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ARTICLE

## NO<sub>x</sub> degradation in a continuous large-scale reactor using full-size industrial photocatalytic tiles

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Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

**Many reactors were proposed to investigate the efficiency of photocatalytic materials in the NO<sub>x</sub> degradation but the operative conditions are often very far from reality: parameters and reactor setup, good for laboratory tests, cannot verify the real efficiency of a photocatalytic material in a real context. To solve this issue, we experimented for the first time a new kind of gas-flow reactor able to test photocatalytic building materials in large size, optimizing the reaction conditions in order to work both with artificial conditions of irradiation (UV-A lamp) and under the direct sunshine.**

### Introduction

Nowadays it is imperative to develop new strategies and, side-by-side, new materials to clean the environment. Every year laws and regulations become stricter with the aim to reduce the greenhouse gases emissions and improve the quality of the air. Among all the pollutants, nitrogen oxides (NO<sub>x</sub>), are continuously monitored all over the world and guidelines on the alarm levels of these molecules in air were published by WHO [1] and often recalled in the legislations of the single Country worldwide. Photocatalysis with titanium dioxide as semiconductor [2,3] seems to be a promising technique to reduce the pollutants concentration thanks to its powerful oxidation property. Literature is full of examples on the preparation and use of TiO<sub>2</sub> in the photodegradation of NO<sub>x</sub> [4,5,6] and also in the market it is very easy to find photocatalytic products.

One of the main problems regarding tests on construction materials (paints, cements, tiles, concretes, etc.) is to find a serious and reproducible way to confirm their photo-efficiency. Many reactors with different configurations were proposed and published [7, 8, 9], in addition to the well-known photocatalytic reactor described in the ISO 22197-1 rule [10]. When photocatalytic materials are tested in gas reactions, many different kinds of reactor are reported. Examples from the most recent literature on NO<sub>x</sub> photocatalytic degradation

include: a gas-tight acrylic flow reactor equipped with a Pyrex window containing the pressed photocatalyst [11]; a photoactive sample coated on a glass plate placed into a quartz reactor [12]; a fixed-bed reactor [9]; a glass holder plate set in the centre of a reactor [13]; a glass substrate coated with the film placed in the centre of an acrylic container [14], etc. Minero et al. [7] investigated different gas/solid reactors such as batch or flow-through either continuous stirred-tank reactor (CSTR) or plug flow reactor (PFR).

The main problem related to all these reactors is that the conditions are often far from reality: although several parameters were already fixed and they are very good for the laboratory photocatalytic tests concerning the NO<sub>x</sub> analysis, there is not a way to verify the real performance of a photocatalytic material in a true realistic context.

Firstly, very small size of the sample are usually tested. Even the ISO reactor requires a sample of 50x100 mm in size, a very small dimension in comparison to the real use of the final material. Secondly, too high NO<sub>x</sub> concentrations and sometimes levels of UV-A irradiation impossible to obtain on earth except with the use of lamps, but far from the solar irradiation power, are used. Referring in particular to the NO<sub>x</sub> real data collected in Milan in the last period, the average value does not get over 100 ppm also during the less windy day [15] and this is luckily the situation in quite all the cities all over the world except for few examples (air of good quality has to have NO<sub>x</sub> concentrations lower than 20 ppb [1] and 200 ppb is the second and last alert threshold).

In the present paper we present a new kind of gas-flow reactor able to test photocatalytic building materials of large size, optimizing the reaction conditions in order to work both with artificial conditions of irradiation (UV-A lamp) and under the direct sunshine. In this latter case, the test can predict the real efficiency of the material when this product is used to cover a building. As testing sample, we chose a photocatalytic

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

porcelain-grès tile by GranitiFiandre SpA, whose photocatalytic properties are known [16]. These tiles are industrially produced making use of a particular micro-sized TiO<sub>2</sub>, according with recent papers on the potential dangerous effect of TiO<sub>2</sub> nanoparticles that can cause negative health effects, as demonstrated in respiratory tract cancer in rats [17–19]. Although the calcination temperature after the TiO<sub>2</sub> addition is higher than 600 °C, it is important to underline that there are no changes in the TiO<sub>2</sub> crystallographic phase from anatase to rutile. The preservation of pure anatase was verified by XRD and reported in a previous work [20], in particular, the presence of SiO<sub>2</sub>, together with TiO<sub>2</sub> inhibits the crystal growth of TiO<sub>2</sub> allowing the preservation of the anatase structure at temperature higher than 600 °C [21, 22].

