THE DEVELOPMENT OF PAVEMENT USING TITANIUM DIOXIDE FOR REDUCTION OF NO_X GAS IN THE AIR

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Abstract: Urban air pollution, with its long- and short-term impact on human health, well-being and the environment, has been a widely recognised problem over the last 50 years. Fuel gases from combustion in motor vehicles, such as nitrogen oxides (NO_x) will be emitted to the ambient air.Nitrogen oxides such as nitric oxides(NO) and nitrogen dioxide (NO_2) are important air pollutants, because they have significant harm to human health and play an important role of being precursor of another dangerous pollutants such as formation of photochemical smog. Anthropogenic activities hold biggest responsibilities for the increasing of NO_x concentration in the ambient air. To anticipate the rapid increase of NO_x concentration, it is important to develop an alternative technology in NO_x abatement.The photocatalytic process using uv light and semiconductor particles is a promising alternative of NO_x abatement. In fact, treatment of pollutants related to environmental problems through photoassisted catalyst has been a much discussed topic in today's literatures, since efficient utilization of solar light for various emission control processes can save the consumption of fossil fuels.Pavementcoated TiO_2anastasewith content of pure TiO_2 of 98.82% at composition of 0.02 g/cm^2 in the photoreactor which flowed by NO_x gas at concentration of 0.327 ppm-0.680 ppm exposed to uv light intensity from 47.9 to 59.0 µW / cm ² within 6 hours, 12 hours, 18 hours and 24 hours. Nitrate and nitrite ions are formed by the photocatalytic paving surface which is diluted with distilled water then measured by ion chromatography. The optimal efficiency of NO_xremoval in this research was 45% which occurred at 18 hours of exposure at 68% -74% humidity. While the resulting of adsorption rate was ranged at 10.932 mg/m^2/day - 19.398 mg/m^2/day, increasing the concentration of NO_3^-in line with the duration of exposure.

Keywords: nitrogen oxides (NO_x), pavement, titanium dioxide (TiO_2), nitrate ion, nitrite ion.

INTRODUCTION

Urban air pollution, with its long- and short-term impact on human health, well-being and the environment, has been a widely recognised problem over the last 50 years. (Gurjar*et. al*., 2008).The Increasingnumber in using motor vehicle as a transportation that use fuel oil (fossil fuels) which produces emissions to be one of factor in the negative impact of air pollution on the environment. Air pollution from the transportation sector in the form of motor vehicle fuel oil (fossil fuels) is triggered again with the higher of amount of fuel use, to be the cause of the air pollution caused by motor vehicle use (Chen *et. al*., 2008). Air pollution from motor vehicles occurred in most of the major cities in Indonesia, one of the city is Jakarta. Contamination that occurred in the Greater Jakarta area alone as much as 85% -90% due to motor vehicle exhaust gas residual as shown by **Table 1**.

Table 1. The Results of Emissions Inventory (Darmanto and Asep, 2011)

Area	Sector	SO_2	NO_2	CO
		Ton/year		
Jakarta	Transportation	21.73%	92.27%	99.94%
	Industry	78.22%	7.63%	0.01%
	Household	0.05%	0.09%	0.03%
	Agriculture	0.00%	0.00%	0.02%
	Total	100%	100%	100%
Bodetabek	Transportation	46.22%	85.79%	93.12%
	Industry	50.15%	13.19%	0.00%
	Household	0.81%	0.62%	0.15%
	Agriculture	2.82%	0.39%	6.73%
	Total	100%	100%	100%

Motor vehicles will emit various gases and particulates consisting of organic and inorganic components that are readily inhaled by humans. Motor vehicle emissions are dangerous because they tend to have a larger fraction and the emissions generated in the middle of bustling urban population (Nasser *et. al*., 2009). Emissions from transportation activity in general are a gas that produced by the combustion process, one of them in the form of nitrogen oxides (NO_x).

Nitrogen oxides (NO_x) is a gaseous compound which is contained in the air (atmosphere) which largely consists of nitric oxide (NO) and nitrogen dioxide (NO_2) and various types of oxides in smaller amounts. Both of these gases have very different properties and both are very harmful to health (Ballari *et. al*., 2010 (a)). NO_x is produced when the fuel burn at high temperatures, in the exhaust gas. Nitrogen oxide (NO) is produced from the burning of waste transportation and will soon be oxidized in the atmosphere to form NO_2 (Parra and George, 2005).

