Development of Green Pavement for Reducing Oxides of Nitrogen (NO_x) in the Ambient Air

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Abstract. The transportation sector is the biggest contributor to air pollution in Indonesia, especially in metropolitan cities. Gases such as oxides of nitrogen (NO_x) are produced during the combustion of fossil fuels in the internal combustion of vehicle engines. Oxides of nitrogen such as nitric oxide (NO) and nitrogen dioxide (NO_2) are important air pollutants, because they cause significant harm to human health and play an important role in being precursors of other dangerous pollutants such as photochemical smog. One of the simple ways to reduce NO_x concentrations is utilizing a catalytic process involving UV light and semiconductor particles such as TiO_2. Illuminated TiO_2 UV light is capable of producing an electron (e^-) and hole (h^-) pair, which initiates a chemical reaction that alters the NO_x to become NO_3^- or NO_2^-. A field scale paving block reactor coated with TiO_2 placed by the roadside was exposed to UV light using various exposure times. The results showed that the sample with a composition of 200 g/m^2 TiO_2 was capable of adsorbing NO_x gas at an average rate of 0.0046 mg/m^2/minute. Additional costs due to TiO_2 coating for every square meter of paving are IDR 13,180.

Keywords: *nitrate ion; nitric ion; nitrogen oxides* (*NOx*)*; paving blocks; photocatalytics; titanium dioxide* (*TiO_2*).

1 Introduction

Fuel used in motor vehicles produces emissions of pollutants such as oxides of nitrogen (NO_x). These gases are formed when fuel is burned at a high temperature. Nitrogen dioxide is a strong oxidizing agent that reacts in the air to form corrosive nitric acid as well as toxic organic nitrates. It also plays a major role in the atmospheric reactions that produce ground-level ozone (smog). Nitrogen dioxide can irritate the lungs and cause lower resistance to respiratory infections such as influenza. The effects of short-term exposure are still unclear, but continued or frequent exposure to concentrations that are typically much higher than those normally found in the ambient air may cause increased incidence of acute respiratory illness in children [1]. Considering the dangers of high NO_x concentrations in the ambient air, it is important to develop

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a cheap and regenerative method for controlling ambient NO_x concentrations. One of the ways to remove NO_x concentrations from the ambient air is utilizing the photocatalytic reaction of TiO_2, which oxidizes NO_x to nitrates or nitrites. The reaction might take place over surfaces such as pavements along the roadside. TiO_2 can be coated on the pavement and activated by the UV radiation directly from the sunlight. This alternative technology can be considered to be a green technology because it utilizes the unlimited energy source from the sun and produces a harmless end product, i.e. very low concentration of nitrates.

TiO_2 is a metal, which is present in nature in various forms. TiO_2 can have three different molecular structures, i.e. brookiet, anatase and rutile [2]. TiO_2 in the rutile pigment known as white paint has low photocatalytic reactivity, while that of anatase is higher. The photocatalytic reaction of anatase occurs well using a wavelength of less than 387 mm. The photocatalyst can be applied in various forms including modules (blocks), in situ made concrete objects and thin over-coated layers (whether made of clear nano crystal line solution or an opaque paint-like solution). Quite often, these types of coatings are referred to as "self-cleaning", since photocatalytic coatings on construction materials also act to prevent the adsorption of soot or dust that tend to stick to grimy surfaces. Although titania-coated surfaces can serve, in principle, for the dual purpose of self-cleaning and outdoor air treatment, optimization for one type of application does not necessarily coincide with optimization for the second type of application. For example, to achieve good self-cleaning properties a low specific surface area, which limits sticking, is desirable, while for air decontamination a high specific surface area is preferable [3].

Photocatalytic materials/constructions have been widely used in various indoor and outdoor environments to reduce NO_x concentrations in the ambient air. For example in a 30 m^3 room at 30 °C and 50% humidity with UV radiation below 2.1 W/m^2 commercial mineral paint plus a 3% TiO_2 concentration achieved NO_x reduction of 0.21 mg/m^2/day [4]. In the same conditions translucent paints containing 5% TiO_2 reduced the NO_x concentration at 0.06 mg/m^2/day. Similarly, a floor covered with a layer of TiO_2 was reportedly able to remove pollutants, including NO_x [5].