The reactor was designed to simulate on a laboratory bench-scale equipment, the actual environment in which a photocatalytic tile works. This situation is very different from a typical chemical reactor because the tiles must perform their activity outdoor, without a defined flow (and concentration) of reactants. Both the concentration of reactants and the way in which these reactants come in contact with the tile are strongly dependent from the weather conditions. In the absence of wind, the contact time between polluted molecules and tile surface can be very high; on the opposite, in conditions of strong wind, the same parameter can be very low. These considerations explain the reason for which this reactor is not based on a traditional engineering approach, but with the aim to reproduce the real working environment of the photocatalytic product. The width and length of the reactor (625 and 625 mm) were requested by the size of the industrial tile (600x600 mm), while the height of the reactor was calculated in order to obtain residence times in the range 0.25–0.35 h using the flowrate indicated in the text (140 and 180 NL h<sup>-1</sup>). Using such a dimension and such a flowrate, the simulation study performed by the Comsol software indicates a good homogeneity in the reactor and residence times suitable for the reproduction of the real working conditions.

The full description and fluid dynamics of the reactor together with the simulation of the kinetics NO<sub>x</sub> degradation were reported using 140 NL h<sup>-1</sup> or 180 NL h<sup>-1</sup> of gas stream polluted either with 100±10 or 200±10 ppb of NO<sub>x</sub> (chosen to be the first and second alarm levels of both WHO and EU regulations, respectively). Specifically, both NO and NO<sub>2</sub> in mixture were constantly monitored. Irradiation of the reactor was obtained both with a commercial UV-A lamp or exposing directly the reactor under the sunlight in Milan (latitude: 45,46 Nord, longitude: 9,18 East) in September 2014. In this latter case, the amount of UV-A was monitored by a radiometer. In all case, target of the experimentation was to verify the reactor performance and confirm the efficiency of a 600x600 mm photocatalytic tile to reduce the air pollution.

## Material and methods

### Catalytic tile preparation and characterization

Industrial porcelain-grès tiles are manufactured under high pressure by dry-pressing fine processed ceramic raw materials

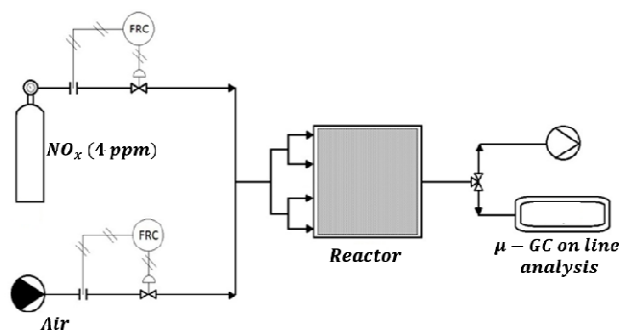
with large proportions of quartz, feldspar, and other fluxes and finally fired at high temperatures (1200–1300 °C) in a kiln. Commercial photoactive porcelain grès tiles by GranitiFiandre S.p.A were subsequently covered at the surface with a mixture of pure anatase micro-TiO<sub>2</sub> (1077 by Kronos) mixed with a commercial SiO<sub>2</sub>-based compound. To ensure the requested product stability, at the end of the preparation procedure tiles were treated at high temperature (680 °C) for 80 min and then brushed to remove the powder present at the sample surface and not completely stuck (samples name: WGActive). Temperature was precisely chosen to maintain the anatase form of the semiconductor and allow the vitrification of the tiles surface [23]. The tiles were characterized by SEM and XRD analysis. The detailed description of the performed analyses is reported elsewhere [24]. By EDX analysis, it was possible to determine the quantity of TiO<sub>2</sub> coated on the tiles surface as 1.1 g m<sup>-2</sup>. A good distribution of the micro-TiO<sub>2</sub> on the porcelain tile surface can be observed. The TiO<sub>2</sub> particles dimension ranges between 100 and 125 nm, results that was confirmed by XRD.

