Evaluation of air cleaning through photocatalytic asphalt mixture functionalized with TiO_2 nanoparticles.

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ABSTRACT: Controlling atmospheric pollution is a challenge for society. Air pollutants, such as NO and NO_2, resulting from the combustion of fuels in the air, can cause acid rain and pose health risks to human beings. Using semiconductor nanoparticles, e.g., TiO_2, in Asphalt Mixtures (AM) to photodegrade NO_x is a promising alternative for air cleaning in urban cities. Asphalt pavements are ideal materials for that due to their large surface area and vicinity to vehicular exhaust gases. Thus, this research aims to evaluate the NO_x reduction effect of a photocatalytic AM sprayed with TiO_2 under the standard ISO 22197-1. The results demonstrate a photocatalytic activity of the functionalized asphalt mixtures, with a reduction of 40% of NO and 20% of NO_x.

KEYWORDS: TiO_2; air cleaning; photocatalytic asphalt mixtures; smart materials; NO_x removal efficiency.

1 INTRODUCTION

Exposure to air pollution is a short- and long-term risk factor for human health, causing respiratory and cardiovascular disease, cancer, and other problems (Schraufnagel et al., 2019). Among the various contributors to air pollution, road traffic is a significant source, with its initial emissions mainly of nitric oxide (NO), which gradually oxidizes in the atmosphere to form nitrogen dioxide (NO_2). The combination of NO and NO_2 is known as nitrogen oxides (NO_x), which are harmful to health and contribute to the formation of acid rain and the intensification of the greenhouse effect (Mills & Elouali, 2015). Removing these pollutants is challenging in urban areas. Thus, environmental agencies have reported the transport sector's impact on air quality. The European Environment Agency (EEA) identified road traffic as the main cause of exceeded air quality standards in northern Europe (European Environment Agency, 2022). Similarly, the Environmental Protection Agency (EPA) indicates that the transportation sector is responsible for approximately 45% of the total NO_x emissions inventory in the United States (Environmental Protection Agency, 2023).

Despite significant efforts to control individual vehicle emissions, such as the promotion of electric vehicles and the enforcement of stricter regulations on diesel vehicles, there remains a need to explore innovative solutions to meet the need to reduce pollution, with a focus on air pollution control through technologies capable of reducing NO_x (Fan et al., 2018). In this context, there is an interest in applying semiconductor materials in civil engineering materials for air purification. This application typically involves functionalization by using semiconductor materials with titanium dioxide (TiO2) on various substrates, such as ceramics, concrete, and glass. TiO_2 is usually a preference due to its low cost, high chemical stability, and non-toxicity (Meng et al., 2019).

The use of semiconductor materials in photocatalysis is part of the Advanced Oxidation Process (AOP), where the generation of hydroxyl radicals ($OH^{\bullet}$) is the primary oxidant involved in the degradation of pollutants (Casagrande et al., 2020). Briefly, the process consists of the absorption of light, producing electron-hole pairs on the surface of TiO_2 (Eq. 1). When the electrons and holes react with O_2 and H_2O, radicals are produced (Eq. 2, 3, and 4). They react with air pollutants, degrading to less toxic forms. In the specific case of NOx, nitrite and nitrate ions are the product of photocatalysis (Eq. 5 and 6), which can be subsequently washed away by rain (Segundo et al., 2021).

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

$$h^+ + HO^- \rightarrow OH^{\bullet} + H^+ \quad (2)$$

$$e^- + O_2 \rightarrow O_2^- \quad (3)$$

$$H + + O_2^- \rightarrow HO_2^{\bullet} \quad (4)$$

$$NO + HO_2^{\bullet} \rightarrow NO_2 + HO^{\bullet} \quad (5)$$

$$NO_2 + HO^{\bullet} \rightarrow NO^{3-} + H^+ \quad (6)$$

Regarding this application in civil engineering materials, the asphalt mixture has grown in recent years as a promising substrate for functionalization (da Rocha Segundo et al., 2023). There are four essential aspects for its efficiency and viability. The first related to the large area and worldwide scale that pavements cover. Second, it is the first external structure in contact with vehicle exhaust gases. Third, a large proportion of asphalt pavements are exposed to sunlight, which presents the initial energy to trigger photocatalysis. Fourth, most pollutants have a higher density than oxygen, i.e., they accumulate in lower spaces close to the asphalt pavement level (Li et al., 2023). Researchers worldwide have studied this application using different functionalization techniques, with the spray coating method usually being selected to apply TiO_2 nanoparticles over the surface of the asphalt mixture (Cao et al., 2017; Carneiro et al., 2013; Tang et al., 2017).

