Photocatalytic removal of NO using TiO$_2$-containing ceramic tiles: evaluation under different reactor's operational mode

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Abstract

Construction materials that incorporate into their structures photocatalysts are found to exhibit a capacity in removing NO from air. Therefore, the development of such innovative materials with both de-soiling and de-polluting properties is a significant step towards the improvement of indoor and outdoor air quality.

It is the purpose of this study to investigate the photocatalytic removal of dominant urban air pollutant (NO) using TiO$_2$-modified ceramic tiles under both static and dynamic conditions. The activity of 4 types of these materials was investigated in an environmental chamber ($0.125m^3$) under a realistic level of irradiation, humidity and compound amount with reference to a typical urban air pollutant concentration. The photocatalytic performance of the materials was evaluated through the calculation of two parameters: the a) photocatalytic decomposition percentage (PD %) and the b) photocatalytic rate (PR µg m^{-2} s^{-1})

Results showed that building materials, such as ceramic tiles, when treated with different layers of 10% TiO$_2$, can be used for the photocatalytic removal of air pollutants under "real" world conditions. A NO degradation percentage high as 75%, and a decomposition rate the size of 0.65 µg m^{-2} s^{-1} were reported for the 4-layer TiO$_2$ material under static mode, whereas the corresponding parameters were found to be 50% and 0.63 µgm^{-2}s^{-1} respectively in the dynamic system. Overall, it was exhibited that the PR parameter presented the same trend and level under both operational modes for all materials, whereas the %PD parameter displayed higher values when studied under static mode.
Keywords: photocatalytic building material, TiO$_2$, NOx, VOCs, air purification.

1 Introduction

Heterogeneous photocatalysis is an efficient and clean technology for the degradation of air pollutants. It represents an emerging environmental control option for the efficient removal of chemical pollutants in air. This process involves a semiconductor catalyst, regularly titanium dioxide (TiO_2), which is activated with ultraviolet light of the appropriate wavelength. The activation generates electrons and holes in the conduction and valence bands, respectively. These species are very reactive and can either recombine or diffuse to semiconductor surface, where they are trapped by adsorbed molecules of water and oxygen. They provoke the formation of hydroxyl radicals and other reactive species that attack the pollutant molecules and thus degrade them (Maggos *et al*. [1]).

Over recent years, heterogeneous photocatalysis has received a great deal of attention and has become a very promising technology for the remediation of environmental pollution owing to the fact that it can lead to the complete destruction of a great number of organic and inorganic compounds with low energy costs. In addition, particular interest has been given to the titanium dioxide (TiO_2) photocatalysis, which is found to exhibit unique advantages in efficiently decomposing low concentrations of inorganics and VOCs under mild conditions in comparison to other available remediation technologies, such as the thermal and catalytic incineration technologies (Fu *et al*. [2], Jacobi *et al*. [3], Blanco *et al*. [4]). For example, while one NOx control methodology is to reduce NOx back to N_2 (Zhang *et al*. [5]), another approach is to oxidize NO to NO_2 and HNO_3 along the general direction of nitrogen fixation. Overall, the NOx photocatalytic oxidation offers the following distinctive advantages: (1) no extra reactants are required and (2) NOx is recycled or recovered as nitric acid, which constitutes a potential raw material for fertilizers.

The use of the TiO_2 photocatalyst in cementitious and other construction materials has become an interesting approach over the last decades for the removal of air pollutants in urban areas (Fujishima *et al*. [6]). Concrete pavement surfaces and external building surfaces constitute optimal media for the application of photocatalytic materials than can reduce air pollution in indoor and outdoor environments. A number of laboratory studies (Strini *et al*. [7], Poon and Cheung [8], Demeestere *et al*. [9]) as well as several pilot projects can nowadays affirm the de-pollution effectiveness of such photocatalytic building materials. Furthermore, it is proven that even in real complex site conditions, the photocatalytic air purification effect of the (photocatalytic) construction materials (cementitious layer) remains effective (Guerrini and Peccati [10], Beeldens [11]).

In addition to the materials' construction quest, in the literature of photocatalysis, special care has also been given to the optimal reactor configuration. Several different laboratory reactor designs are nowadays reported in the literature, including fixed bed annular reactor configurations, batch reactor, semi-batch reactor with quartz flat window, circulating fluidized bed (CFB) reactor, microchannel reactor, honey comp monolith reactor, TiO^2-

coated fibre-optic cable reactor, annular venture reactor etc. (Tomasic *et al*. [12]). In the majority of studies, a continuous-flow air pollutant stream is employed (dynamic systems), and the photo-efficiency of the materials is evaluated by the difference in the air pollutant concentrations, which are recorded at the steady states before and after the system's irradiation. However, further investigation on the matter is needed since there the relationship between the employed photocatalytic reactor configuration, the adopted operational conditions and the photocatalysts' nature still remains quite unexplored.

