ATMOSPHERIC PURIFICATION BY TiO_2-COATED FIRED CLAY TILES: PARAMETRIC STUDY AND COMPARISON WITH OTHER BUILDING MATERIALS

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Abstract

Atmospheric pollution is a major environmental and health concern of the XXIst century. Yet, despite the countless international protocols aiming at reducing the emissions of air pollutants, the European regulatory thresholds are still too often exceeded.

When it comes to atmospheric purification, photocatalytic coatings are known to be efficient. Besides, in France, two thirds of the roofs are built with fired clay tiles. Hence, this study is focusing on the ability of fired clay tiles, functionalized with a photocatalytic coating, to degrade NOx. More specifically, the impact of environmental factors on the dispersion and degradation of nitrogen dioxide (NO_2), one of the main atmospheric pollutants, is evaluated.

To that end, the influence of the initial NO_2 concentration, light intensity, roof inclination and air circulation has been assessed, using TiO_2-coated fired clay tiles. The performance of fired clay coated and uncoated tiles has also been compared to that of other frequently used building materials: concrete tiles, zinc boards, bitumen boards, shingle, glass tiles and raw earth bricks. NO_2 degradation by the several tested materials has been determined, both under illumination and in the dark. All the experiments have been carried out in a dedicated sealed testing chamber.

While results did not highlight a significant influence of the pollutant concentration on NO_2 degradation rate, increasing light intensity led to greater degradation efficiency and allowing air circulation around the samples decreased the degradation rate. The comparative study emphasized the efficiency of coated fired clay tiles to photocatalytically degrade NO_2, whereas the other tested materials, except for raw earth bricks, only exhibited adsorption properties.

Keywords: *atmospheric purification, fired clay products, nitrogen dioxide, photocatalysis*

1. INTRODUCTION

Pollution is one of the major concerns of the XXIst century and atmospheric pollution in particular is monitored with great attention. Since the "Great Smog of London" in 1952, smogs are regularly observed over major cities, harming the environment as well as the human health. Therefore, many protocols have been signed to reduce the emissions of pollutants (Helsinki 1985, Sofia 1988, Geneva 1991, Oslo 1994, Gothenburg 1999…), setting emission ceilings for the main air pollutants [1]. The lifetime of the latter in the atmosphere varying from a few hours for ozone (O_3) to a few months for carbon monoxide (CO), mainly depending on their physicochemical properties, it is crucial to develop methods to eliminate them [1].

According to the French law, "*atmospheric pollution is the introduction by humans, directly or indirectly, in the atmosphere or closed rooms, of substances that can affect human health, living resources, ecosystems, influence climate changes, harm material goods or create odor nuisances*" [2]. The main atmospheric pollutants are sulfur dioxide (SO_2), volatile organic compounds (VOC), nitrogen oxides (NOx), ammonia (NH_3), carbon monoxide (CO) and fine particles ($PM_{1/2.5/10}$) [1]. This paper is only focusing on nitric oxide (NO) and nitrogen dioxide (NO_2).

Nitrogen oxides are all the molecules in which nitrogen is linked to at least one atom of oxygen and for which the oxidation number equals at least 2 (NO, NO_2, N_2O_3, N_2O_5, HONO, HNO_3, $CH_3C(O)OONO_2$). NO and NO_2 are the prevailing oxides in the atmosphere and are collectively known as NOx (**Eq.1**) [3].

$$[NO_X] = [NO] + [NO_2] \qquad (1)$$

In 2019 in France, road transportation was by far the larger NOx emitter (385.6 kt), followed by agriculture (79.7 kt) and residential activities (42.1 kt) [4]. If the amount of NOx released in the atmosphere has been continuously decreasing over the past years, following the emission ceilings imposed by national and international directives, those pollutants are still responsible for acid rains, smogs, heart, respiratory and neurological diseases, leading to premature mortality [1, 5, 6]. NOx are furthermore responsible for a photochemical pollution generating ground-level ozone (O_3) through NO_2 photolysis under ultraviolet radiation (λ<473 nm), following the Chapman cycle [1] (**Fig. 1**).