One way to anticipate a rapid increase in levels of NO_x emissions caused by motor vehicles, namely the development of alternative technologies that are placed as close as possible to the source so the number of NO_x released into the air by the antopogenik activity levels are not dangerous. Contact between motor vehicle emissions with the road surface, then the photocatalytic compounds such as TiO_2 can be used for manufacture of pavement that can be used as an air pollution control is done by coating TiO_2 on the surface of the pavement (Hassan *et. al*., 2012).

NO_xremoval through photocatalytic oxidation of NO to NO_3^-or NO_2^-which is not dangerous by semiconductor particles (TiO_2) is a process that is quite beneficial because it can avoid the use of fossil fuels and the use of additional reactants such as ammonia or ozone (Shen *et. al*., 2012) . Schematic process that occurs in the TiO_2 photocatalytic can be seen in **Figure 1**.

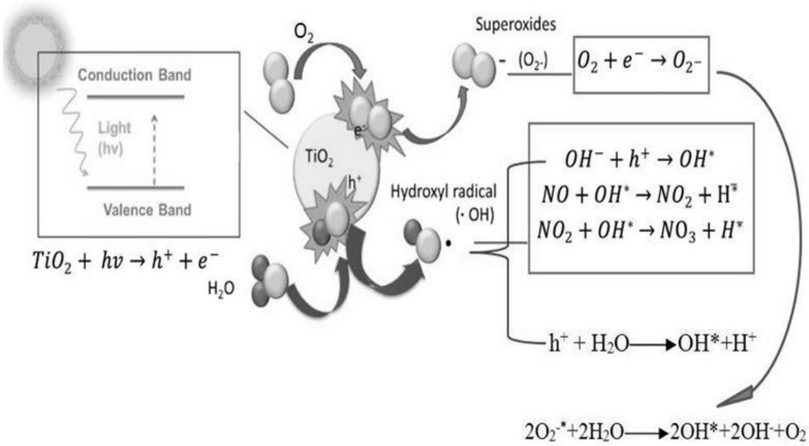


Figure 1. Process Schematic on the Photocatalytic TiO_2 (Dylla *et. al.*, 2011)**.**

The illumination of TiO_2 with light of wavelength less than 400 nm generates excess electrons in the conduction band (e-) and positive holes (h) in the valence band.

$TiO_2 + hv \longrightarrow Oh^+ + e^-$ **(1)** (Folli *et. al.*, 2010)

Holes react with either physisorbed H_2O or chemisorbed OH^- groups to form hydroxyl radicals (OH*).

$h^+ + H_2O \longrightarrow OH^* + H^+$ atau **(2)** (Ballari *et. al.*, 2010(b))

$h^+ + OH^- \longrightarrow OH^*$ **(3)** (Ballari *et. al.*, 2010(b))

Excess electron in the conduction band might probably react with molecular oxygen to form superoxide ions.

$e^- + O_2 \longrightarrow O_2^{-*}$ **(4)** (Ballari *et. al.*, 2010(b))

Which can further disproportionate to form more OH* radicals.

$2O_2^{-*} + 2H_2O \longrightarrow 2OH^* + 2OH^- + O_2$ **(5)** (Ballari *et. al.*, 2010(b))

The OH* radicals are extremely reactive and readily attack NO_x molecules to form NO_3^- and NO_2^- ions (Beelden, 2008).

$NO_2 + OH^* \longrightarrow NO_3^- + H^+$ **(6)** (Beelden, 2008)

$NO + OH^* \longrightarrow NO_2^- + H^+$ **(7)** (Beelden, 2008)

According to Fujushima and Zang, 2006, in Hasan *et. al.*, 2012, photocatalytic compounds can significantly reduce NO_x. The use of compounds on the surface of photocatalytic pavement for its existence close to the source of pollution is a promising technology. However, the application of technology for the manufacture of environmentally friendly pavement is still in its infancy and there are many environmental factors, design, and operational factors that still need to be evaluated. In addition, many factors have not been studied as the effects of exposure time and photocatalytic regeneration compounds on NO_x removal efficiency.

The purpose of this study is as one of the alternative friendly technology development environmentally, which can be applied to reduce the air pollution is mainly generated by the transportation sector. Installation of pavement using a catalyst-coated titanium dioxide (TiO_2) in the upper part is expected to make a significant contribution in reducing the concentration of pollutant gases, especially NO and NO_2. While the objectives of this research which are determine the effect of variations in the time of exposure ultraviolet (UV) to the NO_x removal efficiency, determine the effect degeneration on the photocatalytic compound to NO_x removal efficiency and mass of NO_xremoval compares to the formation of new compounds in the form of nitrate and nitrite compounds through calculation mass balance.

