

Influence of parameters on the photocatalytic oxidation of nitric oxide at the surface of titanium dioxide-modified concrete materials

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1. Introduction – Titanium dioxide (TiO₂) is a well-known photocatalyst leading to the transformation of nitrogen oxides (NO/NO₂) under UV irradiation, via catalytic heterogeneous reactions, to nitric acid (HNO₃), which remains on the TiO₂ surface and can be washed out by rain or other washing processes. Despite the increasing control requirements, NO₂ limits are regularly exceeded on highly populated urban areas. Thus, an additional reduction of such concentrations by using photocatalytic surfaces could be very useful. Nevertheless, the anti-polluting ability in outdoor conditions remains an open question.

In the framework of the LIFE MINOX-STREET European project, co-financed by the EU, some promising photocatalytic materials have been selected in order to evaluate their performance at real scale. The work presented here forms part of a series of systematic studies, carried out within the mentioned European project, whose primary objective has been to evaluate the performance of a wide variety of commercial photocatalytic materials and select several among them promising to be implemented at urban scenarios. To do that, rigorous essays and tests on their physical-chemical properties and expected photocatalytic efficiency, not only under controlled laboratory conditions but also in real atmosphere, have been done and, after evaluating the results, three different photocatalytic materials considered for their application at real scale. One of them has been applied on bituminous concrete pavements –BCP– (a water emulsion –WE–) and two of them have been applied on sidewalk concrete pavements –SCP– (a water emulsion and a photocatalytic coating –PC–), all of them selected for further investigation. More concretely, the influence of several key environmental parameters on their air-purifying capacity, within a range of relevant atmospheric conditions, has been studied and it is presented here.

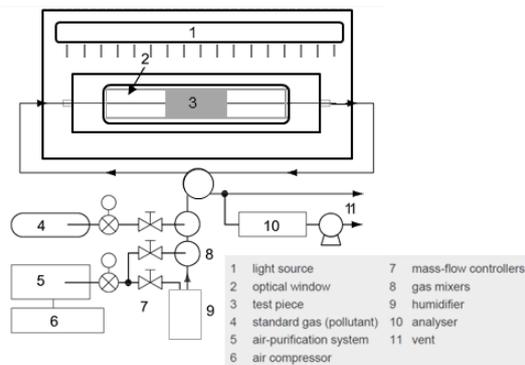
Since some years, a great variety of these so-called air-purifying materials aimed to eliminate the nitrogen oxides from the atmosphere are offered by the market and intense work has been performed to clarify the reaction pathways of the photocatalytic transformation of these compounds and deepen in the kinetics of the oxidation process. To assess the photocatalytic efficiency of air-purifying products a standard operation procedure was developed and published by ISO in 2007 [1]. The suitability of the ISO standard test procedure for the assessment of the efficiency of photocatalytic materials continues being widely discussed elsewhere.

Here, the mentioned international standard has been chosen to minimize the influence of the gas-phase Leighton chemistry as well as unwanted wall losses of reaction compounds or heterogeneous formation of products on the reactor walls and look into the dependence of the nitric oxide (NO) uptake coefficient, γ , on several process parameters as NO inlet concentration, UV-A irradiance intensity, relative humidity and flow rate has been tested.

Further, a first-order rate approximation has been followed to compute analogue surface deposition velocities that can be used in resistance models to estimate deposition flows on photocatalytic surfaces.

2. Experimental - The photocatalytic activity of three promising photocatalytic concrete materials (a bituminous concrete pavement –BCP– and a sidewalk concrete pavement –SCP–) has been essayed under the ISO international standard. In the

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



standard ISO experiment (Image 1), test gas mixture flow (NO, air, H₂O) (50% relative humidity) is passed over the flat rectangular sample of typically 5 cm x 10 cm, placed inside a bed flow photo-reactor, and is irradiated by UV-A light (10 W m⁻²) 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. During the essays, NO inlet and outlet concentrations are analyzed and registered.

