NO_x PHOTOCATALYTIC DEGRADATION EMPLOYING CONCRETE SURFACES WITH TITANIUM DIOXIDE

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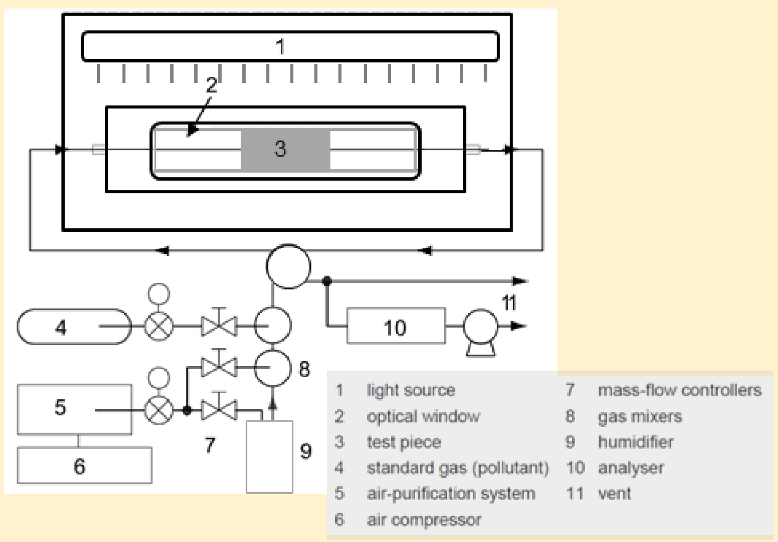
INTRODUCTION

In the framework of the LIFE MINO$_x$-STREET European project, co-financed by the EU, a variety of commercial photocatalytic building and construction materials and coatings has been subjected to rigorous laboratory essays and then, some of these products selected in order to evaluate their depolluting effect at real scale.
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, the air purifying ability of a variety of commercial photocatalytic coatings, applied on different concrete pavements, has been quantified by means of laboratory tests and the kinetic for the nitric oxide (NO) removal of such products investigated. Additionally, a numerical approach for estimating NO deposition velocities has been applied and the estimates presented.

EXPERIMENTAL AND KINETIC APPROXIMATION

After a market study of photocatalytic products available for use in urban settings, several of these products, considered as potentially useful for their application on concrete pavements, were selected for testing their photocatalytic activity under the ISO 22197-1:2007 international standard method [1].



Scheme of the ISO 22197-1 test equipment

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) (300- 400 nm) 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.

Suitable samples need to be available of appropriate dimensions. For bituminous concrete pavements, coring asphalt mix has been needed to carry out firstly. Bituminous and sidewalk concrete pavements samples were cut into 99 mm x 49 mm x 5 mm specimens to be introduced in the photo-reactor.

Bituminous and sidewalk concrete pavement samples

Estimation of NO surface deposition velocity

The kinetic expression based on the Langmuir-Hinshelwood model [2] has been used to derive a NO reaction rate as a superficial rate for a gas-solid heterogeneous system [3]. The disappearance rate of NO reactant r_{NO} can be expressed as:

$$r_{NO} = \frac{kK_{ad}C_{NO}}{1+K_{ad}C_{NO}} \qquad (1)$$

where C_{NO} is the NO concentracion (ppvm^{-1}), k is the reaction rate constant (ppmv m^{-1} s^{-1}) and K_{ad} is the adsorption equilibrium constant (ppmv^{-1} s^{2}).
As this system is not controlled by the interfacial mass transport [4], the conversion is the rate limiting step and then the NO balance equation can be read as:

$$\upsilon_{air}\frac{dC_{NO}}{dx} = a_v r_{NO} \qquad (2)$$

where a_v is the active surface area per unit reactor volume (m^{-1}) and υ_{air} is the air velocity (m s^{-1}).

The integration of (2) using $C_{NO} = C_{NO,in}$ as boundary condition gives:

$$\frac{1}{k} + \frac{1}{kK_{ad}}\frac{ln(C_{NO,in}/C_{NO,out})}{(C_{NO,in}-C_{NO,out})} = \frac{a_v L}{\upsilon_{air}(C_{NO,in}-C_{NO,out})} = \frac{BL}{Q(C_{NO,in}-C_{NO,out})} \qquad (3)$$

where B and L are the reactor width (m) and reactor length (m), respectively, and Q is the flow rate (m^3 s^{-1}).
By varying NO inlet concentration conditions (in the 100 to 1000 ppbv range), the kinetic parameters for NO photocatalytic degradation can be derived setting out $y = BL/Q(C_{NO,in} - C_{NO,out})$ versus $x = ln(C_{NO,in}/C_{NO,out})/(C_{NO,in} - C_{NO,out})$. The intersection with the ordinate corresponds to $1/k$ and the slope to $1/kK_{ad}$. Finally, the NO deposition velocity, $\upsilon_{ph,NO} = \lim_{C_{NO}\to 0}(kK_{ad}/1 + K_{ad}C_{NO})$, in the limiting case given by $K_{ad}C_{NO} \ll 1$, can be approximated by $\upsilon_{ph,NO} = kK_{ad}$.