METHODOLOGY

Based on previous research that have been done by Hassan *et al*. (2010), Dylla *et al*. (2011) andOsborn(2012), the photoreactor used in this study form a box that is equipped with inlet and outlet ports that serve as sampling for measuring the concentration of NO_x. According to research Fujishima et. al. 2000 in Dylla et. al., 2011, stated that the process by photocatalytic TiO_2, the smaller wavelength of 400 nm is required for irradiation. Higher intensities more photons are produced, that increase the rate of oxidation fotokatalitiknya. In accordance with that statement, the ultraviolet light source used in this research was a black light uv lamp with a power of 20 watts, 220V with a maximum wavelength of 352 nm. UV lamps totaling 8 pieces placed on top of the inner wall of the reactor in such a way as to allow ultraviolet light to the entire surface of the pavement underneath. UV light intensity at the reactor has range between 47.9 - 59.0 $\mu W/cm^2$. The light source is in the photoreactor can cause heat inside. To reduce the temperature increase in the need to be equipped with a fan that serves as a cooling device (Hunger *et. al*., 2008). A fan placed in the photoreactor than as a coolant also serves as an agitator air flow so that the concentration of NO_x in the photoreactor spread evenly. Specifications photoreactor used in this study can be seen in **Figure 2** below with illustrations contained in **Figure 3**.

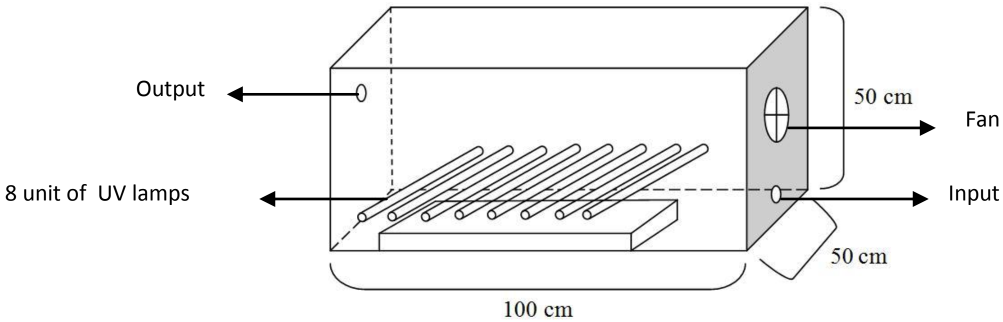


Figure 2. Spesificationof Reactor

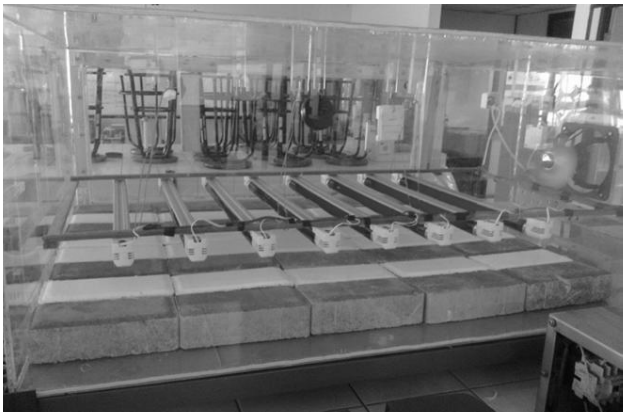
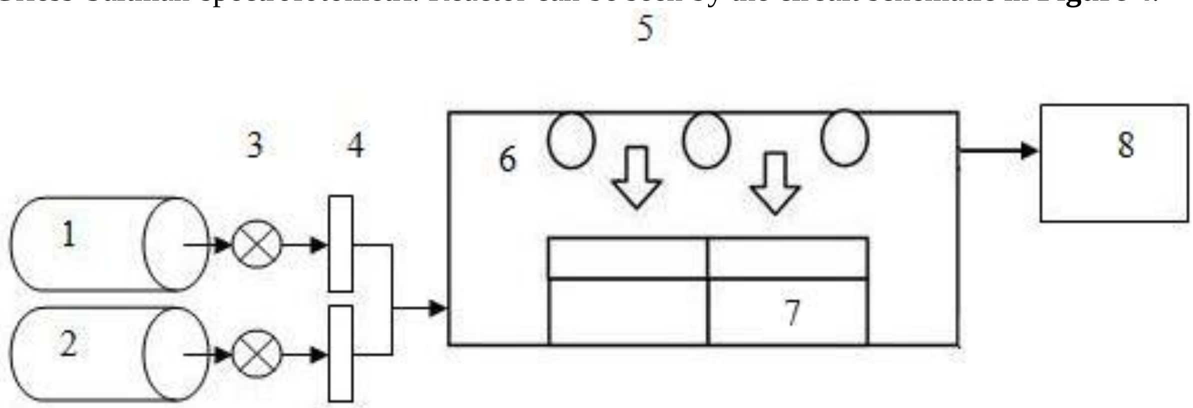