Test conditions were varied for the different parameters under study (Table 1): with NO inlet concentration in 100 to 1000 ppb range, UV-A irradiance intensity in 2 to 40 W m⁻² range, relative humidity in the extended range from 20 to 85 % and flow rate fixed at 3 or 1.5 l min⁻¹.

Assuming NO photocatalytic decomposition follows a first order kinetics under relevant atmospheric conditions, a first-order rate coefficient (k_r , s⁻¹), can be determined from the experimental data obtained:

$$k_r = - \frac{\ln(C_{out}-C_{in})}{t_r} \quad (1)$$

where C_{in} and C_{out} are NO concentration at the inlet and exit of the photo-reactor (ppbv) and t_r is the reaction time of the gas-phase NO and the sample. k_r is directly related to the activity of the sample, on one hand, but also dependent on the geometry of the reactor. Therefore, the dimensionless reactive uptake coefficient, γ , has been introduced in heterogeneous chemistry [2]. The reactive uptake coefficient is defined as the ratio of the number of collisions that lead to reaction over all collisions of the gas-phase reactant with a reactive surface. It can be calculated from k_r as:

$$\gamma = \frac{4 \cdot k_r}{\bar{v} \cdot S/V} \quad (2)$$

considering that \bar{v} is the mean molecular velocity of the gas NO (m s⁻¹) defined by the kinetic gas theory:

$$\bar{v} = \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M}} \quad (3)$$

where R is the ideal gas constant (8.314 J mol⁻¹ K⁻¹), T is the absolute temperature (K) and M is the molecular mass of NO (kg mol⁻¹). Then, an analogue surface deposition velocity can be defined:

$$V_{surf} = \frac{\gamma \bar{v}}{4} \quad (4)$$

In this way, NO uptake coefficients (γ) and surface deposition velocities (V_{surf}) have been estimated from the experimental data.

3. Results and Discussion – In the case of nitrogen oxides, and more particularly NO, the degradation rate of pollutant gas increases with the light intensity in the activation region of the spectrum [3]. Several authors reported a UV illumination at different places registered in countries of diverse continents under different climatic conditions from 7-10 W m⁻² on a cloudy day to 35 W m⁻² on a summer day. During experimental campaigns, values up to 35 W m⁻², under autumn and winter episodic conditions, when most severe nitrogen oxides pollution episodes take place ordinarily in the Community of Madrid, have been registered. All tested materials exhibited two different regimes: a first-order regime where electron-hole pairs are consumed rapidly by chemical reactions and a half-order regime, above 10-20 W m⁻², where the recombination rate is dominant which decrease the photocatalytic reaction rate, according to other studies [4, 5].

Table 1. Summary of the tests conditions.

Operating conditions	Value
Flow rate (l min ⁻¹)	1.5 and 3.0
Flow velocity above reactive surface (m s ⁻¹)	0.1 and 0.2
Temperature (°C)	20 °C
Pressure (kPa)	101.325
NO inlet concentration (ppbv)	250, 500, 750 and 1000
Relative humidity (%)	20, 35, 50, 65, 75 and 85
Reactive surface (mm x mm)	49 x 99
Irradiance (300-400 nm) (W m ⁻²)	2, 5, 10, 20 and 40

Image 2. Dependence of kinetic parameters on UV-A irradiance (BCP/WE).

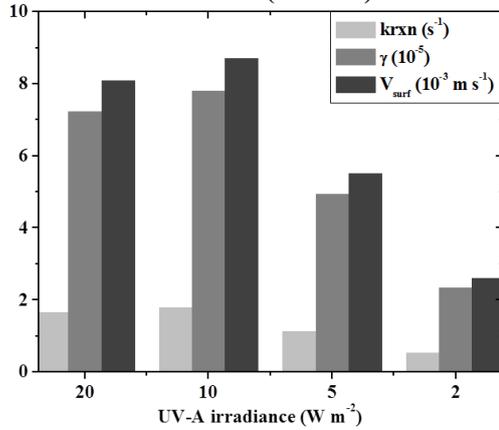
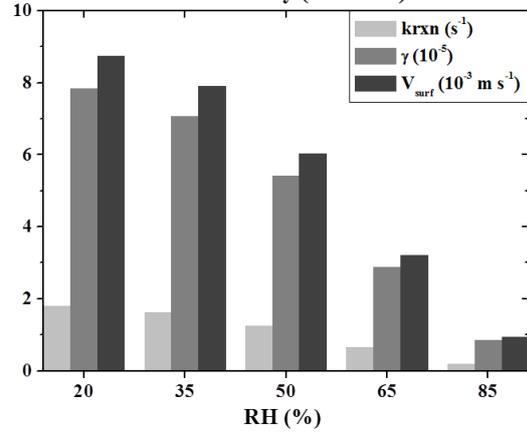