As for NO_x removal outdoors, in a study of photocatalytics a coated paving was able to reduce nitric oxide released by vehicles by 15 percent. Other supporters of the new technology indicate that urban air quality can be improved up to 80 percent if all the roads, sidewalks and building exterior surfaces are treated with photocatalyst [6].

When tested in the outdoor environment, rainfall has shown to have an effect in regenerating photocatalytic activity, similar to that of lab washing. As a result, some researchers have recommended that washing should be executed at least every two months during the dry season [7]. However, water washing or rain have not been effective with respect to adhesives and water insoluble contaminants. In those cases using a degreasing agent may be beneficial. Exposure to different types of contaminants is dependent on location, so exposure to these contaminants can be controlled locally [7]. Other solutions include burning the surface or water washing to eliminate intermediates and restore the active sites on the catalyst surface, as proposed by Zhao [8]. Despite the debate, one thing which researchers agree upon is that the durability of the catalytic activity must be proven before widespread implementation and possible regeneration techniques, e.g. applying water washing, must be evaluated if degeneration occurs [9].

The total porosity of TiO_2 blended pastes decreases and reduction of the pore volume mainly occurs within the capillary pore range. Acceleration of the hydration rate and a change in microstructure also affects the physical and mechanical properties of cementitious materials [10]. Successful commercialization of self-cleaning surfaces, including concrete, glass and ceramic products, enables buildings to maintain their aesthetic appearance over time. The self-disinfecting function provides a convenient way to achieve a microorganism-free environment that satisfies the high hygiene standard demanded in facilities where sterile conditions are crucial [11].

2 Methodology

The present research was divided into three major stages, i.e. determining the optimum mixture for the TiO_2 layer coated over the pavement blocks; wear resistance and durability testing of the coated paving blocks to meet the specifications according to the Indonesian National Standard (*Standar Nasional Indonesia* – SNI); and finally a field scale experiment. The field scale experiment was conducted by placing coated pavement blocks along a road with high levels of road traffic for different exposure times. The formed nitrates or nitrites were then collected by manual washing using deionized water and quantified using ion chromatography. The exact sampling location, at an intersection of Jalan Ir. H. Juanda, Dago, Bandung is shown in Figures 1 and 2.

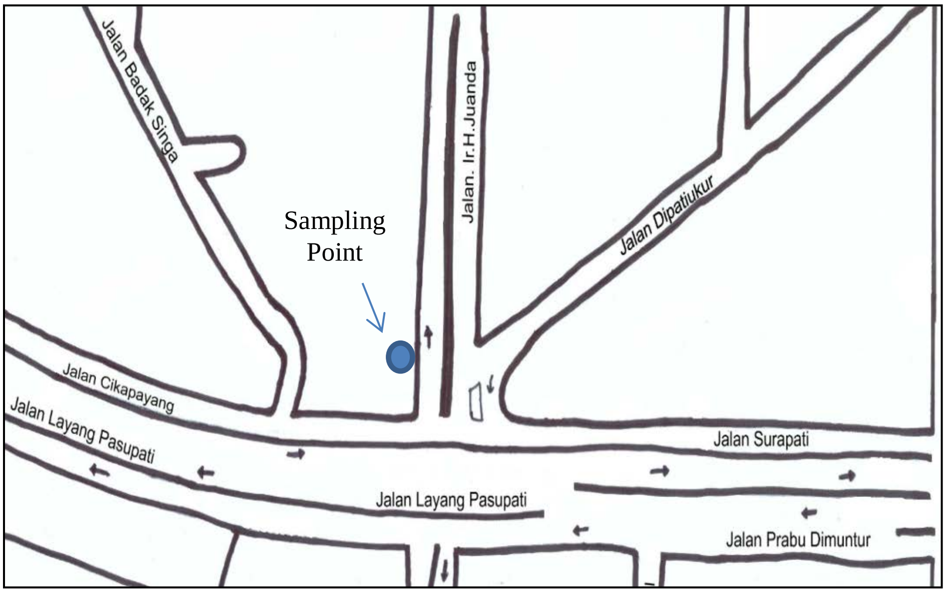

Figure 1 Location of paving blocks coated with TiO_2 by the side of the road (according to a road map of Bandung City).