The advantages of this technique are that it is simple and presents a high efficiency, as most of the nanoparticles are exposed to light (Rocha Segundo et al., 2019).

Standardized gas degradation tests can be performed to evaluate the efficiency of NO_x removal on the photocatalytic asphalt mixture. The test can follow the standard ISO 22197-1, which specifies the air purification process of photocatalytic materials using nitric oxide (NO) as a pollutant. This standard applies to fine ceramics (ISO 22197-1, 2016) but also meets the requirements for measurements on asphalt mixture samples (Wang et al., 2017). In the gas degradation test, it is possible to control various parameters that contribute to the success of the reaction, including humidity, pollutant concentration, irradiance, and dry air (Casagrande et al., 2020). Conducting these tests in a controlled environment is of utmost importance as it allows for analyzing the reaction's performance related to the asphalt mixture.

The experimental setup must include synthetic air, standard gas, humidifier, photoreactor, light source, and NO_x analyzer to ensure that the photocatalytic reactions occur under laboratory conditions (ISO 22197-1, 2016). Synthetic air provides the necessary air source, while bottled gas of standard NO and humidifiers allow for precise pollutant concentration and humidity levels, respectively. The photoreactor, combined with the light source, allows the photocatalytic reaction on the asphalt mixtures, while the NO_x analyzer enables monitoring of the pollutant concentration over time.

Although some studies have evaluated the efficiency of photocatalytic asphalt mixtures through laboratory tests, the studies found often did not discuss the calculation of the removal amount specified in the ISO guidelines. In addition, a part of these studies, including Hassan et al. (2013), Bocci et al. (2016) and Chen et al. (2010), used another type of standard. Thus, this research aims to evaluate the efficiency of NO_x air cleaning using asphalt mixture (AM) functionalized with TiO_2 through gas degradation tests following ISO 221997-1. An analysis of the NO_x reduction of a functionalized asphalt mixture sample by spraying coating technique will be performed.

2 MATERIAL AND METHODS

2.1 *Materials*

The materials used were: (i) asphalt mixture AC10 designed according to the Marshall method, (ii) Ethanol, and (iii) TiO_2 semiconductor nanoparticles (Aeroxide TiO_2 P25) purchased from Quimidroga (Barcelona, Spain) with purity > 99.5%.

The asphalt mixture AC 10 was composed of 5.5% of asphalt binder Elaster 13/60 and aggregate fractions of 4% of filler, 31% of 0/4 mm aggregate, and 65% of 4/10 mm aggregate. AM was cut to dimensions of 12×4×1 cm^3 and functionalized by spraying coating method (Fig. 1). The sample was functionalized with TiO_2 nanoparticles over its surface dispersed in an alcohol solution at a concentration of 0.4 g/L.



Figure 1. Asphalt mixture functionalized with TiO_2.

2.2 *Test Methods, Experimental Equipment, and Conditions*

The evaluation of NO_x degradation was carried out according to the standard ISO 22197-1 (Fig. 2). The equipment consists of a cylinder containing 50 ppm nitric oxide (NO), compressed air, and a humidifier. The equipment also includes three mass flow controllers (MFCs) to regulate the flow of pollutant, dry air and wet air, and a pressure regulator to adjust the outlet pressure of the pollutant. Software developed using LabVIEW2013 was used to maintain the constant temperature at 25ºC. An UV-A lamp (VL-206.BL) and a reactor fabricated to ISO dimensions with a quartz window are also used. The data acquisition by the NO-NO_2-NO_x analyzer (Thermo Scientific™, model 42i). The analyzer determines the concentrations of NO and NO_x, while the concentration of NO_2 is derived by subtracting the NO concentration from the NO_x concentration value. The test results should follow the principles of the measurements shown in Figure 3 to obtain the amount of pollutant adsorbed in the dark, removed by photodegradation and desorbed after the photocatalytic process.