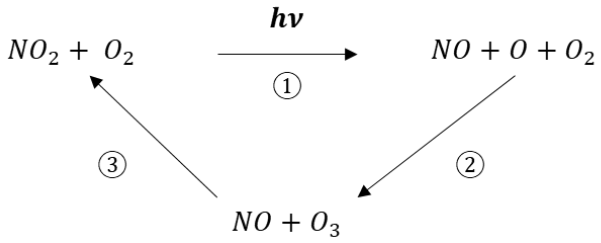

Fig. 1. Chapman cycle: photolysis reaction of NO_2 under ultraviolet radiation [1]

To date, many studies have reported the efficiency of photocatalytic systems to degrade NOx [7 – 14]. Photocatalysis is based on the activation of a photosensitizer, mostly semi-conductors, by a photon – whose energy (hv) equals at least the band gap energy of the semi-conductor – enabling the excitation of an electron (e^-) and the creation of a hole (h^+). If no charge recombination occurs, the photoinduced charges migrate toward the surface of the semi-conductor and react with the water and dioxygen molecules adsorbed on its surface to form highly reactive free radicals. The latter are then responsible for the degradation of the NOx molecules adsorbed on the surface of the semi-conductor (**Fig. 2**) [15].

Three types of semi-conductors are generally used for photocatalytic applications. It can either be compounds alone (TiO_2, ZnO…) or multi-components systems (CeO_2/TiO_2, La_2O_3/TiO_2…), the latter having the ability to avoid charge recombination. Oxides can also be doped (Cu-TiO_2, Ce-TiO_2…) so as to reduce the band gap of the system [9, 11, 16 – 18]. Among those photocatalytic systems, Titanium dioxide (TiO_2) is by far the mostly used semi-conductor due to its effective photocatalytic properties, its availability and its non-expensive cost [12].

$$Semi - conductor + h\nu \rightarrow e^- + h^+$$
$$H_2O + h^+ \rightarrow H^+ + OH^\cdot$$
$$OH^- + h^+ \rightarrow OH^\cdot$$
$$O_2 + e^- \rightarrow O_2^{\cdot -}$$
$$O_2 + e^- \rightarrow O_2^{\cdot -}$$
$$O_2^{\cdot -} + H^+ \rightarrow HO_2^\cdot$$

Creation of free radicals at the surface of the semi-conductor

$$NO + 2\,OH^\cdot \rightarrow NO_2 + H_2O$$
$$NO + HO_2^\cdot \rightarrow NO_2 + OH^\cdot$$
$$NO_2 + OH^\cdot \rightarrow HNO_3$$

Degradation of NOx by the free radicals

Fig. 2. Indirect degradation of NOx via free radicals

Yet, environmental conditions can impact the efficiency of photocatalytic systems to degrade NOx. Previous papers reported that the level of UV-A radiation, the relative humidity, the flow rate and the inlet concentration could in fact influence the rate of degradation [19, 20].

The aim of this study is to assess the impact of environmental conditions such as light intensity and ventilation on the dispersion and degradation of NOx by TiO_2-coated fired clay products. Besides, this paper focuses on the performance of coated and uncoated fired clay products to degrade NOx, as compared to that of other building materials. All the experiments have been conducted in a dedicated sealed NOx chamber developed at CTMNC.

2. MATERIALS AND METHODS

2.1. Preparation of the fired clay samples

Fired clay samples were prepared in the CTMNC laboratory. 237 mm (± 1 mm) long, 51 mm (± 1 mm) wide and 8 mm (± 1 mm) high tiles were extruded from a clay mixture dedicated for the production of roof tiles. After the extrusion, tiles were left to dry at room temperature and controlled humidity for 48 hours before being dried in a ventilated oven at 110°C for 48 hours. The dried tiles were then fired at 940°C for 90 minutes, with a temperature increase of 78°C/hour. The fired tiles were finally cooled down to room temperature at 84°C/hour.