Figure 2 Placement of paving blocks coated with TiO_2 on Juanda Street in Bandung City. (Source: research documentation)

2.1 Determining Optimum Mixture of TiO_2 Coated Over Fabricated Paving Blocks

Grade A paving blocks, produced according to SNI 15-6699-2002 [12], which regulates the quality requirements for paving blocks in Indonesia, were used in this research. The paving blocks were produced by PT. Cisangkan Bandung with an automatic machine using a vibrating and pressing process, equipped with a batching plant and water moisture control. The dimensions of the individual paving blocks are shown in Figure 3.

Figure 3 Paving block dimensions.

The specifications of the TiO_2 used in this research are described in Table 1.

Table 1 TiO_2 Specifications.

Item	Specification	Result
TiO_2 (purity)	98,00% – min.	98.82
Particle size	0.3 ± 0.05 – μm	0.32
Tinting strength of Reynolds	1280 – min.	1280
Oil absorption	25 ml/100g – max.	21.2
Residue (325 mesh)	0.015 % – max.	0.014

Source: Brataco Chemical Data [13]

2.2 Wear Resistance and Durability Test of Coated Paving Blocks

A wear resistance and durability test was performed for the coated paving blocks to see if they meet the quality requirements according to SNI 03-0691-1996 [12]. The results of the tests are shown in Table 2 below. The coated paving blocks that passed the wear resistance and durability tests were then used for performing the field photocatalytic experiment.

Table 2 Paving block quality compared to SNI.

Compressive Strength (kg/cm^2)		Wear Resistance (mm/menit)		Water Absorption (%)	
SNI	**Cisangkan**	**SNI**	**Cisangkan**	**SNI**	**Cisangkan**
400	400	0.090	0.090	3	3

2.3 Field Scale Experiments and Laboratory Data Measurement

A total of 80 paving blocks coated with TiO_2 were placed by the road side, accompanied by 80 other paving blocks without TiO_2 that acted as control. The exposure times were set to 6 hours, 12 hours, 18 hours and 24 hours respectively. The photocatalytic reaction was indicated by the forming of nitrate and nitrite on the paving blocks. The formed nitrate and nitrite on the surface of the paving blocks were collected by diluting them using deionized water and the concentration was then quantified by ion chromatography. To anticipate sources of nitrate and nitrite other than from the photocatalytic reaction, the concentrations of nitrate-nitrite from the surfaces of the uncoated paving blocks were also quantified.

2.3.1 Determination of Ambient Concentration of Nitrogen Oxides (NO_2 and NO)

The ambient concentration of nitrogen oxides in the experimental site were measured using the Griess Saltman method. This is based on the principle that NO_2 from the ambient air reacts with the Griess Saltman reagent to form a purple compound. The intensity of the formed color is then measured by a spectrophotometer at wavelength 550 nm. The NO concentration was also determined by oxidizing this gas using $KMnO_4$ or $K_2Cr_2O_7$ oxidant to form NO_2; the formed NO_2 was then measured using the Griess Saltman method. The measurements of ambient NO_x concentrations were performed every hour during the exposure time of the coated and uncoated paving blocks.

2.3.2 Determination of Other Physical Parameters

Other physical parameters were measured every 15 minutes during the exposure time, i.e. UV intensity (using a UV radiometer A/B in units of $\mu W/cm^2$), humidity and temperature (using a digital hygrometer), and wind speed (using an anemometer).

2.3.3 Determination of Nitrate and Nitrite Concentration, pH and Conductivity

The nitrate and nitrite that were formed over the surface of the coated and uncoated paving blocks were dissolved by deionized distilled water. The total volume of water used for each paving block was 200 mL. The solution was then filtered using filter paper and stored in high density polyethylene bottles and refrigerated at 4 °C and then analyzed within a maximum period of 48 hours. Concentrations of nitrate and nitrite ions were determined by ion chromatography (IC). The value of pH and conductivity of the solution were also determined in order to identify the influence of existing ions.