It is the purpose of this study to evaluate the photocatalytic efficiency of building materials (ceramic tiles) in a homemade photoreactor under different operational modes: a dynamic and a static one. Both the reactor's design as well the adopted photocatalytic experiments procedure was based on the indications ISO 22197-1:2007 standard [13].

2 Experimental

2.1 Material

Four types of ceramic tiles containing 10% TiO_2 were constructed. The TiO_2 paste was prepared using Degussa P25 powder as the starting material. 3 g of the powder were mixed with 1.1ml 10% aqueous solution of distilled acetylacetone in a porcelain mortar, where 4ml deionized water was added dropwise. Finally, the mixture was further homogenized with a non-ionic surfactant, Triton X-100.

The tiles differed on the number of the TiO_2 layers, which were deposited on their surface. Specifically, the following materials were constructed:
#1. 1 layer from 10% TiO_2,
#2. 2 layer from 10% TiO_2
#3. 3 layer from 10% TiO_2
#4. 4 layer from 10% TiO_2

2.2 Photocatalytic experiments

The photocatalytic activity of ceramic tiles was examined employing a photocatalytic system, which comprised of a gas delivery unit, a reactor chamber and a measurement unit (Figure 1). A compressed gas cylinder of 10 ppmv NO (±2%) balanced in N_2 was used for the creation of NO polluted atmosphere in the photocatalytic reactor (Linde Hellas Ltd). Prior to its introduction to the photocatalytic chamber, NO was mixed with the appropriate quantity of synthetic air (20.5% v/v O_2 and 79.5% v/v/ N_2) in order to adjust the initial NO concentration to $C_{NO} \sim 200$ μg m^{-3}. Calibrated flow meters allowed setting and controlling the flow rate at 2-2.5 L/min for the compounded gaseous stream in the case where the system operated under <u>dynamic conditions</u>. The flow rate value was chosen with the criterion to avoid the appearance of mass transfer limitation phenomena above the material's surface. So as to ensure the efficient mixing of the atmospheric constituents within the chamber in the case of the <u>static mode </u>system, a fan was installed and set in operation.
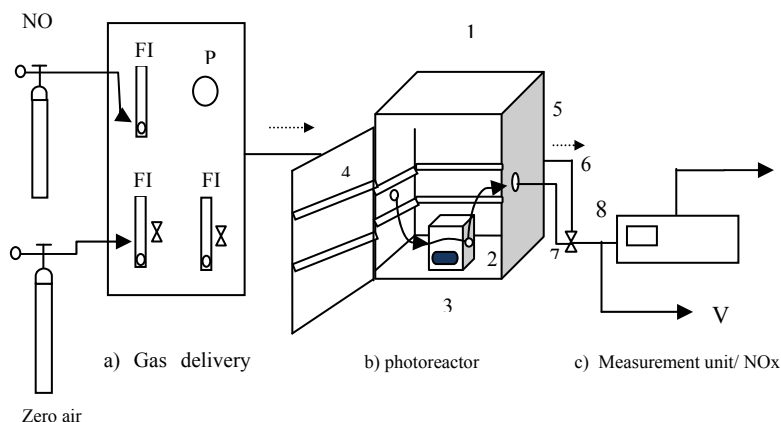
Figure 1:   Schematic presentation of the photocatalytic.

Photocatalytic experiments were carried out in a cubic Pyrex-glass reaction chamber of 0.125 m^3 volume capacity (50 cm x 50 cm x 50 cm), which was placed inside a (light) sealed irradiation box. The photocatalytic tiles were subsequently placed at the bottom surface of the cell. The cell's loading factor l_f (photocatalyst surface/cell volume ratio) was estimated to be about 0.72 m^2 m^{-3} (figure 2).
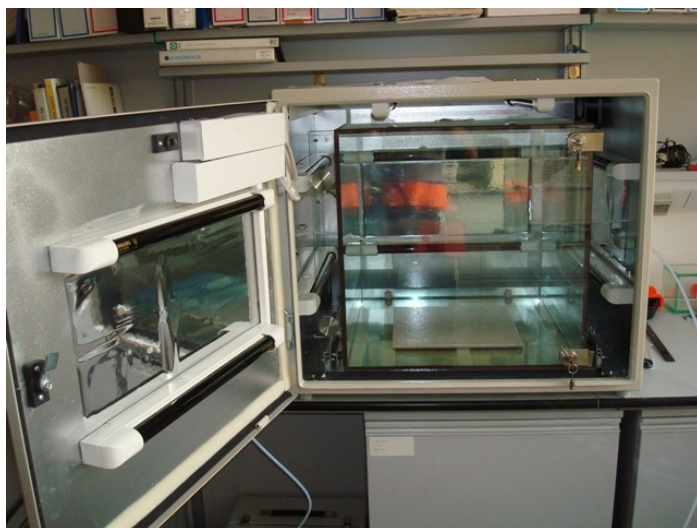

