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Evaluation of the influence of environmental conditions on the efficiency of photocatalytic coatings in the degradation of nitrogen oxides (NOx)

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A B S T R A C T

The incorporation of titanium dioxide (TiO_2) into cement mortars generates materials with photocatalytic properties, that is, a cement matrix able to capture and degrade atmospheric pollutants like nitrogen oxides (NOx). The chemical phenomenon of NOx degradation requires the activation of TiO_2 through ultraviolet radiation (UV-A), as well as water and oxygen molecules necessary for the generation of hydroxyl radicals (OH•), responsible for the degradation of NOx. While photocatalytic materials are in service they are subject to different environmental conditions with regard to the incidence of UV-A radiation, relative humidity of the air and movement of the pollutant masses by the wind. This study aims to evaluate the influence of these different environmental conditions on the efficiency of photocatalytic mortar in the degradation of NOx. Using a specifically-developed test apparatus, the efficiency of a photocatalytic mortar was tested under 27 different environmental conditions, obtained by varying the relative air humidity (30, 50 and 70%), UV-A radiation (10, 25 and 40 W/m^2) and pollutant mass flow rate (1, 3 and 5 l/min). All tests were carried out with an initial concentration of nitric oxide (NO) of 20 ppmv. It was observed that the higher the levels of UV-A radiation the better the performance of the mortar in the degradation of NOx. On the other hand, higher percentages of relative humidity and flow rate caused a decrease in photocatalytic activity. The experimental results verified that the environmental conditions have a considerable influence on the efficiency of photocatalytic mortar in the degradation of NOx.

1. Introduction

Automobile traffic is an important source of atmospheric pollution in urban areas, which is of serious and growing concern, given the substantial risks to public health due to increases in the concentration of pollutants such as nitrogen oxides (NOx).

According to Prodesp [1] the deterioration of air quality in the Metropolitan Region of São Paulo/Brazil (MRSP) is due to the atmospheric emissions of around 2000 industrial plants of high polluting potential and a registered fleet of approximately 9.7 million vehicles. According to 2009 estimates, these pollution sources are responsible for the emission to the atmosphere of 376,300 t/a of NOx. Of this total, vehicles are responsible for 96% of the emissions.

According to Cetesb [2], the annual report on the air quality of São Paulo State shows that ozone was the pollutant which surpassed to the greatest extent the standards for air quality (320 μg/m^3) in 2010, with acceptable ozone levels being surpassed on 61 days in MRSP. This urban area has a high potential for the formation of ozone, since its precursors (NOx) are emitted in large quantities, mainly by vehicles. In this regard, the air quality standard in relation to ozone cannot be reached without a significant reduction in the emissions of nitrogen oxides (NOx) and volatile organic compounds (VOCs).

Due to the large growing fleets of vehicles in cities, the current measures taken to fight air pollution, including the use of fuels derived from renewable sources ("green fuel") and catalytic devices installed in vehicles and industrial plants, are not sufficient to meet the air quality standards established by the current legislation and by the World Health Organization (WHO). This problem has stimulated the search for new technologies in order to reduce levels of urban pollution, with the aim of making cities more inhabitable.

The use of photocatalytic materials is currently one of the most studied methods of combating air pollution [3,4]. A large quantity of such materials consists of the mixture of a semiconductor, such as titanium dioxide (TiO_2), with a cement mortar, allowing a vast array of applications, e.g., in coatings for pavement surfaces and constructions [5–10].

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Photocatalysis, *i.e.*, catalysis that uses photons, is a process that is being increasingly applied and is showing excellent results [11–13] in the degradation of air pollutants. Heterogeneous photocatalysis was discovered by Fujishima and Honda in 1972, while carrying out experiments on the photo-oxidation of water in TiO_2 electrodes. The mechanism of photocatalytic oxidation has been extensively investigated. The degradation process of nitrogen oxides (NOx) through heterogeneous photocatalysis can be represented by Equations (1)–(9) [14–17].

Equation (1) shows the absorption of photons (hν) of ultraviolet A radiation (315–400 nm) by the semiconductor (TiO_2), resulting in the transfer of an electron (e^-) from the valence band (VB) to the conduction band (CB) with concomitant generation of a gap (h^+) in the valence band (VB).

$$TiO_2 + h\nu \rightarrow e^- + h^+ \quad (1)$$

Equations 2–4 show the adsorption of the reagents (H_2O, O_2 and NO) by TiO_2:

$$TiO_2 + H_2O \leftarrow\rightarrow TiO_2\_H_2O \quad (2)$$

$$TiO_2 + O_2 \leftarrow\rightarrow TiO_2\_O_2 \quad (3)$$

$$TiO_2 + NO \leftarrow\rightarrow TiO_2\_NO \quad (4)$$

Equations 5 and 6 show the generation of hydroxyl radicals (OH•) from water molecules adsorbed on the surface of the semiconductor:

$$H_2O_{abs.} \leftarrow\rightarrow OH^- + H^+ \quad (5)$$

$$h^+ + OH^- \rightarrow OH\bullet + H^+ \quad (6)$$

Equations (7)–(9) show the oxidation of NO and NO_2 to nitrate ions (NO_3^-):

$$NO + OH\bullet \rightarrow HNO_2 \quad (7)$$

$$HNO_2 + OH\bullet \rightarrow NO_2 + H_2O \quad (8)$$

$$NO_2 + OH\bullet \rightarrow NO_3^- + H^+ \quad (9)$$

The product of the degradation reaction of nitrogen oxides (NOx) is nitrate ions (Equation (9)) [18]. The removal of reaction products on the surface is carried out by rain as they are dissolved (neutralized) in an aqueous medium. Therefore, the removal of the pollutant is driven only by natural energy [19].