2.4 Reaction Kinetics

The reaction kinetics of the formation of HNO_3^- were determined by applying the rate law of the reaction. The formation reaction of HNO_3^- by the photocatalytic reaction on the surfaces of the TiO_2 coated paving blocks is represented in Equation (1). According to Laufs, *et al*. [14], the photocatalytic reaction occurs on the surface of the paving blocks followed by first-order kinetics with reaction rate constant k (NO_2 + TiO_2) about 0.041 ± 0.007 s^{-1}.

$$NO + NO_2 + O_2 + H_2O \longrightarrow 2HNO_3^- \qquad (1)$$

The kinetics of reaction of HNO_3^- in this paper was determined by following the rate law as follows:

$$r = k\,[NO][NO_2][O_2][H_2O] \qquad (2)$$

where:
r = reaction rate (M/second)
k = reaction kinetics constant ($second^{-1}$)
[ ] = molarity (M)

The reaction rate was calculated by using the value of k from Laufs, *et al*. [14], and the values of NO, NO_2, O_2 and H_2O from the field measurements.

3 Results and Discussion

3.1 Optimum Mixture of TiO_2 Coated Over Fabricated Paving Blocks

The results of the wear resistance test for the TiO_2 and water based resin composition with the best performance are shown in Table 3. The decision of choosing the optimal composition was influenced by the additional price due to coating the paving blocks with TiO_2 and water based resin. The additional cost for each type of composition is shown in Table 4.

Table 3 Composition of TiO_2 and Water Based Resin per 1 m^2.

Paving Code	Number of Paving (piece)	Composition			Endurance (mm/minute)
		TiO_2 (gram)	*Water based resin* (mL)	Water (mL)	
5k	50	200	160	150	0.087
6k	50	250	250	375	0.085
7k	50	200	200	600	0.090
8k	50	150	150	200	0.090
9k	50	200	100	200	0.089

*****1 square meter equivalent to 50 pieces of paving

Table 4 Additional cost estimation for the use of TiO_2 and water based resin per 1 m^2.

Paving code	**Number of *Paving* (piece)**	**Cost (Rupiah)**		**Total (Rupiah)**
		TiO_2	***Water based resin***	
5k	50	9000	6688	15688
6k	50	11250	10450	21700
7k	50	9000	8360	17360
8k	50	6750	6270	13020
9k	50	9000	4180	13180

Considering the costs and the wear resistance, the ratio of the mixture composition with code **9k** was chosen. This composition would require 200 gram of TiO_2 for 50 paving blocks (per 1 m^2) and 100 ml of water based resin at an additional cost of 13,180 rupiah per m^2. This composition still gave a good endurance or wear resistance, i.e. 0.089 mm/minute (the standard according to SNI is 0.09 mm/minute). Figure 4 shows the paving blocks coated with TiO_2 and water based resin that were used during the field experiment.

Figure 4 TiO_2 coated paving block. (Source: research documentation)

3.2 Field Measurement Results

The time durations during which the coated and uncoated paving blocks placed by the road side were exposed to the UV light from the sun were 6 hours, 12 hours, 18 hours and 24 hours respectively. During the exposure time, other supporting physical parameters were measured every 15 minutes, i.e. UV intensity, humidity, temperature and wind speeds. The ambient concentrations of NO_x (NO and NO_2) at the site were measured every hour.

Figure 5 shows the results of the measurement of hourly average concentrations of NO and NO_2 during the respective exposure times. Higher NO_2 concentrations were measured than NO concentrations. The diurnal cycle of NO_2 showed that the peak concentration of NO_2 occurred at 09.00-10.30 in the morning. The average hourly concentration of NO_2 was 0.051. This value is higher than the NO_2 concentration in front of the ITB gate, i.e. 0.014 ppm. The traffic load on Jalan Ir. H. Juanda was the highest contribution to the source of NO_x. However, the concentration of NO_2 by the side of the road was still lower than the ambient standard according to the Indonesian Government Regulation.