Figure 2:   Photocatalytic reactor (environmental cubic chamber).

Irradiation was provided by ten fluorescent black light blue 15W Philips TLD 15W/08 lamps, being located horizontally, in pairs, on each side of the irradiation box at a distance of approximately ~20 cm from the photocatalytic

material. The total UV light intensity measured on the samples' surface was on average 30lum/ft^2 (or 47.3Wm^{-2}). Irradiation time was set at 45min.

The initial concentration of the air pollutant as well as the adopted temperature and humidity levels within the glass cell were chosen with the ultimate criterion of approaching the corresponding levels of the same variables in the outdoor real environment. For that purpose the NO concentration was established at approximately 200 μg m^{-3}, while the temperature and humidity levels were controlled at 24-27°C and 35-45% respectively. For keeping the temperature stable within the chamber, the environmental box was also equipped with two fans. The NO$_x$ concentration was measured with a chemiluminescence NOx analyzer (Environment S.A AC42M), which was connected in line to the outlet of the reactor.

3   Results and discussion

3.1 Static

The principle on which the measurement and evaluation of the materials' photocatalytic activity is based refers to the loss of the pollutant's amount that is observed over the whole photocatalytic process.

The reduction of the air pollutant's concentration within the chamber can be attributed to the appearance of the following four (4) different mechanisms:

1. Sink effect (on the walls of chamber)
2. Absorption on the surface of the sample
3. Photolysis by U.V light
4. Photocatalysis by TiO$_2$ and U.V light.

It then becomes clear that the evaluation of these side-effect mechanisms (1–3) plays a critical role to the assessment of the TiO$_2$-material's ability to photocatalytically remove the air pollutant.

Table 1:   Ceramic tiles photocatalytic parameters for static mode.

Photo-material	% NO removal during experiments 1,2,3	% NO photocatalytic removal	Photocatalytic rate (PR) NO (μg m^{-2}s^{-1})
-	23.4 (Removal due to photolysis & sink effects)	-	-
#1	77.1	**54.4**	**0.34**
#2	97.1	**73.7**	**0.39**
#3	95.8	**72.4**	**0.50**
#4	98.1	**74.7**	**0.65**

Blank tests were initially performed in order to estimate the synergy of these side effects. The tests involved the examination of the performance of a material containing no TiO_2 amount under the same conditions. Calculations showed that in the case of static systems, the contribution of these mechanisms does not exceed the value of 23.4% of the total NO removal recorded during the photocatalytic experiments (Table 1).

For the evaluation of the material's photocatalytic ability, the TiO_2 sample was placed into the chamber and the air pollution mixture was introduced. The system was left for 30 min to stabilize. Subsequently the UV lamps were switched on and the system was left under irradiation for a 45 time period. The NO concentration at the exit of the reactor was constantly measured by the NOx analyzer. The catalytic activity of the materials was then assessed by the following parameters [14]:

a) the Photocatalytic Decomposition Percentage (PD), which displays the percentage of air pollutant that is photo-removed during the photocatalytic experiment, calculated by eq. (1):

$$\% NO_{\text{photo-removed}} = \left(\frac{[NO]_{U.V} - [NO]blank}{[NO]_{U.V}} *100 \right) \qquad (1)$$

where:

$[NO]_{U.V}$: the amount of NO removed/degraded during the irradiation of TiO_2 containing sample ($\mu g\ m^{-3}$), and

$[NO]_{blank}$: the amount of NO removed during blank tests (due to side effects) ($\mu g\ m^{-3}$)

(b) The photocatalytic/oxidation rate (PR, $\mu g\ m^{-2}\ s^{-1}$), which is regarded to provide a more precise estimation of the depollution capacity of a material since for its calculation the sample surface, the chamber volume and the duration of the irradiation period are also taken into account eq. (2):

$$Photocatalytic-rate(PR) = \left(\frac{V * [NO]_{TiO_2UV}}{A * t} \right) \qquad (2)$$

where:

$[NO]_{TiO_2\ U.V}$: the amount of NO removed photocatalytically from the system due to TiO_2 effect ($\mu g\ m^{-3}$)

V: the volume of the experimental chamber (m^3)

A: sample surface (m^2)

T: irradiation time (s).