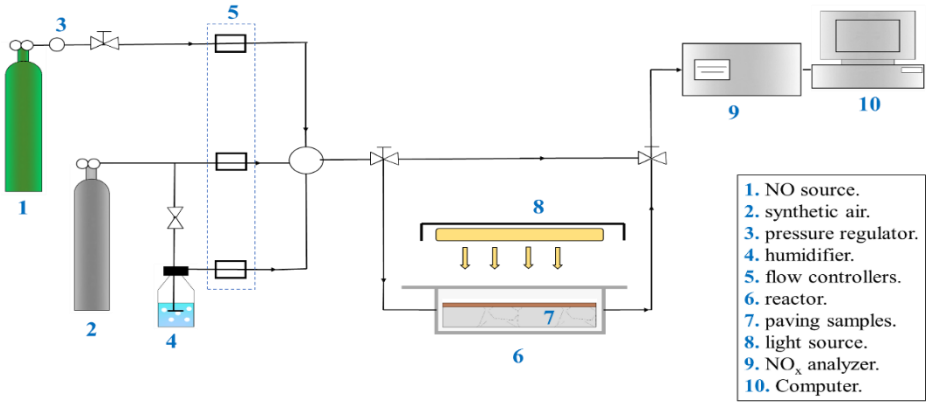


Figure 2. Schematic of the test equipment for photocatalytic degradation of NO_x.

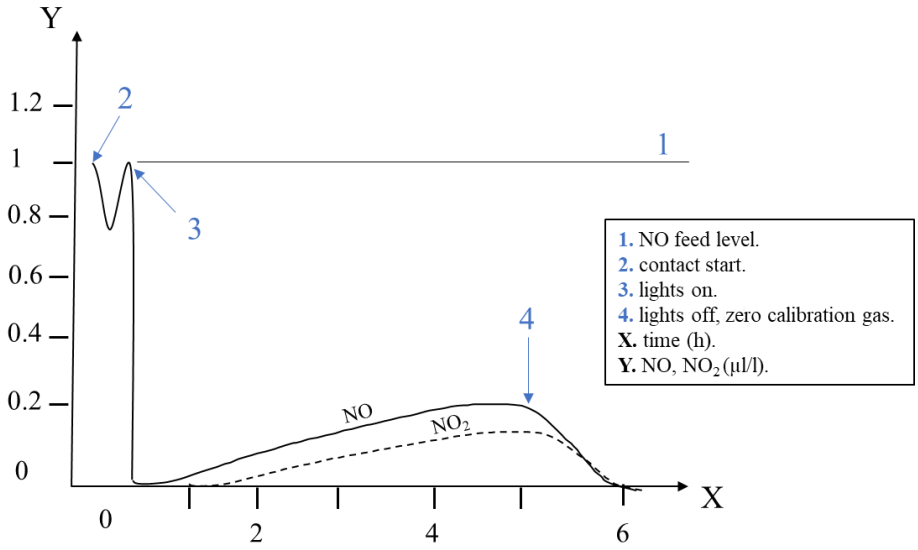


Figure 3. Typical trace of NO_x concentration during the test operation based on ISO 22197-1 (2016).

In this study, the conditions adopted to conduct the test were: i) pollutant initial concentration (NO): 0.45 µl/l; ii) pollutant flow: 0.03 l/min; iii) Dry air flow: 1.3 l/min; iv) wet air flow: 1.3 l/min; v) UV-A irradiance: 29 mW/cm^2.

The functionalized asphalt mixture sample was introduced into the reactor, and the flow controllers were initially programmed for the expected flow of pollutant, dry air, and humid air. The equipment was calibrated during the first 30 minutes of the test, with the monitored gas mix flowing directly into the analyzer, bypassing the reactor until its concentration was adjusted (in Fig. 3, Stage 1: NO feed level). From this point onward, the gas mix flowed through the reactor, and the test was conducted in the dark for one hour (in Fig. 3, Stage 2: contact start). This period was used to evaluate NO adsorption by the sample surface without the influence of the photocatalytic process. After, the light was turned on, and the gas mix was monitored for five hours during the photocatalytic process (in Fig. 3, Stage 3: lights on). The test ended 30 minutes after the light was turned off and the data were exported (in Fig. 3, Stage 4: lights off, zero calibration gas).

The amount of NO_x ($NO + NO_2$) removal was calculated through Equation 7:

$$n_{NO_x} = n_{ads} + n_{NO} - n_{NO_2} - n_{des} \tag{7}$$

Where: n_{ads} and n_{des} represent the amount of NO_x adsorbed and desorbed from the test piece, respectively. n_{NO} and n_{NO2} refer to the amount of NO removed and NO_2 formed in the test. These values are calculated from the equations listed below:

$$n_{ads} = (\frac{f}{22.4})\{\int(\phi_{NO_i} - \phi_{NO})dt - \int \phi_{NO_2} dt\} \tag{8}$$

$$n_{NO} = (\frac{f}{22.4})\int(\phi_{NO_i} - \phi_{NO})dt \tag{9}$$

$$n_{NO_2} = (\frac{f}{22.4})\int \phi_{NO_2} dt \tag{10}$$

$$n_{des} = (\frac{f}{22.4})\{\int \phi_{NO} dt + \int \phi_{NO_2} dt\} \tag{11}$$

Where: f is the air-flow rate converted into that at the standard state (0 °C, 101,3 kPa) (l/min); $\emptyset_{NOi}$ is the supply volume fraction of nitric oxide (µl/l); $\emptyset_{NO}$ is the nitric oxide volume fraction at the reactor exit (µl/l); $\emptyset_{NO2}$ is the nitrogen dioxide volume fraction at the reactor exit (µl/l).