[1] International standard ISO 22197-1:2007, Geneve, 2007.
[2] D. F. Ollis, in: D. F. Ollis, H. Al-Ekabi (Eds.), "Photocatalytic Purification and Treatment of Water and Air", Elsevier Science, Amsterdam, 1993.
[3] M. Hunger, G. Hüsken and H. J. H. Brouwers, *Cem. Concr. Res.*, ***40***, (2010) p. 313.
[4] M. Hunger, H. J. H. Brouwers, in: M. C. Limbachiya, H. Y. Kew (Eds.), "Proceedings International Conference Excellence in Concrete Construction-through Innovation, 2008", CRC Press, United Kingdom, 2008.

RESULTS AND DISCUSSION

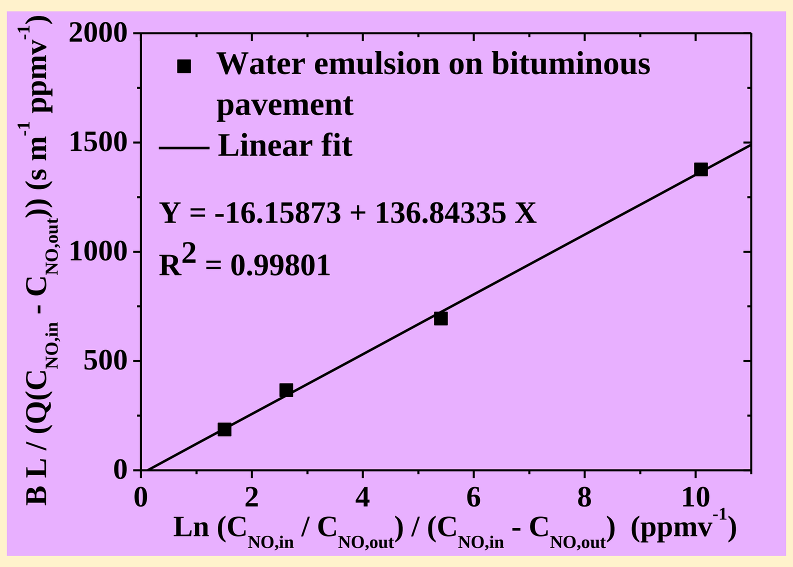
Substrate	Photocatalytic product	χ (%)	η_{NO} (µmol)
Bituminous pavement	Water emulsion	32.2±7.7	12.1±2.5
Sidewalk pavement	Water emulsion	34.2±7.2	12.9±2.6
Sidewalk pavement	Photocatalytic coating	53.0±17.0	19.5±6.2

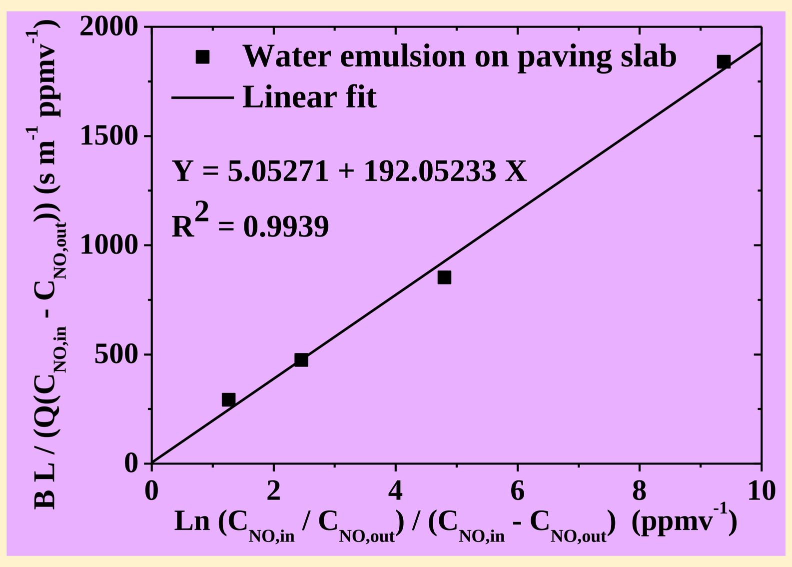
NO removal efficiency for different photocatalytic materials