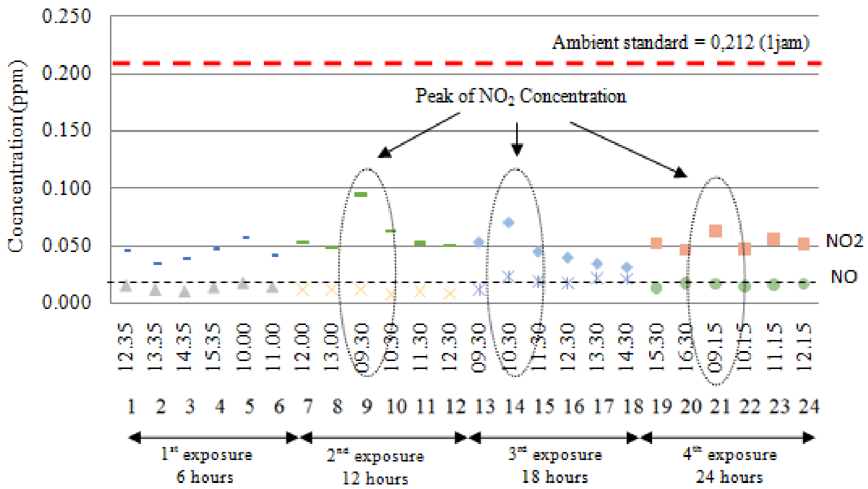

Figure 5 Hourly NO_2 and NO concentrations during exposure time.

The results of the experiment showed a significant increase of nitrate concentration after UV exposure while, in contrast, a significant increase of the nitrite concentration could not be identified. Therefore it was concluded that the main product of the NO_x-TiO_2 photocatalytic reaction was in the form of nitrate. Figure 6 shows the results of the nitrate measurements for the coated paving blocks (with TiO_2) and uncoated paving blocks (without TIO_2) as well as the ambient NO_2 concentrations. The nitrate concentration from the coated paving blocks was higher than that from the uncoated paving blocks, which indicates TiO_2 photocatalytic activity on the coated paving blocks. The nitrate from the uncoated paving blocks mostly originated from windblown dust precipitated over the paving blocks. Figure 6 also indicates that the longer exposure time, the higher the production of nitrate. The nitrate stayed on the top of the surface of the paving blocks if there was no cleaning activity such as rinsing by rainwater.

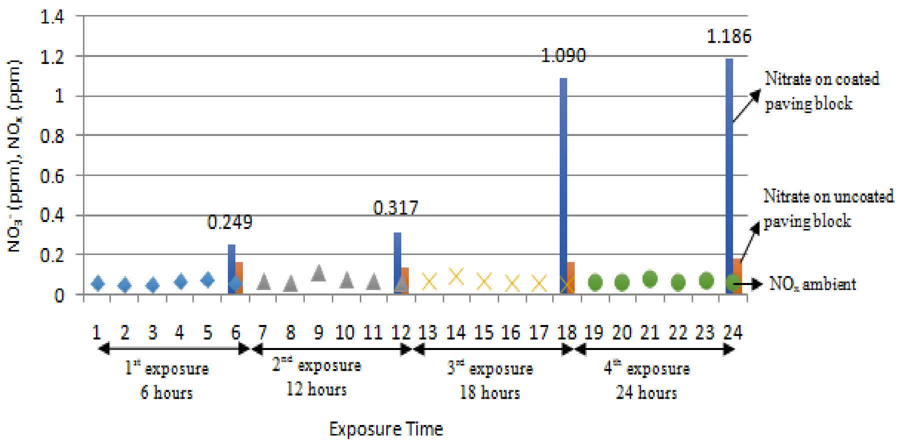

Figure 6 Nitrate formation over coated and uncoated paving blocks.

During the wet season, the produced nitrate may be washed off and carried away through the drainage system and end up in water receiving bodies such as rivers, lakes and the ocean. From the measurement results, the highest nitrate concentration which may be washed out is about 1.186 ppm or 1.186 mg/L, a value that is still far lower than the limit of nitrate concentration allowed for raw water for drinking water, i.e. 10 mg/L according to Government Regulation Nr. 82 concerning Water Quality Management and Water Pollution Control from 2001.