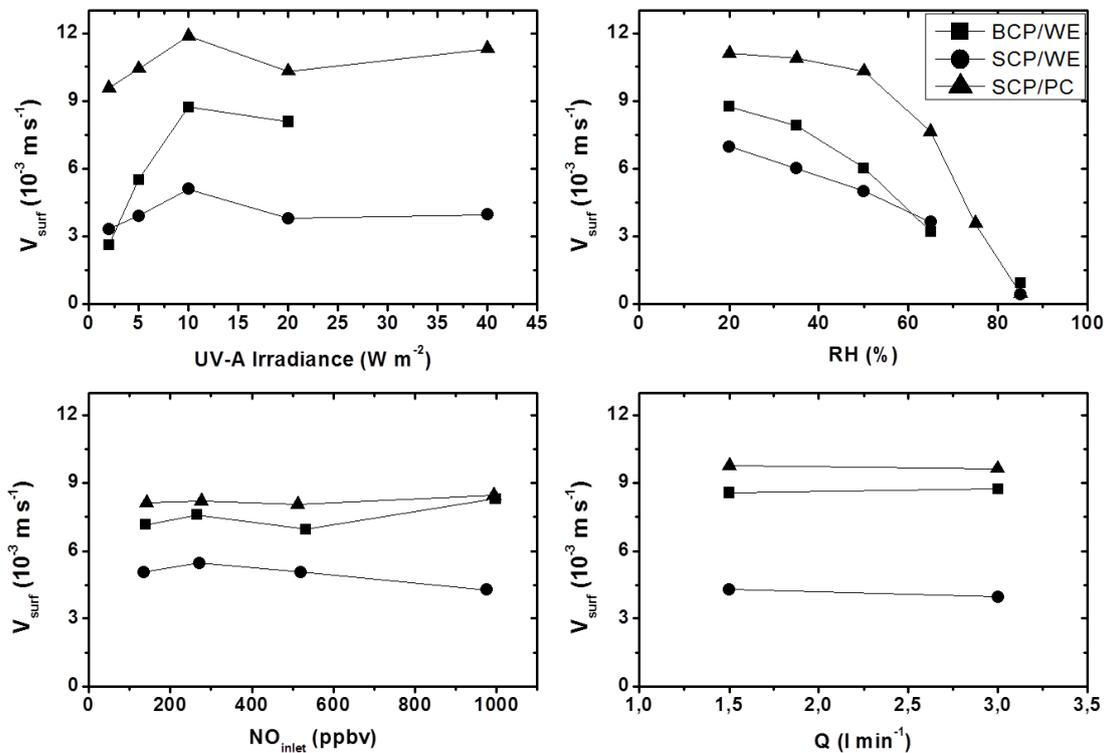
Image 3. Dependence of kinetic parameters on relative humidity (BCP/WE).



The results from the experiments described showed a negative dependence of the NO removal capacity of all materials tested (and corresponding kinetic parameters) on the irradiance intensity below $10 W m^{-2}$ (Image 2). Average γ (10^{-5}) values estimated under tested varying irradiance conditions were 5.58 ± 2.49 , 3.61 ± 0.68 and 9.58 ± 0.81 (given for BCP/WE, SCP/WE and SCP/PC, respectively). Based on the experimental data obtained in the work presented here, estimated kinetic parameters related to air-purifying ability of all materials essayed showed a negative dependence on irradiance intensity below $10 W m^{-2}$ (Image 2).

