NO_x photocatalytic degradation employing concrete surfaces with titanium dioxide

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1. Introduction – One of the dominant sources of NO_x emissions affecting environmental living quality in urban areas is road traffic-induced air pollution. Planning effective measures to improve air quality is, therefore, crucial[1].

Photocatalytic compounds such as titanium dioxide (TiO_2) are used to build air purifying concrete pavements by embedding nanoparticles in the concrete or by applying coatings containing these nanoparticles to the surface pavement. This technology could be promising in inner-city areas where traffic road emissions produce, under certain climate-weather conditions, air pollution episodes with high levels of NO_x, even higher than the limit values given by the directive 2008/50/EC [2].

Local authorities need information on air pollution levels that give not only the pollution levels for few measurement stations within a city (macro-level) but also pollution levels for the individual streets (micro-level) [3]. Therefore air pollution models have been introduced. In practice, 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. Such information helps decision makers to optimize e.g. urban design.

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. Here, the air purifying ability of a variety of commercial photocatalytic coatings, designed to be applied on concrete surfaces, has been quantified by means of laboratory tests. The combining degradation of NO and the appearance of NO_2 have been characterized in a standard laminar flow photo-reactor irradiated with UV lamps employing only NO as the contaminant source. The kinetic parameters present in the NO reaction rate are estimated employing experimental data obtained in the standard method used. Additionally, a numerical approach for estimating NO deposition velocities has been applied and the estimates presented.

2. Experimental – 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 [4]. In order to perform the work, suitable samples need to be available of appropriate dimensions. From a comparative study on photo-active concrete pavements, some of the photocatalytic materials with the highest efficiency were selected for further experiments and kinetic studies. The used photo-reactor operates in steady state. A schematic diagram of the reactor is given in Image 1. The light intensity is kept constant at 10 W m^{-2} (300-400 nm). The fixed operating conditions are summarized in Table 1.

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

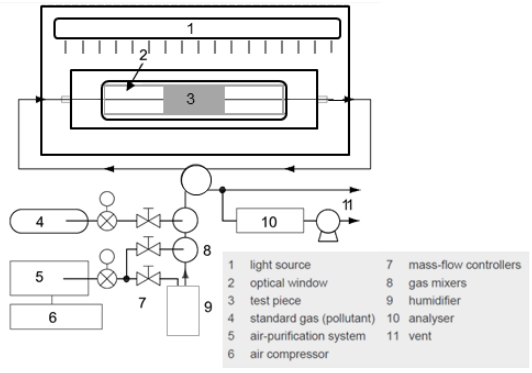


Table 1. Summary of the ISO test conditions.

Operating conditions	Value
Flow rate	3 l min^{-1}
Flow velocity above reactive surface	0.2 m s^{-1}
Temperature	20 °C
Pressure 101.325 kPa	101.325 kPa
NO inlet concentration	1.0 ppmv
Relative humidity	50%
Reactive surface	49 mm x 99 mm
Irradiance (300-400 nm)	10 W m^{-2}

The photocatalytic materials selected were then tested by varying NO inlet concentration in a 100 to 1000 ppb range and maintaining the rest of test conditions as ISO international standard establishes. Next, it was a priori assumed that the conversion of NO into NO_2 is the limiting step more than diffusion of NO from the gaseous phase to the concrete surface. For the prevailing photocatalytic gas-solid surface reaction, only adsorbed NO can be oxidized. The kinetic expression normally proposed for modelling the NO degradation rate is based on the Langmuir-Hinshelwood model which is widely employed for the photocatalytic degradation of a large number of pollutants [5] and it has been used here to derive the reaction rate as a superficial rate for a gas-solid heterogeneous system [6]. The disappearance rate of NO reactant r_{NO} can be expressed as:

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

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}).
It has been have found that this kind of experimental systems employing a photocatalytic concrete stone in a flow reactor is not controlled by the interfacial mass transport [7]. So, it is reasonably assuming the conversion as the rate limiting step and then the NO balance equation can be read as:

$$v_{air}\frac{dC_{NO}}{dx} = a_v r_{NO} \quad (2)$$

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

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

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

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 employing the equation (3) and experimental data under variable 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, $v_{ph,NO}$, can be define as $v_{ph,NO} = \lim_{C_{NO}\to 0}(k\,K_{ad}/1 + K_{ad}C_{NO})$. In the limiting case given by $K_{ad}C_{NO} \ll 1$, the deposition velocity $v_{ph,NO}$ corresponds to the concentration-independent kinetic constant of a first-order rate law of a chemical surface reaction of NO, and $v_{ph,NO}$ can be approximated by $v_{ph,NO} = kK_{ad}$.