Figure3. Photoreactor

In a research of photocatalytic in laboratory scale required equipment as follows: NO_x sources, photoreactorand a NO_x analyzer (Dylla *et. al*., 2011). The resulting concentration of NO_x in the gas container is still very high so it needs to be diluted with ambient air. Flowmeter necessary as controlling the flow rate into the photoreactor in order to obtain the desired discharge. NO_x in the gas container and the ambient air is pumped into the photoreactor with each discharge of 0.4 L / min and 20 L / min. NO_x gas concentration after passing through photoreactor be measured continuously every 30 minutes by the method of Griess-Saltman-spectrofotometri. Reactor can be seen by the circuit schematic in **Figure 4**.



Description:

1. Sources of NO_x gas
2. Sources of diluent gas
3. Air pump
4. Flowmeter
5. TiO_2- photocatalytic reactor
6. UV lamp
7. Pavementcoated TiO_2
8. Griess method-Saltman-spectrofotometri

Figure 4. Schematic of Photocatalytic Reactor for Researching NO_xAbatement by the PavementCoated TiO_2

Variations used in this research includes the time of exposure to UVdevided into 6 hours of exposure, 12 hours of exposure, 18 hours of exposure and 24 hours of exposure. This variation of the exposure time aims toobserve thedegeneration.

The type of Titanium dioxide as a catalyst used in this research are anatase, anatase has been chosen because this type is the best of the three existing types of TiO_2. Purity of TiO_2 used to reach 98.82% with a particle size of 0.32 µm. Specifications TiO_2 used in this research are shown in **Table 2**.

Table 2. TiO_2 Specifications (Brataco Chemical)

Item	Specification	Result
TiO_2 (purity)	98.00 % - minimum	98.82
Particle size	0.3 ± 0,05 - µm	0.32
Tinting Strength of Reynolds	1280 – minimum	1280
Oil Absorption	25 ml/100g - maximum	21.2
Residue (325 Mesh)	0.015 % - maximum	0.014

TiO_2 layer on the surface of pavement consists of a mixture of anatase TiO_2 powder, water based resin and water with composition of 4 grams: 2mL: 4mL. Water-based resin used as glue on the surface so TiO_2 can stick to pavement. In a research laboratory scale about photocatalytic require equipment including: sources of NO_x, photoreactor, and a NO_x analyzer (Dylla et. al., 2011). The research design is shown in **Figure 5**.