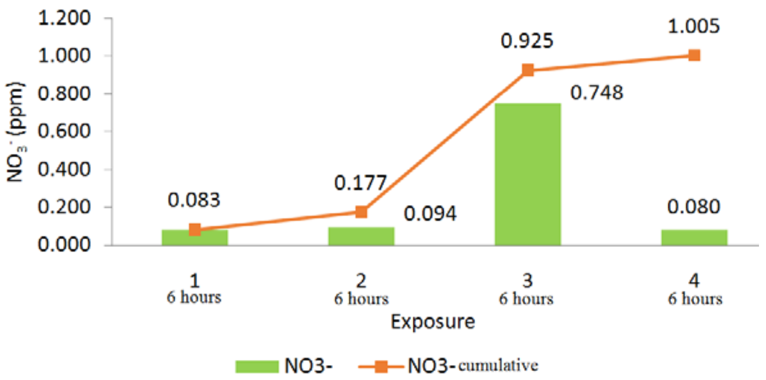

Figure 7 Photocatalytic nitrate production over six hours.

In order to be able to analyze the nitrate production over 6 hours of UV illumination only, Figure 7 was drawn. It shows that the highest nitrate production occurred during the third 6 hours of exposure time. The highest photocatalytic activities were strongly related to the value of UV intensity, as shown in Figure 8.

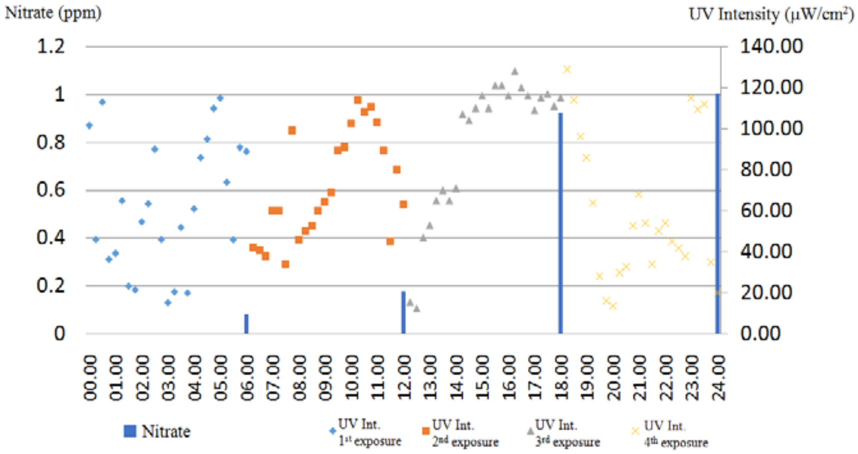

Figure 8 Photocatalytic nitrate production related to UV intensity.

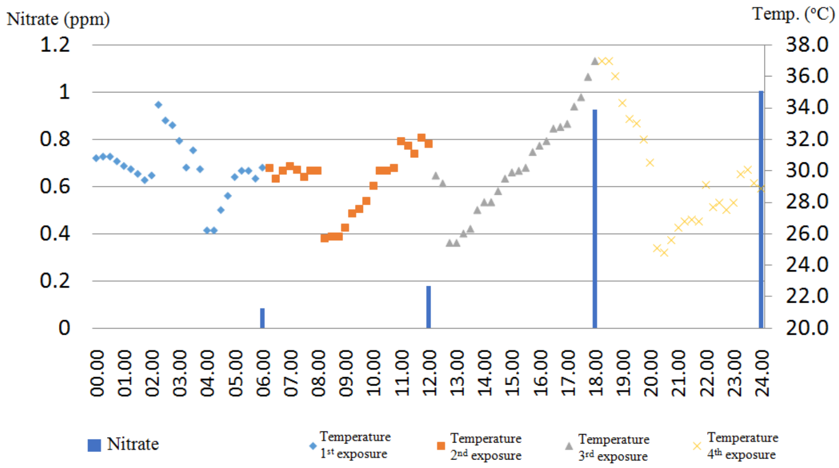

Figure 9 Photocatalytic nitrate production related to ambient temperature.

Temperature and humidity played an important role in the photocatalytic process in forming nitrate on the coated paving blocks (see Figures 9 and 10). A higher temperature may result in a higher nitrate formation and, in contrast, a lower humidity results a higher nitrate formation. Humidity reflects the existence of water vapor as the main source of hydroxyl radicals. These radicals react with NO_2 to form nitrates. However, the relation analysis between nitrate formation and humidity gave a value of -0.978, which means a strong relation in the opposite direction, i.e. higher nitrate levels should be produced when the humidity gets lower. The hydrophilic properties of the TiO_2 surface causes competition between NO_x and water vapor to be adsorbed on top of the paving block surface, hindering the NO_x to reach the active sites of the catalyst.