### Photocatalytic Tests

The reactor (Figure 1), with walls of 10 mm of thickness, has an internal size of 625 x 625 x 115 mm with four inlets and one opposite outlet and can house a sample of 600 x 600 x 10 mm. It is equipped with a thermo-hygrometer model HT-3006A to measure temperature and humidity during the tests. Humidity inside the reactor is maintained constant through bubbling the gas flow into a gas bubbler (containing water and saturated aqueous vapour) to obtain a relative humidity (RH) value between 40–50%. The experiments were carried out either using UV lamps or using the sunlight of July and September 2014.

For what concerns the former runs, the irradiation was emitted by two iron halogenide lamps (Jelosil, model HG 500) positioned at 770 mm centre-to-centre distance. The light intensity incident on the sample surface in the UV-A region was measured with a Delta Ohm radiometer, and regulated at 20 W m<sup>-2</sup> by adjusting the distance of the lamp from the reactor. The degradation was performed at different initial NO<sub>x</sub> concentrations ranging from 100±10 ppb to 200±10 ppb, at room temperature and working with a total gas flow of 140 and 180 NL h<sup>-1</sup>. The initial concentration of the NO<sub>x</sub> was obtained by diluting the stream of NO<sub>x</sub> from the cylinder (4 ppm) with air using two different mass flow meters. The concentration values were chosen in order to work closely to the limit values reported on the Directive 2008/50/EC, in particular, 106 ppb (equal to 200 µg m<sup>-3</sup>, value not to be exceeded more than 18 times in a calendar year) and 213 ppb (400 µg m<sup>-3</sup>, alert threshold). On the other hand, all the runs under direct sunlight were performed with a pollutant concentration of 100±10 ppb, obtained as described previously. The time zero of each test corresponds to the moment in which the UV-lamp is switched on. This operation is made only when the flow outgoing the reactor, in dark condition, corresponds to the incoming one for what concerns both the volumetric flow (there are no leaks in the reactor) and the pollutants concentration (the concentration is uniform

in the whole experimental plant). The pollutants concentration was monitored using chemiluminescence instrument (Serinus



40 Oxides of Nitrogen Analyser) and used to check the final conversion of the pollutant. The duration of each continuous run was set at 6, 12 or 24h.

Figure 1. Scheme of the experimental set-up

After filling the reactor, the reactant flow is maintained unchanged, and light powered on. The output concentration of pollutant [NO<sub>x</sub>] outlet is measured.

The final design of the reactor was selected among several possibilities by considering the results of the corresponding simulation studies of other possible solutions. The size and the inlet/outlet position assure a good homogeneity of the reactant in gas phase and a contact between reactant and photocatalytic tiles that well reproduce the real working conditions.

### Simulations

We performed two sets of simulations with two different aims, i.e. fluid dynamic simulations and kinetic simulations. The fluid dynamics simulations were performed with COMSOL Multiphysics® 4.0a to study the reactor configuration under flowing conditions, coupling the laminar flow with the transport of diluted species physics in a 3D space with each geometry resembling the relevant reactor dimensions and considering steady state conditions.

These simulations were performed in order to verify the homogeneous distribution of the gas flow over the tile surface and to visualize the concentration gradients that build up during the NO<sub>x</sub> treatment under steady-state conditions. Each simulation of this first set was carried out using the following values: C<sub>0,in</sub> = 4.132 10<sup>-6</sup> mol m<sup>-3</sup> (initial NO<sub>x</sub> concentration, equivalent to 100 ppb of NO<sub>x</sub>); D = 1.54 10<sup>-5</sup> m<sup>2</sup> s<sup>-1</sup> (diffusion coefficient of NO<sub>x</sub> in air at 21.1 °C) [25].

Simulations were performed considering air as medium (using the relevant constant provided by the software) and two inlet fluxes: 5.0 10<sup>-5</sup> m<sup>3</sup> s<sup>-1</sup> (180 NL h<sup>-1</sup>) or 3.8 10<sup>-5</sup> m<sup>3</sup> s<sup>-1</sup> (140 NL h<sup>-1</sup>). The kinetic modelling simulations were performed to study the NO<sub>x</sub> degradation reaction. The NO<sub>x</sub> concentration is the sum of the NO and NO<sub>2</sub> concentrations; the general mechanism of NO<sub>x</sub> oxidation by photocatalysis implies their oxidation to nitric or

nitrous acids by active oxygen species produced on the TiO<sub>2</sub> surface [26].