For the coated fired clay samples, the photocatalytic coating has been applied on the dry tiles before the firing step. The Anatase TiO_2-based coating has been applied on the tiles as an aqueous solution by pulverisation.

Tiles size fluctuations were considered to be insignificant, but in order for the surface to be significant enough, a tested sample was constituted of six tiles (**Fig. 3**).

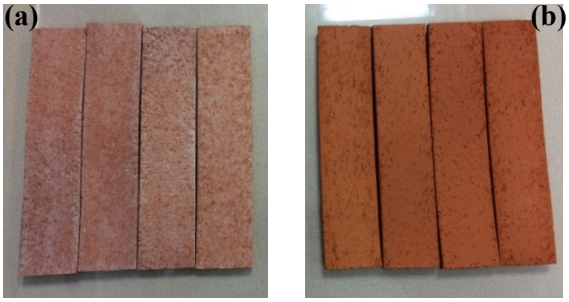

Fig. 3. Fired clay coated (a) and uncoated (b) tiles prepared by extrusion and used for the experiments

2.2. Other building materials used for the comparative study

The efficiency of coated and uncoated fired clay tiles to degrade NOx was compared to that of other frequently used buildings materials. The latter were bought in stores specialized for building materials. The following materials have been used for the comparison: concrete tiles, bitumen boards, shingles, glass tiles, zinc boards and raw earth bricks.

2.3. Testing NOx chamber

A sealed chamber has been developed in order to test the different chosen materials under a NOx enriched atmosphere and variable environmental conditions (**Fig. 4**).

The walls of the chamber are made of polymethylmethacrylate (PMMA). The tightness is ensured by a mechanical seal and junctions are covered with mastic and seals. A tiltable metallic structure has been mounted inside the chamber to support the samples.

The gas mixture Crystal prepared by *Air Liquide* is injected inside the chamber. The mixture is composed of 80 mol% of nitrogen (N_2), 19.99 mol% of dioxygen (O_2) and 0.01 mol% of nitrogen dioxide (NO_2). NO_2 concentration inside the chamber is continuously monitored by the gas detector PORTASENS II C16 from *ATI*. The latter is able to detect a concentration of NO_2 ranging from 2 ppm to 200 ppm with an accuracy of 0.1 ppm.

The lamp used as a light source is a 30W *Philips* MASTER TL-D fluorescent tube. The emission wavelengths are located in the UV-Visible region, which enables the similarity with the solar spectrum. A reflector can be installed on the top of the lamp to direct light rays toward the surface of the samples. The chamber is also equipped with an 18 W fan enabling an air circulation of 2.4 m/s in its vicinity. Finally, a device monitoring the temperature and relative humidity inside the chamber is installed.

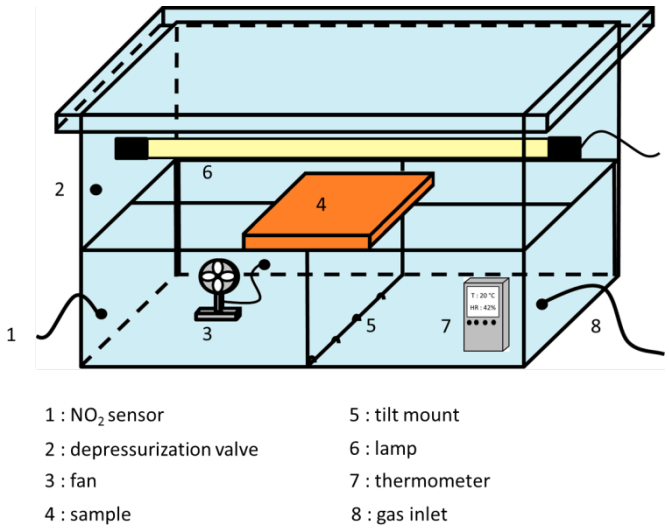

Fig. 4. Schematic view of the NOx chamber

2.4. Evaluation of the impact of environmental conditions on photocatalysis efficiency

The sample used to study the influence of environmental conditions on the degradation of NO_2 was composed of six fired clay tiles functionalized with a photocatalytic Anatase TiO_2-based coating. Considering that the photocatalytic properties of the coating can decrease over the cycles, the sample has been regularly replaced by a new one. For all the tested environmental parameters, evolution of NO_2 concentration inside the testing chamber has been monitored with the PORTASENS gas detector.