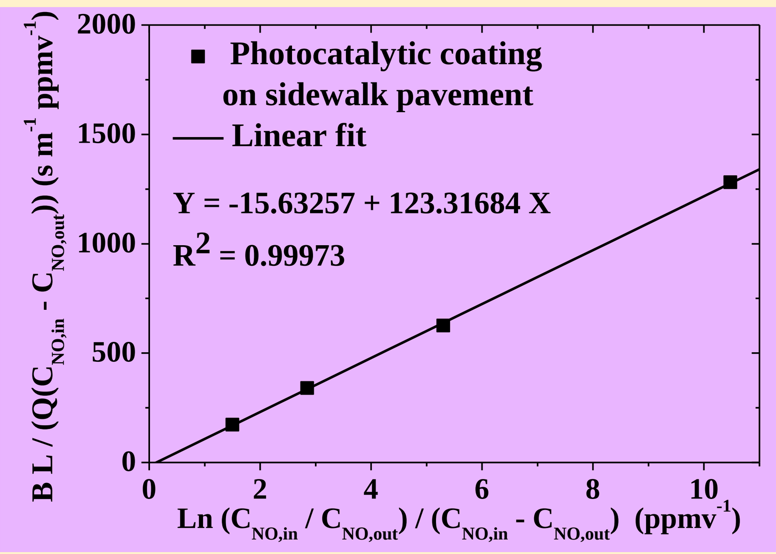
The average NO removal efficiency for different photocatalytic products applied on diverse types of bituminous mixtures (open graded or close graded) and sidewalk concrete pavements (several paving slabs and blocks) are presented. In spite of the noticeable standard deviation selected photocatalytic materials present a NO removal capacity greater than 30% in average (as χ, $(NO_{input}-NO_{output})/NO_{input}*100$) or 12 µmol of NO removed.

Among these photocatalytic materials two highly efficient water emulsions, applied on a sidewalk and a bituminous concrete pavements, respectively, and further, a notable efficient photocatalytic coating applied on a sidewalk pavement, were chosen to carry out additional tests and compute surface deposition velocities.

Linear regression employing the approximate solution of the NO differential mass balance







By employing the equation (3) and the experimental data under variable NO inlet concentration (100 to 1000 ppbv), the Langmuir-Hinshelwood kinetic model was used to estimate kinetic parameters (reaction constant, k, and adsorption equilibrium constant, K_{ad}). Following, the deposition velocity, $\upsilon_{ph,NO}$, which corresponds to the concentration-independent kinetic constant of a first order law of a chemical surface reaction of NO, has been estimated.

Regression fit to approximate solution by using NO mass balance data is presented for a photocatalytic water emulsion coating applied on a sidewalk concrete pavement (paving slab), another water emulsion applied on a bituminous concrete pavement and, additionally, a photocatalytic coating applied on a sidewalk concrete pavement. The inverse of the slope allowed to derive the corresponding surface deposition velocities for the three selected photocatalytic materials.

NO removal efficiencies, kinetic parameters and estimated deposition velocities for three highly efficient photocatalytic for different photocatalytic materials

Substrate	Photocatalytic product	χ (%)	η_{NO} (µmol)	$[k]$ (ppmv m^{-1} s^{-1})	kK_{ad} (ppmv^{-1}s^{2})	$\upsilon_{ph,NO}$ ($\cdot 10^{-3}$ m s^{-1})
Bituminous pavement	Water emulsion	46	16.8	16.159	136.84	7.30763
Sidewalk pavement	Water emulsion	41	15.7	5.053	192.053	5.20692
Sidewalk pavement	Photocatalytic coating	65	23.9	15.668	123.32	8.10898

The greater NO removal capability of the photocatalytic material, the lower the slope of the regression fit and, consequently, the greater its inverse, the deposition rate estimated. The average NO deposition velocities computed by means of these kinetic parameters for the different photocatalytic materials selected were of the order 6.875±1.499 (standard deviation) (10^{-3} m s^{-1}).

CONCLUSIONS

Several TiO_2-based photocatalytic products commercialized to be applied on concrete surfaces have been essayed to test their NOx removal performance. Among them, several photocatalytic coatings, applied on both sidewalk and bituminous concrete pavements, have been chosen to carry out a kinetic study of the NO photocatalytic degradation based on a suitable ISO international standard. Different operating conditions were selected to develop the experiments (varying NO inlet concentration in a range of 100 to 1000 ppb, representative for air pollution episodes) while relative humidity, temperature, flow rate and irradiance remained constant during the tests (50%, 20 °C, 3 l min^{-1} and 10 W m^{-2}). Using these experimental data and the kinetic expressions derive from a Langmuir-Hinshelwood model, the kinetic parameters for NO were computed and NO surface deposition velocities estimated. These estimates can be used for modelers to be implemented into microscale atmospheric dispersion models and predict the possible effects of photocatalytically active surfaces on the air pollution of highly populated and polluted urban areas.

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