The simulation was made by integrating the reactor mass balance showed in Eq. 1:

$$F_{out} = F_{in} + r_{NOx} \quad (1)$$

Where F are the molar fluxes expressed in mole min<sup>-1</sup> entering (in) and exiting (out) the reactor and r<sub>NOx</sub> is the rate of the photocatalytic reaction expr, expressed using the Langmuir-Hinshelwood model and reported in Eq. 2:

$$r_{NOx} = -dNOx/dt = -k_{NOx} (A * W * K_{NOx} * n_{NOx}) / (1 + K_{NO} * n_{NO} + K_{NO2} * n_{NO2} + K_{NO3} * n_{NO3}) \quad (2)$$

where k are the kinetic constants while K are the adsorption constants and NO<sub>x</sub> represents either NO or NO<sub>2</sub>. A and W represent the catalytic surface and the specific lamp power measured on the tile surface respectively. The reaction products are expressed as NO<sub>3</sub> and their concentration is calculated by molar balance, i.e. summing the reacted moles of NO and NO<sub>2</sub>.

The kinetic parameters used for the simulation of the catalytic tile performance are reported in Table 1.

Table 1: NO<sub>x</sub> degradation kinetic parameters

NO <sub>2</sub> Adsorption constant, K <sub>NO2</sub> (mol <sup>-1</sup> )	NO <sub>2</sub> Kinetic constant, k <sub>NO2</sub> (mol min <sup>-1</sup> W <sup>-1</sup> )	NO Adsorption constant, K <sub>NO</sub> (mol <sup>-1</sup> )	NO Kinetic constant, k <sub>NO</sub> (mol min <sup>-1</sup> W <sup>-1</sup> )
194.7	8.00	77.3	3.20

The values of both the kinetic and the adsorption constants were regressed in a previous work by some of the authors, in which the NO<sub>x</sub> photooxidation reaction was studied in a 20 L batch reactor [27], assuming a parallel first order reaction that follows the Langmuir- Hinshelwood mechanism.

Similarly to the previous work, an adsorption constant of the species irreversibly adsorbed of 10<sup>6</sup> mol<sup>-1</sup> was used. MatLab version R2015a by „The MathWorks, Inc.“ software was used for the integration of the differential equation, adopting the ODE 15s algorithm, for the kinetic simulation assuming a uniform activity of the tile. Moreover, we also simulated the reaction using COMSOL, which considers the 3D geometry of the reactor and the local concentration upon the tile. In any case, the kinetic constants were considered proportional to UV light intensity.

## Results and Discussion

### Reactor fluid dynamics

With the aim of studying the reactor fluid dynamics, simulations were carried out. Figure 2 shows the x-y and the y-z views of the reactor and the red lines represent the gas flow streams in the reactor volume. The gas flux is relatively high



and leads to turbulence, at least for the region closer to the reactor inlet.

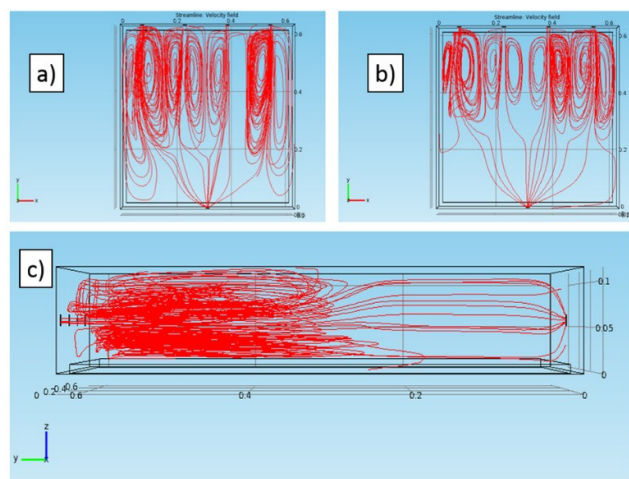


Figure 2: Flow lines of the gas stream in the reactor in the 3D simulation for a) 180 NLh<sup>-1</sup> and b), c) 140 NLh<sup>-1</sup>. Views of the a), b) x-y and of the c) y-z planes.

Notwithstanding this, simulations confirm that the presence of four inlets and one outlet is an ideal choice to allow a good gas stream and an adequate distribution of the gas on the photoactive tile.