To evaluate the impact of NO_2 initial concentration on its degradation rate by photocatalytic products, the initial concentration on NO_2 inside the chamber was varied from 7.6 ppm to 23.4 ppm.

To study the influence of light intensity on NO_2 degradation rate, tests have been carried out without (3405 lm/m²) and with (8150 lm/m²) a reflector mounted on the fluorescent tube. Besides, the sample has also been indirectly lighted by the reflection of the light rays on the walls of the chamber (755 lm/m²). The light intensity received at the surface of the sample was measured with a luxmeter.

The impact of the inclination of roof tiles on the efficiency of NO_2 degradation was determined by tilting the fired clay tiles on their support, from 0° to 30°. For each inclination, the light intensity at the surface of the samples has been measured using the luxmeter.

The influence of the available photocatalytic surface area was studied by varying the number of tiles simultaneously exposed to the light source. Three different exposed surface areas have been tested: 120 cm², 360 cm² and 730 cm².

Eventually, the impact of air circulation on the NO_2 degradation rate was evaluated using a fan. Degradation cycles were carried out with and without powering on the fan and different locations of the fan in the chamber were tested.

2.5. Comparative study with other building materials

The efficiency of coated and uncoated fired clay tiles to degrade NO_2 was compared to the efficiency of other building materials: concrete tiles, bitumen boards, shingles, glass tiles, zinc boards and raw earth bricks. Each material was tested separately, under the same following environmental conditions, with and without illumination: the initial NO_2 concentration was set to 12 ppm, the samples were placed horizontally, the fan remained switched off and the reflector was mounted on the fluorescent tube when the light was switched on.

NO_2 concentration inside the testing chamber has been continuously monitored with the PORTASENS gas detector.

3. RESULTS AND DISCUSSION

3.1. Impact of NO_2 initial concentration

It is widely acknowledged that NO_2 molecules adsorption on the photocatalytic substrate follows the Langmuir-Hinshelwood law [21 – 25]. The degradation rate r is defined by the following equation (**Eq. 2**):

$$r = k\frac{KC}{1+KC} \qquad (2)$$

where k represents the reaction rate constant, K the adsorption equilibrium constant for NO_2 on the active site and C the gas concentration. In this study, since NO_2 concentration is very low ($KC \ll 1$), the degradation rate equation can be simplified as follows (**Eq.3**):

$$r = k'C \qquad (3)$$

where k' is the reaction rate constant and C the gas concentration given by the following equation (**Eq.4**):

$$C = C_0 e^{-k\prime t} \qquad (4)$$

with C_0 the initial NO_2 concentration inside the chamber and t the space time. Therefore, NO_2 is degrading in the atmosphere according to a first-order reaction in the studied gas concentration range [26]. The reaction rate constant k' (written k in the rest of this paper) of each degradation cycle is calculated from **Eq.5** and is used in the rest of this study to compare the influence of the environmental parameters on the degradation efficiency.

$$\ln\left(\frac{C_0}{C}\right) = kt \qquad (5)$$

Results presented **Fig. 5** show that the degradation rate of NO_2 is not significantly influenced by the initial NO_2 concentration. This observation is consistent with the study conducted by Bengtsson (2010), concluding that the absence of impact of the initial concentration on the reaction rate confirms that the degradation rate follows a first-order reaction.