3 RESULTS AND DISCUSSIONS

Figure 4 shows the variation of NO_x concentration during the test. It was observed that the NO concentration varied from 0.45 µl/l to 0.27 µl/l and the NO_x concentration varied from 0.45 µl/l to 0.36 µl/l at the end of 5 hours with the UV lamp on, followed by an increase when the lamp was turned off. In relative terms, this represents a decrease in NO and NO_x concentrations of 40% and 20%, respectively. The differences in concentration and the formation of NO_2 confirm the occurrence of the oxidation process by photocatalysis. These results are consistent with the recently published work by Suárez et al. (2020), using ISO standards, which showed that a photocatalytic asphalt sample removed 29% of NO and 22% of NO_x.

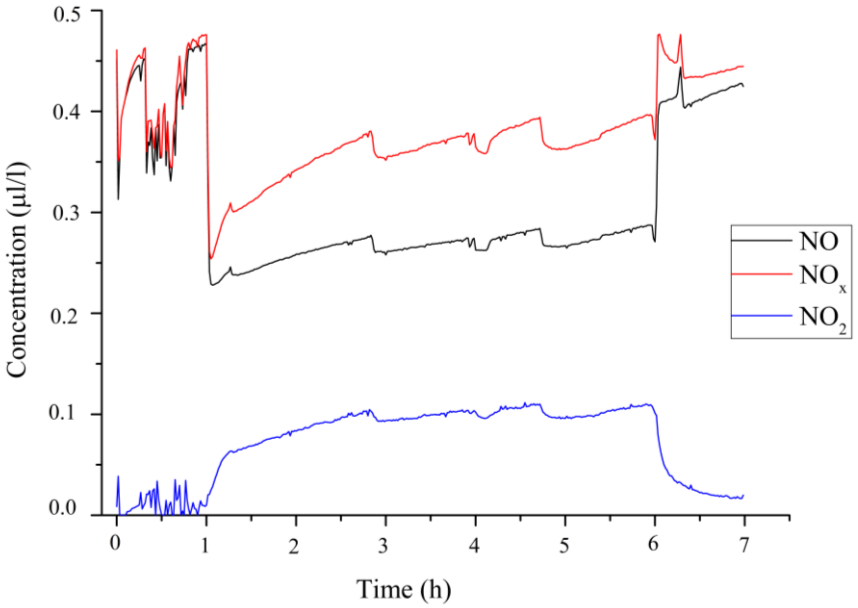


Figure 4. Variation of NO_x concentration during the test.

According to the ISO calculation, the sample adsorbed 0.20 µmol under dark conditions and removed 6.43 µmol of NO and formed 3.33 µmol of NO_2 in the photocatalytic process, after photodegradation desorbed 3.18 µmol. The amount of NO_x removed was 0.12 µmol. This reduction is related to a sample area of 48 cm² exposed to 5 hours of irradiation.

Although the initial concentration of 1 µl/l typically outlined in the test was not reached (Figure 3), the trends observed reflect the principles described in the ISO standard (Figure 4). Therefore, for future studies, different initial concentrations will be evaluated, including 1 µl/l. In addition, other parameters, such as flow rate, irradiance, and temperature, can be varied to understand their influence on the photocatalytic process.

4 CONCLUSIONS

This work evaluated the air-cleaning properties of the asphalt mixture containing TiO_2 over its surface. The main conclusions are:

- The sample can effectively degrade the NO_x.
- Variations in NO and NO_x concentrations occurred during the test, with 40% and 20% reductions, respectively, over 5 hours of UV light.
- The data generated and graphically presented are consistent with the theoretical predictions of the standard. However, it is important to note one limitation: the initial concentration did not reach the equivalent of 1 µl/l.
- The functionalized sample removed 0.12 µmol of NO_x and 6.43 µmol of NO and formed 3.33 µmol of NO_2 during the photocatalytic process for an initial concentration of 0.45 µl/l.

The efficiency of the samples in reducing pollutants should explore the effect of the testing parameters on the photocatalytic process, such as flow rate, irradiance, and temperature.

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