As it can be seen by the results of Table 1, the increase of the number of the TiO_2 layers deposited on the material's surface, leads to a constant increase of the photocatalytic rate (from the value of 0.34 $\mu g\ m^{-2}\ s^{-1}$ up to a value of 0.65 $\mu g\ m^{-2}\ s^{-1}$). On the contrary, after a given point (after the deposition of 2 layers) the % photocatalytic removal seems to remain almost unaffected (at the same level) (~ 74%) regardless of the number of the deposited TiO_2 layers. Consequently, it

can be assumed that the PR parameter gives a more precise picture of the material's photocatalytic ability.

3.2 Dynamic

The measurement of the material's ability to photocatalytically decompose the air pollutant in the case of dynamic systems is based on calculation of the difference between the final (after irradiation) and the initial (before irradiation) steady state concentration of the air pollutant.

For this purpose, the ceramic tiles were placed into the reaction chamber. The reactor was flushed with synthetic air in order to check the cleanness of the system and to allow any possible contaminants to be removed from the sample's surface. With the use of flow meters the inlet NO concentration was set to the desired value, while the flow rate was controlled to 2.5 L/min.

The air mixture was initially driven through the by-pass line directly to the NOx analyzer in order to set the initial NO concentration at the desired value and check the response of the measurement system. Subsequently, the air mixture was channeled to the reaction chamber. Data acquisition began and the system was left to equilibrate. The non-irradiation equilibrium value of the NO concentration was regarded to provide information on the amount of NO which was removed due to its adsorption onto the material's surface and/or on the reactor's glass walls. After the concentration appeared to be stable (steady state), the lamps were activated and the system was left to equilibrate. The concentration of the NO was constantly recorded in respect to the reaction time. The value of the irradiated steady state concentration was regarded to provide information on the amount of NO removed due to light photolysis but more importantly due to photocatalysis. After the NO concentration reached a steady state, the lamps were turned off and the system was allowed to re-equilibrate to the non irradiated condition and a last sample was taken to confirm the previously measured concentration levels.

Once again in order to quantify the photocatalytic performance of the TiO_2 material the PD and PR parameters were calculated according to eq. (3) and (4):

$$\%NO_{photo-removed(PPD)} = \left(\frac{[NO]in - [NO]final}{[NO]in} * 100 \right) \tag{3}$$

where:

$[VOC]_{in}$: the initial VOC concentration ($\mu g\ m^{-3}$)
$[NO]_{final}$: the final NO concentration ($\mu g\ m^{-3}$)

$$Photooxidation-rate(PR) = \left(\frac{F * [NO]_{TiO_2UV}}{A} \right) \tag{4}$$

where:

$[NO]_{TiO2\ U.V}$: the amount of NO removed photocatalytically from the system due to TiO_2 effect (final-initial) ($\mu g\ m^{-3}$)
A = Sample surface (m^2).

As it can be seen in Table 2, increasing the number of the TiO_2 layers both the % photo-removal and the photocatalytic rate are found to increase. Specifically, results displayed that in the case of the continuous-flow (dynamic) system the % NO PD and the PR parameters ranged from 14.2% up to 50.1% and from 0.20 μg $m^{-2} s^{-1}$ up to 0.63 μg $m^{-2} s^{-1}$ respectively. This result comes to opposition with the observed trend of the corresponding parameters in the case of the static system, where it was found that only the PR parameter was increased with increasing the number of TiO_2 layers.

Comparing the results obtained by the two different operational systems (dynamic-static systems) (Figs. 3 and 4), it can be concluded that for the same material, the % PD values present significant differences. As a matter of fact, the

Table 2: Photocatalytic parameters for dynamic mode.