Relative humidity has a complex influence on photocatalytic reaction. Nevertheless, at ppmv level, several authors found a linear decrease in the degradation rates of NO with increasing humidity in the 10-70% range [6]. CIEMAT's meteorological towers have registered values in the 30 to 65% range during autumn and winter nitrogen oxides pollution episodes in Madrid. Therefore, the values to be found in episodic conditions are highly variable and within the range of relative humidity tested. The results from

Image 4. Average V_{surf} (10^{-3}) ($m s^{-1}$) obtained from experimental data.



the experiments also showed a negative dependence of the NO removal capacity on relative humidity in the whole range studied (Image 3). And average γ (10^{-5}) values estimated for varying relative humidity conditions were 4.81 ± 2.92 , 3.95 ± 2.28 and 6.57 ± 3.94 (for BCP/WE, SCP/WE and SCP/PC, respectively). On the other hand, the dependence of k_r on NO inlet concentration did not show a clear trend for any of the essayed materials, as it was expected by following the numerical approximation used. Thus, estimated average γ (10^{-5}) values and their standard deviation were 6.72 ± 0.53 (BCP/WE), 4.44 ± 0.39 (SCP/WE) and 7.36 ± 0.13 (SCP/PC).

At the same time, k_r is independent on the flow rate and reaction time applied. As a consequence, estimated average γ (10^{-5}) values and the corresponding standard deviation values showed clearly this effect (7.76 ± 0.11 for BCP/WE, 3.70 ± 0.20 for SCP/WE and 8.69 ± 0.07 for SCP/PC).

Analogue surface deposition velocities were also computed for each case. Image 4 presents a summary of average analogue surface deposition velocities, V_{surf} , obtained from experimental data. As it is reasonable, the described influence of every key parameter on the NO removal efficiency was also reflected in the estimated values of deposition rates.

The test conditions used in the work have covered the range of typical atmospheric conditions found under nitrogen oxides pollution episodes. A UV-A light intensity lower than 10 W m^{-2} or relative humidity values above 20-40% have, as a result, a significant drop in the photocatalytic activity of all materials tested.

4. Conclusions – The standard test procedure described in ISO 22197-1: 2007, developed to test the air-purifying performance of photocatalytic materials, has been successfully applied to determine the photocatalytic activity of three different types of photocatalytic products, designed to be applied on both bituminous and sidewalk concrete pavements. Moreover, the influence of several key parameters (as UVA irradiance, relative humidity, NO inlet concentration and flow rate) on the NO removal capacity has been investigated.

In addition, a first-order kinetics approximation is proposed to estimate kinetic parameters (as uptake coefficient or analogue surface deposition velocities) independent of the experimental photo-reactor configuration and the studied concentration levels, allowing a previous evaluation of the potential NO removal capacity of the photocatalytic materials tested under realistic weather conditions.

The nature of photocatalytic products and substrate on which they are applied determine the NO remediation activity measured and, consequently, the first-order rate constants, uptake coefficients and analogue surface deposition velocities estimated.

The amount of NO removed from the gas phase by photocatalytic oxidation is strongly affected by changes of the light intensity as well as of the relative humidity.

5. References

- [1] International standard ISO 22197-1:2007, Geneve, 2007.
- [2] B. J. Finlayson-Pitts, L. M. Wingen, A. L. Sumner, D. Syomin and K. A. Ramazan. *Phys. Chem. Chem. Phys.*, **5**, (2003) p. 223-242.
- [3] S. Devahasdin, C. Fan, K. Li and D. H. Chen., *J. Photoch. Photobio. A*, **156**, (2003) p.161-170.
- [4] W. A. Jacoby, D. M. Blake, R. D. Noble, C. A. Kovel, *J. Catal.*, (1995), 157 p. 87-96.
- [5] T. H. Lim, S. M. Jeong, S. D. Kim and J. Gyenis., *J. Photoch. Photobio. A*, **134** (3), (2000) p. 209-17.
- [6] G. Husken, M. Hunger and H. Brouwers, *Build. Environ.*, **44**, (2009) p. 2463-74.