especially to the initial NO_x concentration and the relative humidity inside the reactor (RH_{int}), which, as mentioned in section 3.2, is an almost constant value (≈ 25%) that is not related to the outdoor relative humidity. Further data must be incorporated in the future to validate and increase the robustness of the prediction models.

5. Conclusions

The present study addresses the in situ evaluation of the NO_x removal efficiency of photocatalytic pavements by means of a specifically develop device (PHOTONSITE). The device has been employed to measure the performance of different photocatalytic products placed in or on different substrates, exposed during 17 months to realistic outdoor conditions. Based on these measurements, prediction models for the NO_x removal capacity of the materials were derived. The main conclusions of this study are summarised as follows:

- Materials belonging to the same type of photocatalytic product and substrate behave in a similar way: the emulsions on asphalt (E/A) experience the most significant loss of activity over time, irrespective of the climatic conditions. On the contrary, slurries on asphalts (S/A) show a relatively constant behaviour over time with fluctuations mainly attributable to the variations of the humidity of the substrate. The concrete tiles (T) are likewise influenced by the humidity of the substrates, while, with one exception, the time-dependant deactivation of the tiles is not identified as a statistically significant influence variable.
- Due to the hygrometric inertia of construction materials, the instantaneous relative air humidity (recorded during the in-situ measurement) is not representative for the humidity of the substrate. Instead, the mean value of the relative air humidity over a time-period of X days before the in-situ evaluation of NO_x removal can be adopted as a measure for the humidity of the substrate. For the

slurries on asphalts and concrete tiles, periods of $X = 28$ days and $X = 3$ days, respectively, were found to be adequate.

- The present study enhances the scope of available models for NO_x removal prediction of construction materials from standardized laboratory conditions to real world environment exposure. However, the scope of applicability of the herein derived models is still restricted to the specific constraints imposed by the in-situ test conditions.

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