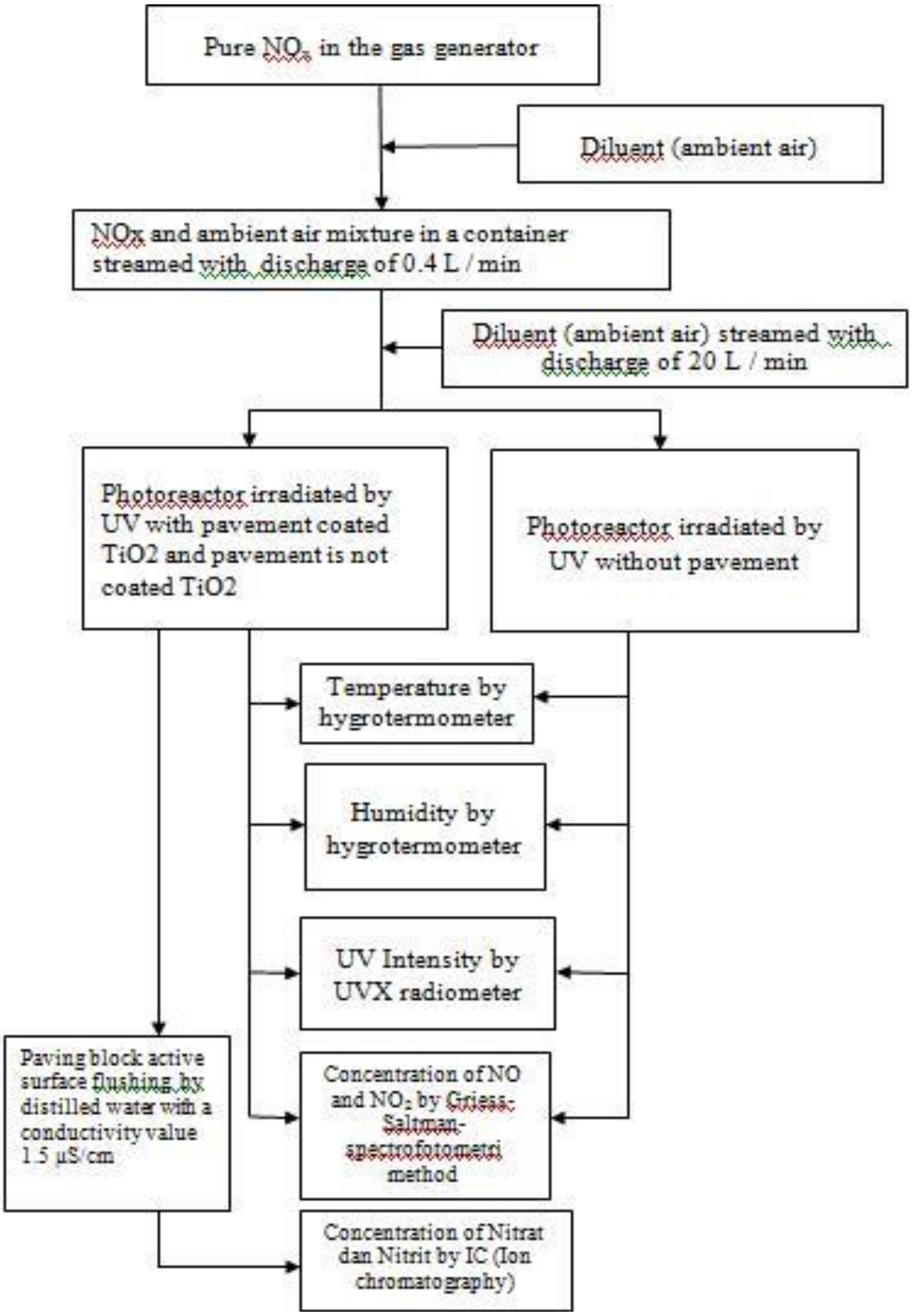


Figure5. The Design of Research

To get the adsorption rate of nitrate ions and nitrite ions from the photocatalytic pavment in units mg/m^2/menit, determined by using the following equation:

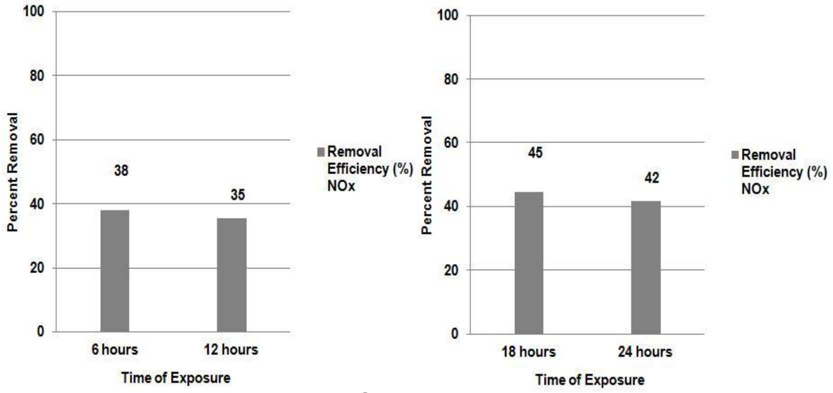
$$\text{Adsorption rate} = (T - B) \times \frac{V_{water}}{A \times t} \qquad \textbf{(Equation1)}\text{(Khair, 2013)}$$

where,

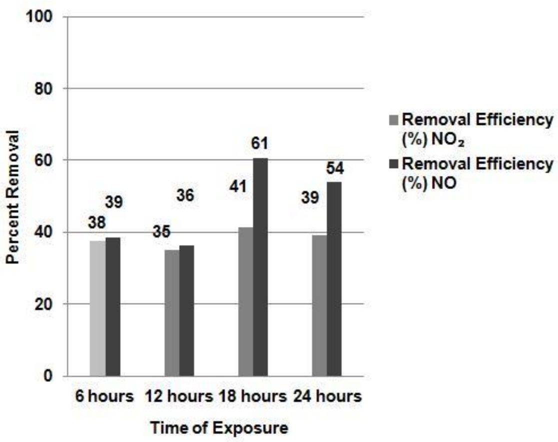
T is the concentration of ions in the TiO_2-coated pavement after exposure (mg / L)
B is the concentration of ions in the TiO_2-coated pavement before exposure (mg / L)
V_{water} is the amount of water used in flushing (L)
A is the active surface area of pavment (m^2)
t is the exposure time pavment (day)