In the literature, studies focusing on the degradation rates of several atmospheric pollutants (NO, VOCs…) suggest that different initial concentrations lead to various reaction rates. Most of the works concluded that an increase of the inlet gas concentration conducted to a lower degradation rate [20, 24, 25], while Kim (2005) noticed the increase of the photocatalytic degradation of VOCs when increasing the initial concentration. Those observed differences could be partially explained by the fact that the degradation rate of atmospheric pollutants can be simultaneously influenced by several parameters (relative humidity, light intensity, catalyst load…), especially at low reaction rate [27]. The nature of the substrate, and thus its intrinsic properties, may also impact the degradation rate.

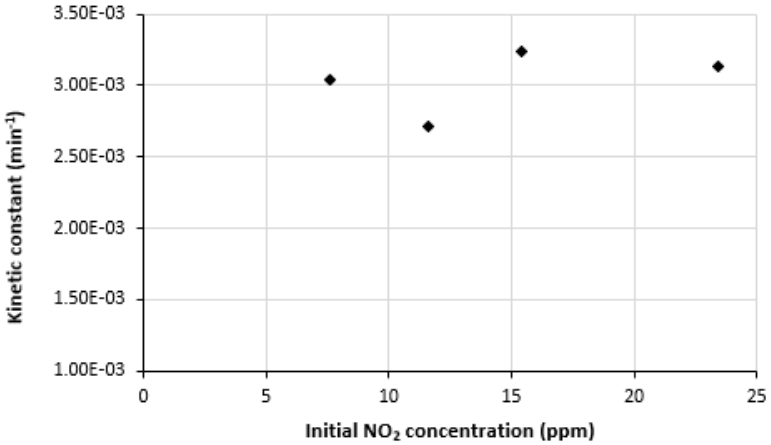

Fig. 5. Impact of the initial NO_2 concentration on NO_2 degradation rate

3.2. Impact of light intensity

The influence of light intensity on the degradation rate of atmospheric pollutants has been widely studied [19 – 21, 27, 28]. When it comes to light intensity, photocatalytic reactions are known to occur in two regimes [28]. At lower radiation intensities, the reaction rate follows a linear first-order regime: the chemical reaction is faster than the electron-hole pairs recombination. On the contrary, the reaction rate follows a half-order regime at higher radiation intensities: the electron-hole pairs are consumed more rapidly by the recombination process than by the chemical reactions.

Results obtained in this study suggest that NO_2 degradation rate increases with an increase of the irradiance before reaching a plateau, the degradation curve being asymptomatic (**Fig. 6**). Those results are consistent with the two theoretical regimes of the degradation rate. An increase of light intensity enables more photons to reach the photocatalytic coating, thus increasing the formation of electron-hole pairs. Above a certain intensity, all the available photocatalytic sites may have been activated: the photocatalyst load becomes the limiting factor.

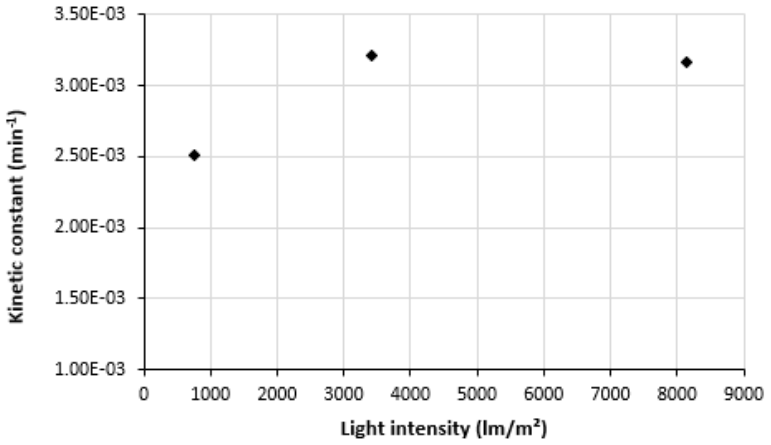

Fig. 6. Influence of light intensity on NO_2 degradation rate

3.3. Impact of fired clay roof tiles inclination

Since NO_2 degradation rate is influenced by light intensity, it is appropriate to consider that samples inclination can have an impact as well. French regulation requires roofs to have a minimum slope, mainly to permit water evacuation. The magnitude of the slope depends on regional criteria, on the type

of fired clay tiles used and on the eventual association with other roofs elements. Because of this inclination, solar radiations do not arrive perpendicularly to the surface of the tiles, thus limiting the light intensity reaching the surface.