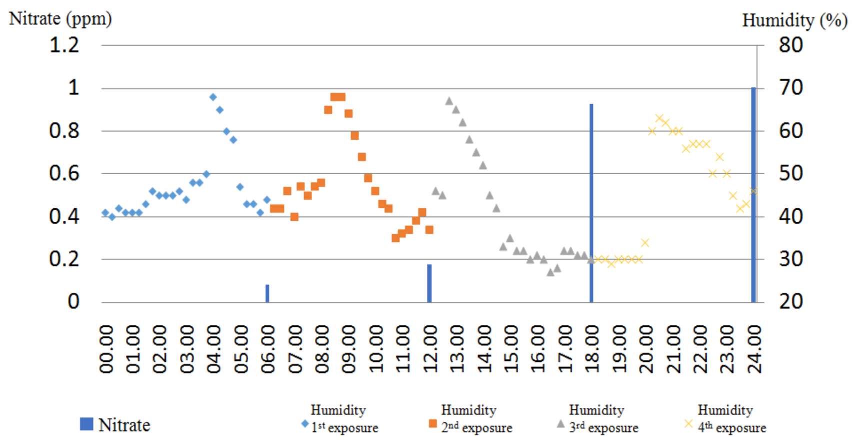

Figure 10 Photocatalytic nitrate production related to ambient humidity.

A correlation analysis between nitrate formation and other parameters such as wind velocity, UV intensity, and ambient NO_x concentration is described in Table 5. A strong positive correlation was shown by nitrate–UV intensity and also nitrate–humidity. A weak correlation was shown by nitrate formation–ambient NO_x concentration due to the relatively constant NO_x concentration during exposure. NO_x gas was constantly emitted by vehicles burning fuel on the road.

Table 5 Results of correlation analysis of environmental parameters.

	Temperature	**Humidity**	**Wind Velocity**	**UV**	**NO_x**	**NO_3^-**
Temperature	1.000					
Humidity	-0.706	1.000				
Wind Velocity	-0.965	0.818	1.000			
UV	0.489	-0.879	-0.541	1.000		
NO_x	-0.016	-0.405	-0.241	0.079	1.000	
NO_3^-	0.685	-0.978	-0.760	0.952	0.232	1.000

According to Laufs, *et al*. [14], the photocatalytic reaction occurs on the surface of the paving blocks shows first-order kinetics with rate constants k (NO_2 + TiO_2) of 0.041 ± 0.007 s^{-1}. By applying the rate law of reaction, the rate constant from Laufs, *et al*. [14], and concentrations of NO-NO_2-O_2 and H_2O from the site measurements, the average reaction rate during the experiment was 3.49×10^{-7} M/s. Meanwhile, the nitrate adsorption rate could be calculated from the amount of nitrate formation due to photocatalytic activity divided by the active surface area and exposure duration, as shown in Table 6. For comparison, nitrate adsorption rates were collected from several sources, as listed in Table 7.

Table 6 Nitrate adsorption rate over coated paving blocks.

Exposure	Nitrate (ppm)		Area (m2)	Exposure Duration (minutes)	Nitrate Adsorption Rate (mg/m^2/min.)
	Coating Paving (with TiO_2)	Uncoated Paving, Control (Without TiO_2)			
1	0.249	0.166	0.2205	360	0.00209
2	0.317	0.140	0.2205	720	0.00223
3	1.090	0.165	0.2205	1080	0.00777
4	1.186	0.181	0.2205	1440	0.00633

Table 7 Adsorption rates from various sources.