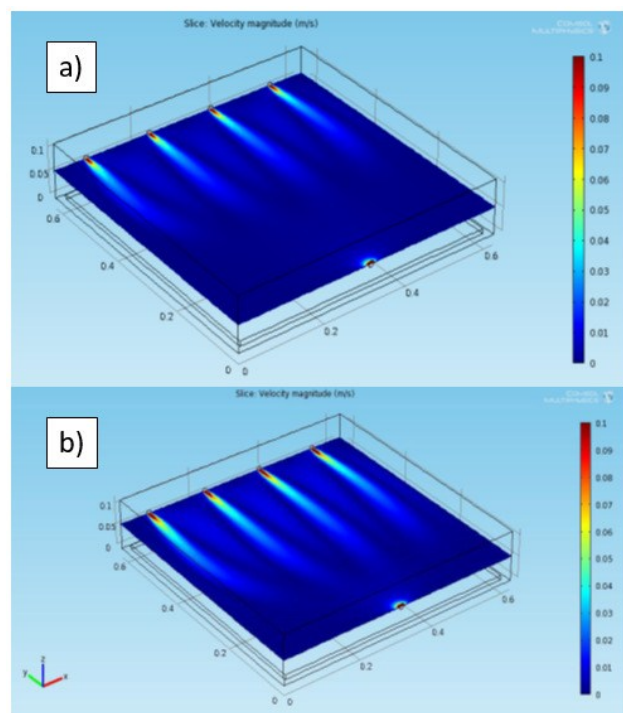


Figure 3: Local velocity as x-y sections (at  $z=57.5$  mm, i.e. in correspondence of the inlets centre height of the gas stream in the reactor) in the 3D simulation for (a) 140 NL h<sup>-1</sup> and (b) for 180 NL h<sup>-1</sup>. The maximum range was limited to 0.1 m s<sup>-1</sup>

Figure 3 represents two cross-sections (in the x-y plane) of the 3-D simulated velocities of gas in the reactor for the two fluxes.

Because the highest local velocities are located close to the inlet and the outlet, (about three orders of magnitude higher than in the reactor “bulk”), the maximum value of the visualized range was limited to 0.1 m s<sup>-1</sup>, whereas the simulated maximum speed are 0.3 m s<sup>-1</sup> for 140 NL h<sup>-1</sup> and 0.4 m s<sup>-1</sup> for 180 NL h<sup>-1</sup>, in both cases located at the outlet.

Both simulation study (Fig. 3) and the experimental values of the NO<sub>x</sub> concentration in the exit stream of the reactor seem to indicate that dead zone can be considered as negligible in this configuration.

#### Kinetic simulations

Together with the fluid dynamic study, a kinetic simulation was performed by considering the reactor as a well-mixed reactor. Firstly, a 1D simulation using MatLab, considering both an average distribution of the pollutants and an average activity of the photocatalytic tile was performed.

In Figure 4 a-b are reported the experimental and simulated results for the experimental runs performed under the UV lamps (intensity= 20 W m<sup>-2</sup>) using a NO<sub>x</sub> concentration of 100 ppb and monitoring the reaction for 70 min.

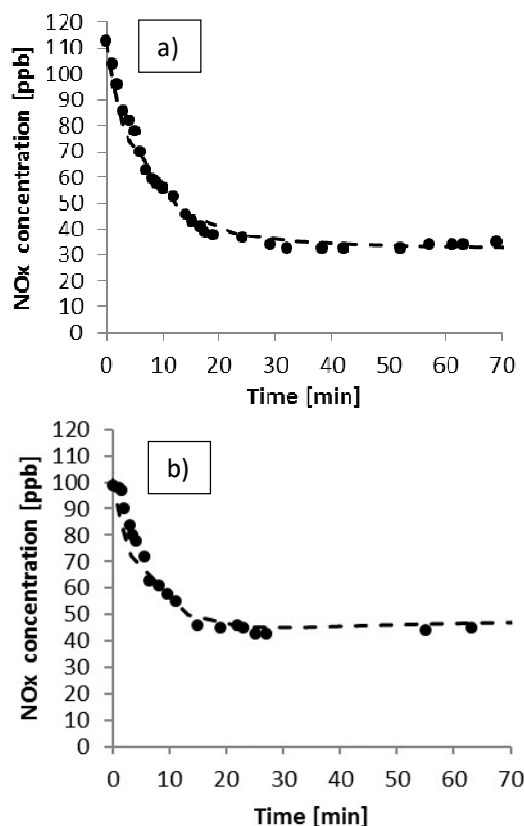


Figure 4: NO<sub>x</sub> photo degradation under 20 W m<sup>-2</sup> of UV-A light. a) total flow rate 140 NL h<sup>-1</sup>; b) total flow rate 180 NL h<sup>-1</sup>.