Through the NOx degradation mechanism, represented by Equations (1)–(9), it is clear that the efficiency of the catalyst in the process depends directly on the radiation at a wavelength of 315–400 nm and on the presence of water molecules. The effect of these two parameters on the efficiency of the degradation of NOx is reported in several publications [13,20,21], including by Hüsken et al. [11], who identified that the efficiency of the degradation mechanism increases with UV-A radiation and decreases with relative humidity. Nevertheless, studies performed by Yu and Brouwers [22] provided results which led to the conclusion that water plays an important role in the generation of hydroxyl radicals (OH•), improving the efficiency of heterogeneous photocatalysis. Other studies [11,13,23,24] have also highlighted the influence of the flow rate on the efficiency of photocatalytic materials.

In service, photocatalytic coatings will be subject to the interference of different environmental conditions and the chemical kinetics of the pollutant degradation reaction may be influenced by changes in the environmental parameters, such as relative humidity, UV-A radiation, velocity and wind direction. This paper presents the results of a study that evaluated the influence of different environmental conditions (UV-A radiation, relative humidity and flow rate) on the efficiency of a photocatalytic mortar in the degradation of nitrogen oxides (NOx).

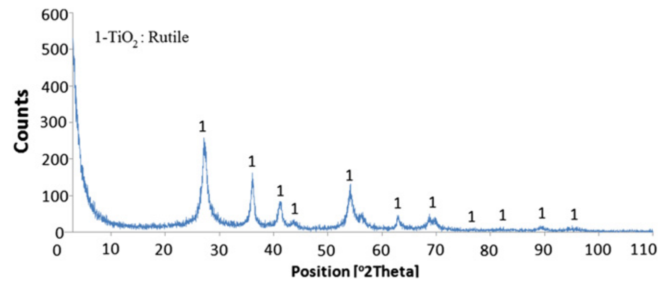

Fig. 1. X-ray Diffraction of the Rutile sample (10 × 40 nm).

2. Materials and methods

2.1. Materials used in the Research

For the production of the photocatalytic mortar, Portland cement with Pozzolan - CP II Z 32 was used, with a density of 2.97 g/cm^3. A nanometric titanium dioxide (TiO_2) sample in the form of a rutile bar with a diameter of 10 nm, length of 40 nm, 98% purity, specific surface of 150 ± 10 m^2/g and real density of 4.23 g/cm^3 was used as the catalyst. The crystalline structure of the rutile is shown in the x-ray diffraction spectrum in Fig. 1.

The photocatalytic mortar was produced with an aggregate of granitic origin, and the sieve size through which 100% of the sample particles passed was number 4 (4.8 mm). Fig. 2 and Table 1 present the granulometry of the aggregate used.

2.2. Production of the photocatalytic mortar

The photocatalytic mortar was developed with a view to its application as the surface layer of precast concrete paving (PCP). Initially, optimization of the photocatalytic mortar was performed. Mortars with the addition of 3, 6 and 10% TiO_2 were studied, and layers of photocatalytic mortar with thicknesses of 3, 6 and 10 mm were applied to samples of PCP. The evaluation of the cost/photocatalytic efficiency led to a mortar with a thickness of 3 mm and the incorporation of 3% of TiO_2.

To evaluate the influence of environmental conditions on the degradation of NOx, the optimized mortar was produced with the

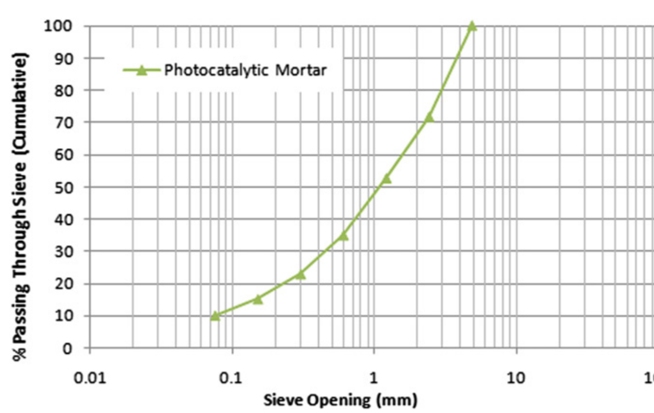

Fig. 2. Particle size of aggregate.