RESULTS AND DISCUSSION

There are many factors that affect the efficiency of the photooxidation, one of them is the possibility of degeneration in photocatalytic properties. It seen at 6 hours of exposure time compared to 12 hours of exposure time whereas 18 hours of exposure time compared to 24 hours of exposure time which each can be seen in **Figure 6 (a)** and **Figure 6 (b)**. From **Figure 6 (a)**appears that there has been a decline of 3% between 6 hours of exposure time and 12 hours of exposure time. The same pattern also occurs in **Figure 6 (b)**. According to Sleiman *et. al*., 2009 in Dylla *et. al*., 2011, stated that the degeneration and accumulation of this product is the result of a function of time and concentration of pollutants.



(a) NO_xRemovalEfficiency per $m^2$of Pavement**(b)**NO_xRemovalEfficiency per $m^2$of Pavement
at the Exposure Time 6 and 12 Hoursat the Exposure Time 18 and 24 Hours



(c)NO_2 and NORemovalEfficiency per $m^2$of Pavement

Figure 6. RemovalEfficiencyof Pollutan Gas by Photocatalytic Pavement

Effect of uv on gas removal efficiency of NO_2 and NO gas can be clearly seen from **Figure 6 (c)**. This is reflected in NO removal efficiency which has greater value than NO_2 removal efficiency. NO gas will oxidize to form NO_2 if illuminated by uv light. Equation is as follows:

$N_2 + O_2 \longrightarrow 2NO$ (Dylla *et. al*., 2011)

$2NO + O_2 \longrightarrow 2NO_2$ (Dylla *et. al*., 2011)

Oxidation process by the amount of oxygen that is also contributing to the reduction ofNO. When sunlight (source of uv) is available, NO_2 will undergo photolysis reactions and form O_3.

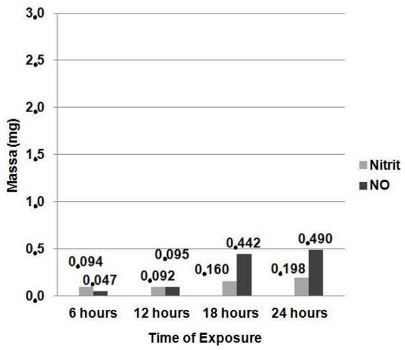
$NO_2 + hv \rightarrow NO + O$ (Dylla *et. al*., 2011)

$O + O_2 + M \rightarrow O_3 + M$ (Dylla *et. al*., 2011)

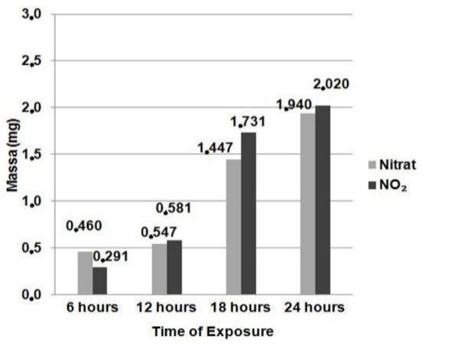
M may be either N_2 or O_2 or other third molecule will absorb excess energy, thus stabilizing the O_3 formed. At the time of O_3formation, reaction with NO to form NO_2 by the following equation:

$O_3 + NO \rightarrow NO_2 + O_2$ (Dylla *et. al*., 2011)

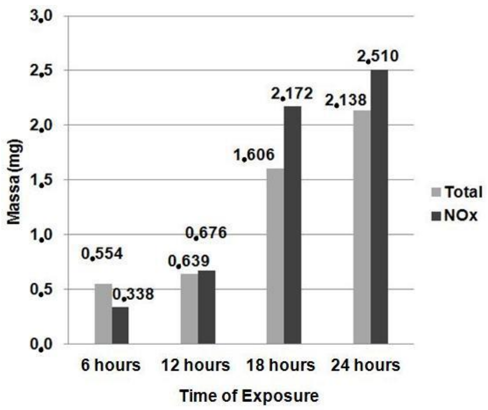
Mass balance in the photocatalytic reactor can be evaluated from the mass elimination of NO_x and the formation of new compounds in the form of nitrate and nitritcompounds. Formation of nitrite and nitrate by hydroxyl ions can be seen in the equation **(6)** and **(7)**.