Obtained results (**Fig.7**) confirm that the light intensity received at the surface of the samples decreases with the inclination. NO_2 degradation rate slightly decreases with the increase of the slope, the most significant variation being from 10 to 15°. Those results are in line with the observations made studying the impact of light intensity on NO_2 degradation rate.

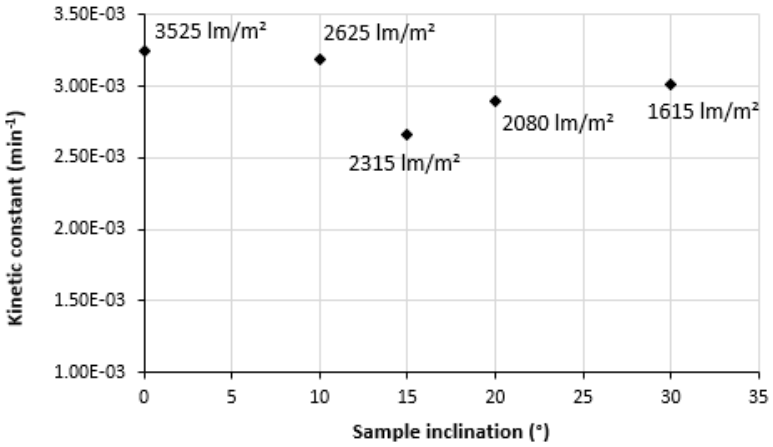

Fig. 7. Influence of samples inclination on NO_2 degradation rate

3.4. Impact of the extent of the exposed photocatalytic surface area

The impact of the extent of the photocatalytic surface area on NO_2 degradation efficiency was studied varying the exposed surface from 120 cm² to 730 cm², adapting the number of tiles simultaneously exposed. For each test, the initial NO_2 concentration was set to 13 ppm.

Results outline that the larger the exposed surface, the faster the NO_2 degradation. The evolution of the kinetic constant as a function of the extent of the surface area appears to increase linearly (**Fig. 8**).

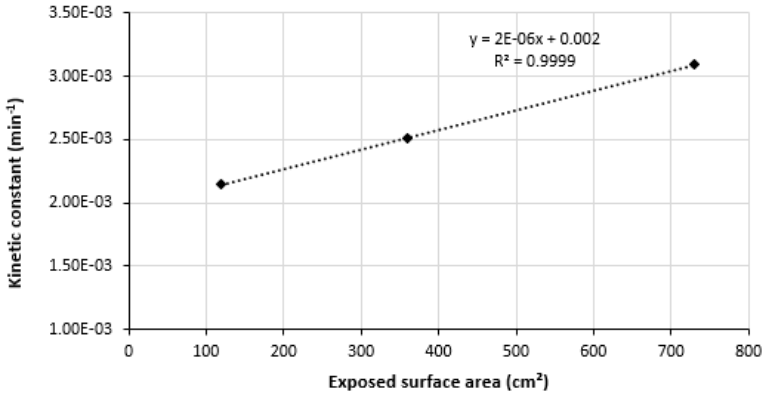

Fig. 8. Influence of the extend of the exposed photocatalytic surface area on the kinetic constant of NO_2 degradation