It can be observed that the pollutants are successfully degraded and that the maximum conversion is reached after about 40 minutes for both the flows. The minimum

concentration of  $\text{NO}_x$  is reached in the first experiment (Figure 4a) because the reactant flow was set to  $140 \text{ NL h}^{-1}$ , which allows a higher residence time in the reactor. The simulation agrees with the experimental data, confirming the validity of this model and its kinetic parameter obtained in the 20 L reactor simulated in [27], as previously described.

The experimental results of the run performed at  $140 \text{ NL h}^{-1}$  and with a concentration of 200 ppb of  $\text{NO}_x$  are reported in Figure 5, together with the simulations. These experiments were conducted for a longer time, i.e. 24 hours.

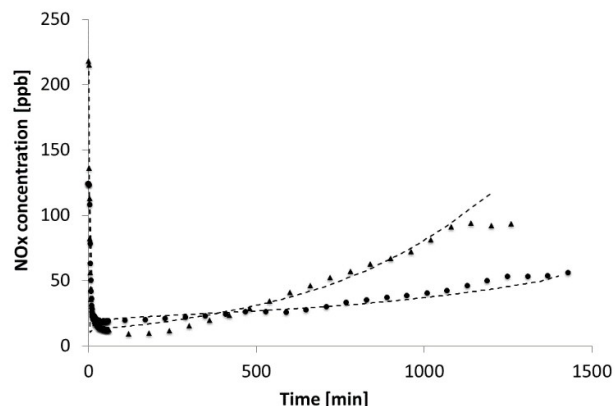


Figure 5:  $\text{NO}_x$  photodegradation, light power:  $20 \text{ W m}^{-2}$ , total flow rate of  $140 \text{ NL h}^{-1}$ ,  $\text{NO}_x$  concentration of 124 ppb (circles) 217 ppb (triangles). Dotted lines stand for the simulated trends.

Due to the longer experiment time, the formation of the adsorbed species become important and affects the tile performance. From Figure 5 it can be observed that the formation of  $\text{NO}_3^-$  onto the catalyst surface led to a decrease in the reaction rate. The model can reproduce the behaviour of the experimental  $\text{NO}_x$  concentration, showing that the value chosen for the irreversible adsorbed species is well estimated. The real situation is better at higher  $\text{NO}_x$  concentration as the model foresees a faster degradation of the photocatalytic material that, on the contrary, still shows a good photoactivity with a different trend of the experimental data in comparison to the simulated line (triangles and dotted line in Figure 5).

The results of the runs conducted under the sunlight are reported in Figure 6. The variation of the specific UV power from sunlight respect the relative time of the test is reported in Table 2.

The sunlight power is greater during July. Since the experiments were conducted in a relative short time (about 2 hours), the power increases proportionally with the time, for this reason in the model, the dependency of the light intensity on time was approximated as linear.

These results demonstrate how the photoactivity of the product is actually dependent from the light intensity. The data gathered in July are characterized by a greater  $\text{NO}_x$  final conversion compared to the one of September. The calculated values fit the experimental ones, confirming the right choice to consider the kinetic constant proportional to the UV-light intensity.

Table 2: Specific sunlight power in UV-A region measured during the experimental degradation tests performed under sunlight.