(a) Mass of Nitrit ion (NO_2^-) and NO



(b) Mass of Nitrat ion (NO_3^-) and NO_2



(c) Total Mass and NO_x

Figure 7. Mass Balance

From **Figure 7 (a)**, **Figure 7 (b)** and **Figure 7 (c)** shows that the difference between input and output mass covering NO_x, NO and NO_2, have a greater value than the mass that formed after the reaction include nitrite ion (NO_2^-), nitrate ion (NO_3^-) and total mass (mass of $NO_2^-$and NO_3^-). Presence of oxidation-reduction mechanisms which can occur on the surface of TiO_2 illuminated by UV cause equilibrium of the mass balance equation can not be obtain, because the detection of the formation of new compounds is only performed on the results of the oxidation reaction. The formation of new compounds in the form of N_2O can not be done because of limited gas detectors available. Therefore there are a number of missing mass that formed to nitrite or nitrate as a result of a number of NO or NO_2abatement, due to limited gas detectors are available.

To get the adsorption rate of nitrate ions and nitrite ions from the coated TiO_2 photocatalytic pavmentin units mg/m^2/day, determined by using **Equation 1**. Data of load abatement can be seen in **Table 3**.

$$\text{Adsorption rate} = (T-B)\times\frac{V_{water}}{A\times t}$$

$$\text{Adsorption rate} = (0.460-0)\times\frac{2}{0.2\times 0.25}=18.386 mg/m^2/day$$

Table 3. The Calculation of Photocatalytic Adsorption Rate on TiO_2 Coated Pavement

Exposure time (hours)	UV intensity μW/cm²	Humidity (%)	Application	NO3- on Pavement with TiO₂ before Exposure (ppm)	NO3- on Pavement with TiO₂ after Exposure (ppm)	Surface Area (m²)	Vol. Diluent	Time (day)	Adsorption Rate NO3⁻
6	47.9-59.0	65-75	paving	0	0.460	0.2	2	0.25	18.386
12	47.9-59.0	65-75	paving	0	0.547	0.2	2	0.5	10.932
18	47.9-59.0	68-74	paving	0	1.447	0.2	2	0.75	19.289
24	47.9-59.0	68-74	paving	0	1.940	0.2	2	1	19.398

The highest adsorption rate occurs in the 24-hour measurement of exposure time, with a value of 19.938 mg/m^2/day and the lowest adsorption rate of 10.932 mg/m^2/day. If the results of this research compared with the few research that have been conducted by other researcher, it can be said that the results of this research are quite promising. However, several aspects need to be repaired again linked pavement coated TiO_2 and apply the mixture used. In **Table 4** are presented the results of photocatalytic TiO_2 comparison of data from several studies.

Table 4. Comparison of Photocatalytic TiO2 from Multiple Research.

Data Source	UV intensity	Humidity	Application	Adsorption rate
Maggos, et. all., 2007	1 W/cm^2	20 %	Paint	13.824 mg/m^2/day
Maggos, et. all., 2005	0.21 mW/cm^2	50 %	Paint	0.21 mg/m^2/ day
Yu, 2002	0.9 mW/cm^2	25 %	*Pavement*	230 mg/m^2/ day
Khair, 2013	71.82 μW/cm^2	45%	*Pavement*	6.624 mg/m^2/ day

Penelitian ini	**47.9-59 μW/cm^2**	**65-75 %**	*Pavement*	**19.398 mg/m^2/** day

CONCLUSION

The experimental results showed that the photocatalytic process has occurred in pavement coated with titanium dioxide (TiO_2) with a purity of 98.82% anastase much as 0.02 g/cm^2 in the photoreactor which flowed gas at a concentration of 0.327 ppm-0.680 ppm exposed to uv light with intensity 47.9 to 59.0 μW/cm² within 6 hours, 12 hours, 18 hours and 24 hours. This is indicated by the amount of NO_xremoval optimal efficiency in this research that reached 45% which occurred at 18 hours of exposure at 68% -74% humidity. Decrease in gas NO_x removal efficiencies indicate that there has been a degeneration and accumulation of products in the photocatalytic surface that occurs as a result of a function of time and concentration of pollutants.Presence of oxidation-reduction mechanisms which can occur on the surface of TiO_2 illuminated by UV cause equilibrium of the mass balance equation can not be obtain, because the detection of the formation of new compounds is only performed on the results of the oxidation reaction. While the resulting adsorption rate was ranged10.932 mg/m^2/day - 19.398 mg/m^2/day, the increasing concentration of $NO_2^-$and NO_3^-as the exposure time.

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References

Ballari, M. M., M. Hunger, G. Husken, and H.J.H. Brouwers. 2010.(a) Modelling and Experimental Study of the NO_x Photocatalytic Degradation Employing Concrete Pavement with Titanium Dioxide. *Catalysis Today*,**151**: 71-76.