Research	UV Intensity	Humidity	Application	Adsorption rate
Pichat [15]	0.6 mW/cm^2	50%	Paving	0.29 $\mu g/m^2$/day
Maggos *et al.* [4]	1 mW/cm^2	20%	Paving	13.824 $\mu g/m^2$/day
Maggos *et al*. [4]	0.21 mW/cm^2	50%	Paving	0.21 $\mu g/m^2$/day
Yu [7]	0.9 mW/cm^2	25%	Paving	230 $\mu g/m^2$/day
This research	**0.72 mW/cm^2**	**45%**	**Paving**	**6.624 $\mu g/m^2$/day**

4 Conclusion

This research has shown that illuminated TiO_2 coated on paving blocks is capable of altering ambient NO_x to nitrates due to photocatalytic activity. Approximately 200 gram of TiO_2 per 1 m^2 square paving block was capable of changing ambient NO_x to nitrate at an average rate of 0.0046 mg/m^2/minutes, with average temperature 29.89 °C, humidity 45.31%, and wind speed 0.84 m/s. The average UV intensity was measured as 71.82 $\mu W/cm^2$ and the average ambient NO_x concentration 0.066 ppm. Additional costs resulting from the addition of TiO_2 and water based resin on the surface of the paving blocks are approximately Rp. 13,180 per m^2 of paving block. From this research it can be concluded that the development of coated paving blocks is a promising green technology for reduction of ambient NO_x concentrations.

Acknowledgements

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References

[1] USE EPA, Retrieved from https://www3.epa.gov/airtrends/aqtrnd95/no2 .html (January 15th, 2013).

[2] Fujishima, A., Hashimoto, K. & Watanabe, T., *TiO_2 Photocatalysis: Fundamentals and Applications*, BKC, Tokyo, 1999.

[3] Paz, Y., *Application of TiO_2 Photocatalysis for Air Treatment: Patents' overview*, Applied Catalysis B: Environmental, **99**, 2010, pp. 448-460.

[4] Maggos, Th., Kotzias, D., Bartzis, J.G., Leva, P., Bellintani, A., Vasilakos, Ch., *Investigations of TiO_2-containing Construction Materials for the Decomposition of NOx in Environmental Chambers*, 5th International Conference on Urban Air Quality, Valencia (Spain), March 2005, pp. 29-31.

[5] Toulan, E., Maze, M., Rousseau, P., *De-Polluting Device with Tio2 Photocatalyst Particles in Hydraulic Binder Coating Activated by UV Lamp for Confined Spaces*, EP 1652827, 2006.

[6] Chusid, M., *FCSI, Next up.. Self-Cleaning Concrete! Photocatalysts Can Keep Concrete Clean and Reduce Air Pollution*, Concrete Décor, 2005.

[7] Yu, J.C-M., *Ambient Air Treatment by Titanium Dioxide (TiO_2) Based Photocatalyst in Hong Kong*, Environmental Protection Department, HKSAR. AS 00-467, 2002.

[8] Zhao, J. & Yang, X., *Photocatalytic Oxidation of Indoor Air Purification: A Literature Review*, Building and Environment, **38**, 2003, pp. 645-654.

[9] Berdahl, P. & Akbari, H., *Evaluation of Titanium Dioxide as a Photocatalyst for Removing Air Pollutants*, California Energy Commission, PIER Energy-Related Environmental Research Program, CEC-500-2007-112, 2008.

[10] Chen, J., Kou, S-C. & Poon, C-S., *Hydration and Properties of Nano-TiO_2 Blended Cement Composites*, Cement & Concrete Composites, **34**, 2012, pp. 642-649.

[11] Chen, J. & Poon, C-s., *Photocatalytic Construction and Building Materials: from Fundamentals to Applications*, Building and Environment, **44**, 2009, 1899-1906.

[12] SNI 03-0691-1996, Concerning Paving Block Specification, 1996.

[13] Brataco Chemical, *Information of TiO_2 Characteristics*, 2012.

[14] Laufs, S., Burgeth, G., Duttlinger, W., Kurtenbach, R., Maban, M., Thomas, C., Wiesen, P. & Kleffmann, J., *Conversion of Nitrogen Oxides on Commercial Photocatalytic Dispersion Paints*, Atmospheric Environmen, **44**, 2010, pp. 2341-2349.

[15] Pichat, P., *Private Communication of Results* by J. Bartzis, et al., National Scientific Research Centre, Demokritos, Greece, Lawrence Berkeley National Laboratory Workshop, Passive Photocatalytic Oxidation of Air Pollution, June 29, 2007.