	July (Zenith angle= $38.70^\circ$ )	September (Zenith angle= $49.91^\circ$ )
Time [min]	Light intensity [ $\text{W m}^{-2}$ ]	
0	4.15	3.55
8	4.35	3.68
21	4.79	4.06
47	5.93	4.56
62	6.68	4.71
77	7.58	4.91
105	9.37	5.54

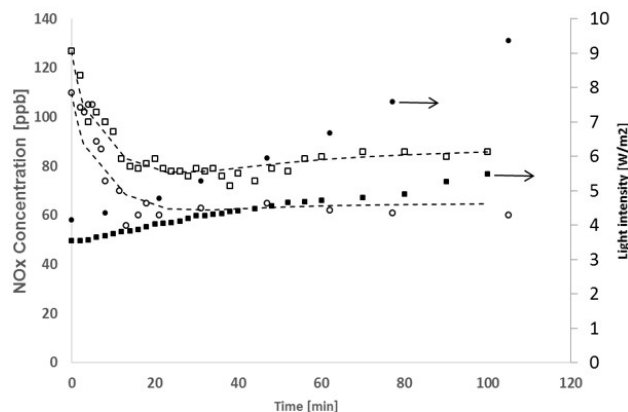


Figure 6:  $\text{NO}_x$  photodegradation under sunlight, feed flow of  $140 \text{ NL h}^{-1}$ , circles stand for the experiment performed during July, squares for the one performed in September. Full points indicate the light intensity (UV fraction) while empty points the  $\text{NO}_x$  concentration exiting the reactor.

Even if the first simulation set showed that the gas is well distributed in the reactor, we also simulate the reaction using COMSOL. In this way, the local concentration of  $\text{NO}_x$  can be considered. The results are reported in Figure 7 for the two conditions considered in the present manuscript, namely  $140 \text{ L Nh}^{-1}$  and  $180 \text{ L Nh}^{-1}$  with an  $[\text{NO}_x]_{\text{in}} = 100 \pm 10 \text{ ppb}$ .

In both cases, the maximum concentration of  $\text{NO}_x$  corresponds to the four inlets and, as soon as the gas streams enter the reactor,  $\text{NO}_x$  diffuses (or is transported by convection) laterally

and is consumed at the tile surface. The latter phenomena is well visible by the dramatic concentration gradient observed in the y-z sections in correspondence to the tile, which is located at the bottom of the reactor.

In addition, in this case, the images show the advantages of using four inlets: as visible from the x-y sections, NO<sub>x</sub> are well distributed over the whole tile surface. Comparison between the two operative conditions does not lead to appreciable differences in the concentration gradients but for the fact that the highest flux leads to a lower contact time and thus to higher NO<sub>x</sub> concentration in the region close to the outlet.