Ballari, M. M., M. Hunger, G. Husken, and H.J.H. Brouwers. 2010.(b) NO_x Photocatalytic Degradation Employing Concrete Pavement Containing Titanium Dioxide. *Journal of Aplplied Catalysis B: Environmental*,**95**: 245-254.

Beeldens, A. 2008. *Air purification by pavement blocks: final results of the research at the BRRC.* Transport Research Arena Europe, Ljubljana.(http://www.brrc.be/pdf/tra/2008_Beeldens.pdfaccessible on april 15, 2013)

Chen,H., Namdeo, A., Bell, M., 2008, Classification of Road Traffic and Roadside Pollution Concentrations for Assessment of Personal Exposure. *Environmental Modelling & Software*,**23**: 282-287

Darmanto, Nisrina Setyo dan Asep Sofyan. 2011. *Analisis Distribusi Pencemar Udara NO_2, SO_2, CO, dan O_3 di Jakarta dengan WRF-CHEM*. Undergraduate thesis. Environmental Engineering FTSL ITB.

Dylla, H., Hassan, M.M., Schmitt, M., Rupnow, T., Mohammad, L.N., Wright, E. 2011. Effects of Roadway Contaminants on Titanium Dioxide Photodegradation of Nitrogen Oxides. *Journal of the Transportation Research Record*, Washington D.C., **2240**: 22-29.

Folli, Andrea and Donald E. Mac phee. 2010.Photocathalytic Cement: Influence of TiO_2Particle Size on Photocatalytic Performance,presentedon*The 8th FIB PhD symposium in civil engineering*, 20-23 Juni 2010.

Khair, Hafizul. 2013. *Pemanfaatan Titanium Dioxide pada Trotoar untuk Mengurangi Gas Pencemar NO_x di Udara*. Graduate *thesis*. Environmetal engineering FTSL ITB.

Hassan, Marwa, Somayeh Asadi, John T. Kevern and Tyson Rupnow. 2012. Nitrogen Oxide Reduction and Nitrate Measurements on TiO_2 Photocatalytic Pervious Concrete Pavement. *Construction Research Congress 2012 © ASCE 2012*: 1920-1930.

Hunger, M.; Husken, G.; and Brouwers, Jos. 2008. Photocatalysis applied to concreteproducts, Part 1: Principles and test procedure. *Materials Science, ZKG International*, **61**: 77-85.

Khair, Hafizul. 2013. *Pemanfaatan Titanium Dioxide pada Trotoar untuk Mengurangi Gas Pencemar NO_x di Udara*. Thesis. Teknik Lingkungan FTSL ITB.

Maggos T., Plassais A., Bartzis J., VasilakosC., Moussiopoulos N., Bonafous L. 2005. Photocatalytic Degradation of NO_xin a Pilot Street Canyon Configuration Using TiO_2 -Mortar Panels, 5thInternational conference on urbain air qualityn Valencia, Spain, 29-31 March 2005, Picada section.

Maggos, Th, J.G Bartzis, M Liakou, dan C Gobin. 2007. Photocatalytic Degradation of NO_xUsing TiO_2-Containing Paint: A real scale study.*Journal of Hazardous Materials*,**146**: 668-673.

Naser,T.M., Isao Kanda, Toshimasa Ohara, Kazuhiko Sakamoto, Shinji Kobayashi, Hiroshi Nitta, and Taro Nataami. 2009. Analysis of Traffic-Related NO_x and EC Concentrations at Various Distances from Major Roads in Japan, *Journal ofAtmospheric Environment*,**43**: 2379–2390.

Osborn, David James. 2012. Quantifiqation of NO_x *Reduction Via Nitrate Accumulation on a TiO_2 Photocatalytic Concrete Pavement*. Thesis. B.S. Lousiana State University, Lousiana.

Parra,J., and George, L. 2005. Performance and Application of an Inexpensive Method for Measurement of Nitrogen Dioxide, Portland State University, (http://www.mcnairprogram.pdx.edu/OnlineJournal 20200405, accessible on June 20, 2013).

Shen, S, B Maria, J Bertram, dan H Liv. 2012. Pervious Concrete with Titanium Dioxide as a Photocatalyst Compound for a Greener Urban Road Environment. *Construction dan Building Materials*,**35**: 874-883.

Yu, Jimmy Chai-Mei. 2002. *Ambient Air Treatment by Titanium Dioxide (TiO_2) Based Photocatalyst in Hong Kong.*AS: Environmental Protection Department. (http://www.epd.gov.hk/epd/tc_chi/environmentinhk/air/studyrpts/files/finalized_technical_report.pdfaccessible on June 25, 2013)