Table 1 summarizes some characteristic values of NO_2 degradation, $t_{1/2}$, $r_{1/2}$ and $r_{1/2,m^2}$. $t_{1/2}$ (min) is defined as the time needed for half of the initial NO_2 concentration (C_0) to be degraded and is calculated

knowing the kinetic constant k (**Eq.6**). $r_{1/2}$ (ppm/min) is the degradation rate of half of the initial NO_2 concentration and is calculated according to **Eq.7**. $r_{1/2,m^2}$ (ppm/min/m²) is defined as the degradation rate of half of the initial NO_2 concentration per unit area (**Eq.8**). $C_{1/2}$ is the NO_2 concentration at $t_{1/2}$.

$$t_{1/2} = \frac{\ln(2)}{k} \quad (6)$$

$$r_{1/2} = \frac{C_0 - C_{1/2}}{t_{1/2}} \quad (7)$$

$$r_{1/2,m^2} = \frac{r_{1/2}}{exposed\ surface\ area\ (m^2)} \quad (8)$$

Those data highlight that relative to the exposed photocatalytic surface area, NO_2 degradation rate is higher for smaller surfaces. In this case, the pollutant concentration may thus to be the limiting factor.

Table 1. Characteristic values of NO_2 degradation rate according to the exposed surface

	Exposed photocatalytic surface area (cm²)		
	120	360	730
$t_{1/2}$ (min)	322	276	224
$r_{1/2}$ (ppm/min)	0.020	0.021	0.028
$r_{1/2,m^2}$ (ppm/min/m²)	1.7	0.6	0.4

3.5. Impact of air circulation on NO_2 degradation rate

Gas molecules at the surface of roofs are constantly more or less rapidly windswept, depending on the strength of the wind. This air circulation may have distinct effects on the efficiency of NO_2 degradation by photocatalytic coatings. On the one hand, new pollutants molecules are constantly brought at the surface of the photocatalytic active sites, and on the other hand, the residence time of the pollutants molecules on the active sites is reduced. The tests carried out in this study were meant to determine whether one or the other effect is predominant.

In order to simulate air circulation around the samples, a fan was installed inside the testing chamber. Results show that air circulation tend to decrease the degradation rate of NO_2 (**Fig.9**) and are consistent with the observations made by Staub de Melo (2012) and Hüsken (2009). This result suggests that a minimum residence time is required for the pollutants on the active sites to be degraded. Therefore, on days with strong winds, the residence time of pollutants molecules being reduced, the degradation efficiency will be lower.

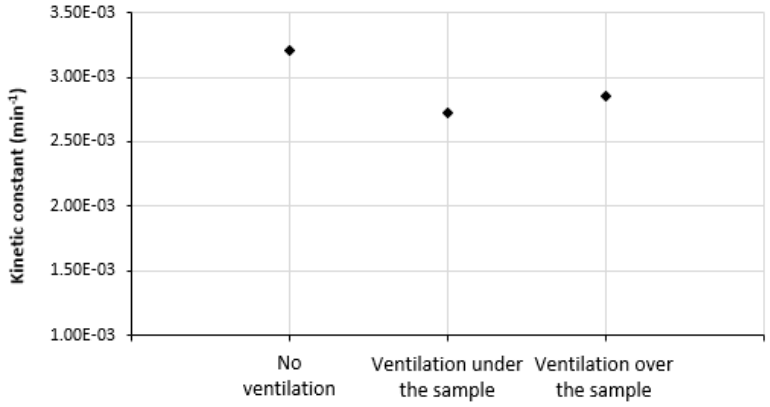

Fig. 9. Influence of air circulation on NO_2 degradation rate

3.6. Comparison study with other building materials

The efficiency of fired clay samples coated with a photocatalytic coating to degrade NO_2 was compared to the efficiency of other selected building materials. For each material, two degradation cycles have been carried out, one under illumination and the other in the dark. This testing method enables thereby to highlight the possible NO_2 adsorption properties of the tested materials as well as their potential intrinsic photocatalytic properties.

To compare the NO_2 degradation efficiency of the different building materials, $r_{1/2,m^2}$ (ppm/min/m²), the degradation rate of half of the initial NO_2 concentration per unit area was calculated for each material (Table 2).