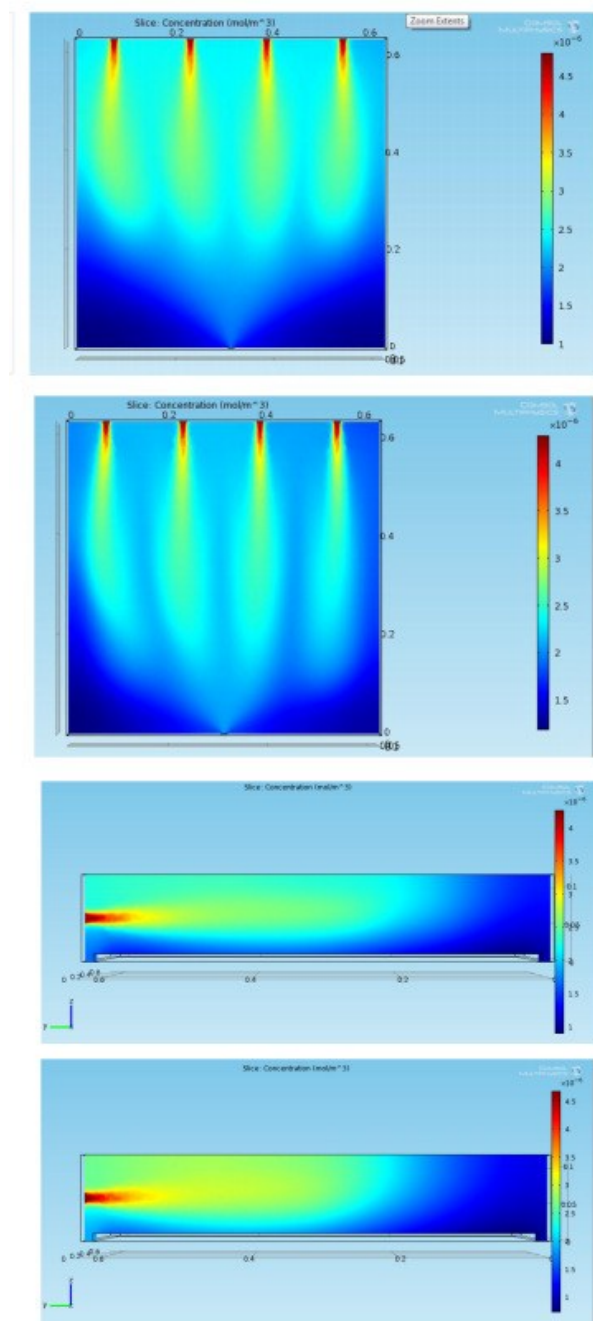


Figure 7: Local concentration of NO<sub>x</sub> as x-y sections (A and B, at z=57.5 mm, i.e. in correspondence of the inlets centre height) and y-z sections (C and D, at x=75.7 mm, i.e. in correspondence of the centre of the first inlet hole) of the reactor considering (A and C) a gas flow of 140 L N h<sup>-1</sup> or (B and D) a gas flow of 180 NL h<sup>-1</sup> with [NO<sub>x</sub>]<sub>in</sub> = 100 ppb.

## Conclusions

In this work, the NO<sub>x</sub> photodegradation was studied using a continuous bench-scale reactor.

Differently from other works already published in literature, an entire (600x600 mm) photocatalytic tile was tested toward this reaction. 3D simulations showed that the design allows good reactant dispersion inside the reactor, confirming the right design of the reactor.

Different conditions in terms of reactant flow, pollutant concentration and test duration were varied, obtaining in all experiments a good photoactivity. Also the tests performed under sunlight showed that the catalytic tile is active using the natural light. The proposed kinetic model is able to fit all the experimental data.

## Acknowledgements

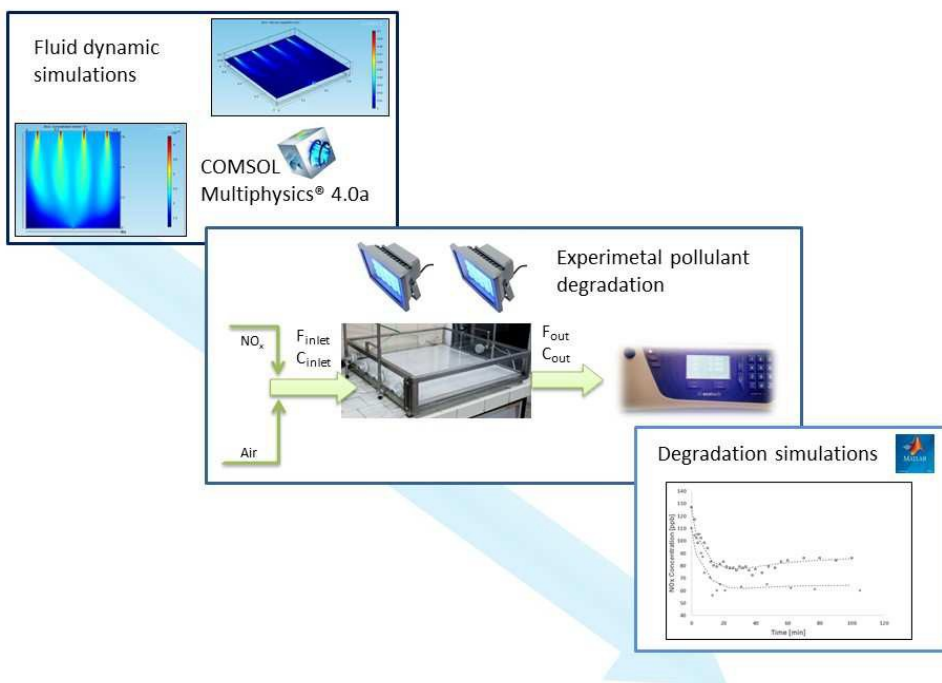
This research was supported by LIFE+ Environment Policy and Governance project Digitalife LIFE13 ENV/IT/000140. The authors would like to thank R. Pellini and G. Campione (GranitiFiandre) for the preparation of the photocatalytic slabs and the construction of the large-scale reactor, respectively.

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Gas-flow photoreactor working with a UV-A lamp or under the direct sunshine to test materials in large size