3. Results and Discussion - The experimental method used, based on a bed flow photo-reactor, has revealed different values of air-purification performance for some promising photocatalytic concrete pavements essayed under ISO conditions, depending on the photocatalytic product itself and the substrate on which the product is applied. In Table 2, 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. As it can be seen, the standard deviation is, in some cases, noticeable. Nevertheless the 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.

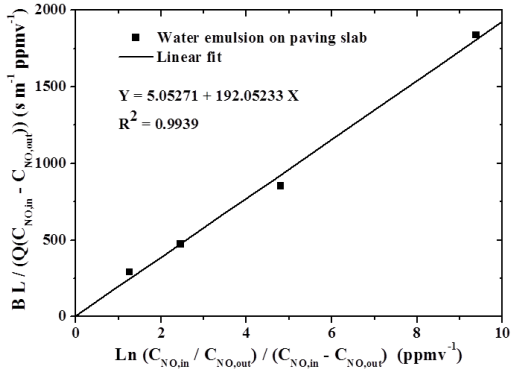
Among these photocatalytic materials two highly efficient water emulsions, applied on a sidewalk and a bituminous concrete pavements, respectively, and further, a notable efficient photocatalytic coating applied on a sidewalk pavement, were chosen to carry out additional tests and compute deposition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

Employing experimental data, the Langmuir-Hinshelwood kinetic model has been utilized to estimate corresponding reaction rate and adsorption equilibrium constants. In Image 2, 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) with a χ equal to 41 and η_{NO} equal to 15.7 µmol. The data fit the line $y = 5.053 + 192.053\,x$. The inverse of the slope allows to derive a corresponding $v_{ph,NO}$ of $5.207 \cdot 10^{-3}$ m s^{-1}.

Table 2. NO removal efficiency for different photocatalytic materials.

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

Image 2. Linear regression employing the approximate solution of the NO differential mass balance.



In the same way, a regression fit to approximate solution by using the same numerical approximation has been done for a photocatalytic water emulsion applied on a close graded bituminous concrete pavement with χ equal to 46 to and η_{NO} equal to 16.8 µmol. The data fit the line $y = -16.159 + 136.84\,x$. The inverse of the slope allows to derive a corresponding $v_{ph,NO}$ of $7.308 \cdot 10^{-3}$ m s^{-1}.

Finally, a regression fit to approximate solution was computed, additionally, for a photocatalytic coating applied on a sidewalk concrete pavement (paving slab) with a with a χ equal to 65 and η_{NO} equal to 23.9 µmol. The data fit the line $y = -15.668 + 123.32x$. The inverse of the slope allow to derive a corresponding $v_{ph,NO}$ of $8.109 \cdot 10^{-3}$ m s^{-1}.

As it can be observed in Table 3, 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}).

Table 3. NO removal efficiencies, kinetic parameters and estimated deposition velocities for three highly efficient photocatalytic materials.

Substrate	Photocatalytic product	χ (%)	η_{NO} (µmol)	$[k]$ (ppmv m^{-1} s^{-1})	kK_{ad} (ppmv^{-1}s^{-2})	$v_{ph,NO}$ ($\cdot 10^{-3}$ 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

4. Conclusions – Several TiO_2-based photocatalytic products commercialized to be applied on concrete surfaces have been essayed to test their NO_x 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 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.

5. References

[1] Europe's environment: the third assessment. Environmental Assessment Report 10, European Environment Agency, Copenhagen, 2003.
[2] Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, European Environmental Agency, European Union, 2008.
[3] G. Wang, F. H. M. van den Bosch and M. Kuffer, "The International Archives of the Photogrammetry, Remote Sensing and Spatial Information Sciences", Vol. XXXVII, Part B8, Beijing, 2008.
[4] International standard ISO 22197-1:2007, Geneve, 2007.
[5] D. F. Ollis, in: D. F. Ollis, H. Al-Ekabi (Eds.), "Photocatalytic Purification and Treatment of Water and Air", Elsevier Science, Amsterdam, 1993.
[6] M. Hunger, G. Hüsken and H. J. H. Brouwers, *Cem. Concr. Res.*, ***40***, (2010) p. 313.
[7] 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.