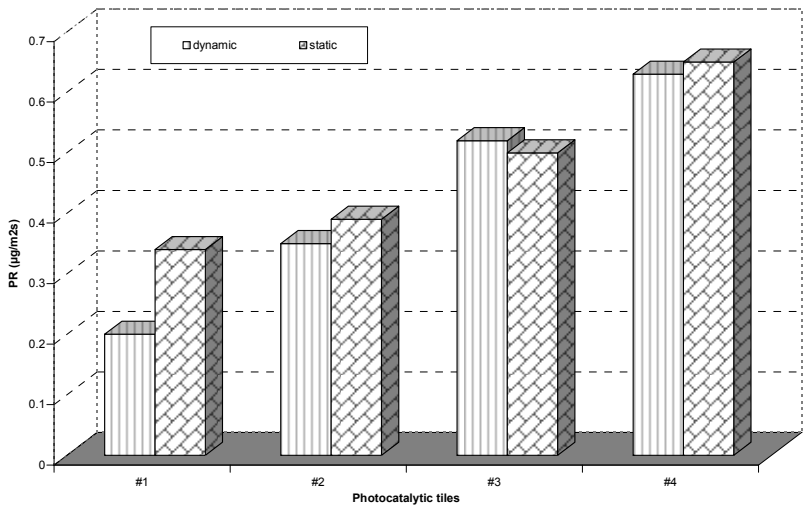| Photo-material	% NO photocatalytic removal	Photocatalytic rate (PR) NO ($\mu g\ m^{-2} s^{-1}$)
-	-	-
#1	14.2	0.20
#2	29.8	0.35
#3	40.2	0.52
#4	50.1	0.63

Figure 3: Photocatalytic rates of the 4 materials under static and dynamic mode.

level of the %PD parameter is found to be higher in the static than in the dynamic system. This difference can be attributed to the total degradation of NO during static experiments, which leads to a higher C_{init}-C_{final} difference (eqn. (1), eqn. (2)) and subsequently to a higher value of the %PD parameter.
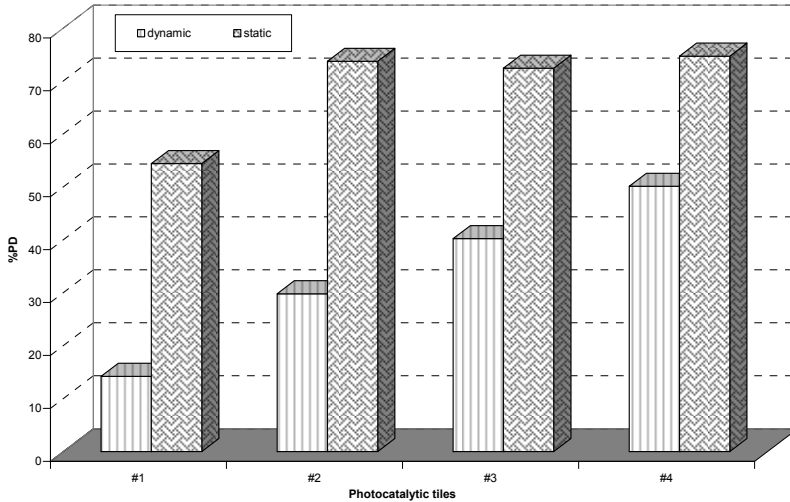

Figure 4:   % PR of the 4 materials under static and dynamic operational mode.

On the other hand, the PR values are found to be very close under both static and dynamic experiments. It could then be asserted that contrary to the % PD, the PR parameter constitutes a more ideal parameter and could be used as a common measurement unit for the presentation and comparison of these two functionally different systems, whereas the %PR parameter could be regarded as a parameter that can only describe the photocatalytic behaviour of a material within a specific photocatalytic system under specific operational conditions.

4   Conclusion

The ability of ceramic tiles containing different layers of TiO_2 (1 up to 4) to photocatalytically degrade NO was examined in a cubic glass photocatalytic reactor under two different operational modes: a static and a dynamic operation. Overall, results displayed that in both cases, the 4-layer tile presented the highest photocatalytic decomposition rate (PR ~0.65 $\mu gm^{-2}s^{-1}$). The photocatalytic ability of the tiles was found to decrease while decreasing the number of the deposited TiO_2 layers, with the PR parameter following a similar downward trend in both static and dynamic systems. Unlike to the PR parameter, the %photocatalytic decomposition percentage (PD%) presented significant differences for the same materials under the two operational modes. For

example, whereas the #3 tile depicted a high %PD value (72%) under static conditions, yet, in the case of the dynamic ones, it displayed a significantly lower performance (40.2%). Additionally, the same variable could not display any specific trend under static conditions with varying the number of TiO_2 layers, a result which was apparent under dynamic conditions. Overall, it is proved that the PR parameter can accurately describe the photocatalytic behaviour of a material independently of the operational mode of the photo-reactor used for the experiments.

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