With no illumination, NO_2 degradation is mainly imputed to the adsorption properties of the building materials. The differences observed between the materials in terms of degradation rate may be partly justified by the fact that the adsorption capacity of a material highly depends on its specific surface and its pore size [29]. Higher degradation rates are measured for the fired clay and concrete tiles and for the raw earth bricks, the three of them being porous materials. The extent of the exposed surface area might as well partly explain the adsorption rate differences, as it has been highlighted in the parametric study (3.4).

The tests carried out under illumination highlight the photocatalytic properties of TiO_2-coated fired clay tiles. Besides, NO_2 degradation rate by uncoated raw earth bricks is greatly enhanced under illumination, suggesting some intrinsic photocatalytic properties, although raw earth products are not known to possess such properties. For all the other tested materials, no significant NO_2 degradation rate improvement has been identified under illumination. The slight degradation rate increase may be imputed to the natural decomposition of NO_2 to No and O_3 according to Chapman cycle under UV irradiation.

Table 2. Comparison of NO_2 degradation efficiency by different building materials in the dark and under illumination

		$r_{1/2,m^2}$ (ppm/min/m²)	
	Exposed surface area (cm²)	Without illumination	Under illumination
Uncoated fired clay tiles	0.073	0.28	0.33
TiO_2-coated fired clay tiles	0.073	0.28	0.43
Concrete tiles	0.139	0.28	0.32
Zinc boards	0.090	0.20	0.20
Bitumen boards	0.150	0.16	0.21
Shingle	0.109	0.16	0.23
Glass tiles	0.112	0.13	0.17
Raw earth bricks	0.034	0.57	0.97

4. CONCLUSION

This paper addresses one of the major current environmental concerns, atmospheric pollution.

The study assessed the influence of several environmental factors on the atmospheric NO_2 degradation by fired clay tiles functionalized with a photocatalytic coating. All the tests have been carried out in a dedicated sealed testing chamber.

The experiments did not highlight a significant impact of NO_2 initial concentration on the degradation rate. However, results showed that NO_2 degradation rate increases with an increase of light intensity, before reaching a plateau when all the active sites of the photocatalytic substrate are being occupied by pollutants molecules. Similarly, the study observed that roofs inclination may lower NO_2 degradation rate as a result of a decrease of the light intensity reaching the surface of inclined tiles.

Besides, the extent of the exposed photocatalytic surface area was found to influence the degradation rate: on the one hand, a larger photocatalytic surface caused a greater NO_2 degradation efficiency and on the other hand, the increase of the surface led to the decrease of the degradation rate per unit area. Eventually, air circulation inside the testing chamber decreased the residence time of pollutants on the active sites, leading to a decrease of the degradation efficiency and suggesting that the latter might be impacted on days with strong winds.

The NO_2 degradation efficiency by coated and uncoated fired clay tiles was compared to that of other frequently used building materials. The study highlighted the photocatalytic properties of fired clay tiles coated with TiO_2, while uncoated raw earth bricks also seemed to exhibit intrinsic photocatalytic properties.

The results of the parametric study are to be understood as a trend of the impact of several environmental factors on atmospheric NO_2 degradation. The obtained values must be considered with a measurement uncertainty estimated at 0.03 ppm/min/m². Moreover, this study did not take into account the influence of relative humidity. Other studies concluded that an increase of the relative humidity led to a decrease of the degradation rate [19, 20].

Besides, the present study could be supplemented by an assessment of the impact of intrinsic properties of fired clay tiles on NO_2 degradation rate. Coated fired clay tiles efficiency to degrade NO_2 could be compared according to their open porosity rate, their chemical and mineralogical compositions, or their surface wettability.

When it comes to field conditions, even though it does not seem easy to gather all the optimal environmental factors to degrade atmospheric pollutants, their impact have to be considered to assess the efficiency of such an installation.

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