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# The Use of Photocatalytic Cementitious Coatings to Reduce Nitric Oxide from Ambient Air

***Abstract-*** *Titanuim dioxide represents a novel photocatalyst material that can be used in different ways for air pollutants remediation. Air pollutants that are spreaded in the surrounding air could be transferred to more complex materials, especially in the presence of sunlight. To study the possibility for the reduction of these pollutants a laboratory tests have been conducted on the coated specimen substrate by using nitric oxide as pollutant gas, and there efficiency in gas removal was monitored with time. Two different particle sizes of $TiO_2$ have been used; micro with particle size range between 150-200 nm and nano PC105 with particle size 20± 5 nm, both are 100% anatse. Two coatings methods were applied on cementitious substrate material dip and spray to study the photochemical reaction with $TiO_2$, aqueous solution prepared by dispersing 3g/L of $TiO_2$ with deionized water and ethanol. Results show that using nano and micro size $TiO_2$ aqueous solutions were effective in the removal of nitric oxide with variations in the time consumed for the removal. Using nano aqueous solution in both dip and spray methods gives the same removal efficiency reached to 98.85% ,while using micro aqueous solution the removal reached to 98.08% when dip method was used and 87.69% when spray method was used.*

***Keywords-*** *Air Pollution, Cementitious, Coatings, NO, Photocatalysis, Titanium Dioxide*

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## 1. Introduction

The utilization of the photocatalytic building materials began from the early of 1990s[1], and have been taken a great of interest as an application particularly from Europe and Japan [2]. The use of TiO2 has been applied in the exterior structure materials and the interior finishing material, like cement mortar, tiles, paving blocks, glass, etc. The specification of cement matrix is compatible with TiO2 particles. The whole degradation process of pollutants on the building surface is happened by natural energy alone by using UV from solar light, then washed by rain (Figure 1)

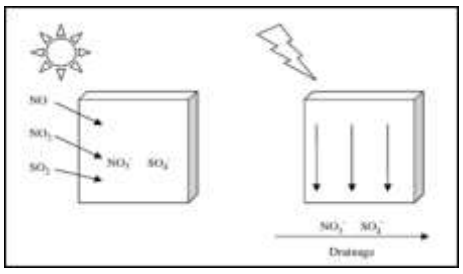

**Figure 1: Removal of Pollutants by using photocatalytic in building materials [3]**

The photocatalytic reactions that take place on the $TiO_2$ surface are [4]:

$$4NO + O_2 + 2H_2O \xrightarrow[UV]{TiO_2} 4HNO_2 \quad \text{.....(1)}$$

$$4HNO_2 + O_2 \xrightarrow[UV]{TiO_2} 4NO_2 + 2H_2O \quad \text{.....(2)}$$

$$2H_2O + 4NO_2 + O_2 \xrightarrow[UV]{TiO_2} 4HNO_3 \quad \text{.....(3)}$$

The conversion of NO to NO2 as shown in the reaction (4) reduces the NOx removal capability due to accumulation of HNO3 over the surface of the photocatalyst:

$$2HNO_3 + NO \xrightarrow[UV]{TiO_2} 3NO_2 + H_2O \quad \text{.....(4)}$$

Reactions (1) to (3) represent a gradual accumulation of $HNO_3$ over the surface of the $TiO_2$, reaction (4) ensures that eventually an equilibrium or saturation level of $HNO_3$ will be reached and that the rate of production will be equal to its rate of the removal, at this level the $TiO_2$photocatalyst is only able to convert the

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oxidation of NO to $NO_2$. The effect of $HNO_3$ could be reduced by using a base or alkaline surface to prevent undesirable reaction [4]. One of the most effective ways to apply $TiO_2$ is by adding a thin coating to the weathering layer [2]. In addition to surface reaction, applying coating solutions lead to lower consumption of $TiO_2$ [5]. Studied showed high photocatalytic activity of $TiO_2$ in suspended form than using in immobilized form [6]. $TiO_2$ is widely used with no chemical additives are required [7]. Films could be deposited on substrates from solutions/suspension, by a sol-gel dip technique, spin coating or through sputtering and spray coatings [8- 9]. In a study compared 5% nano-$TiO_2$ intermixed mortars with dip-coated mortars in nano-$TiO_2$ solution; dip-coated mortars displayed a highly improved photocatalytic activity [10]. The choice of the manufacturing process depends on the specific application requirements of coatings [11].

The application of photochemical reaction panels at the surfaces of car park buildings covered with white $TiO_2$ is investigated in European; results appeared a significant $NO_x$ gases reduction. The removal percent of $NO_2$ and NO gases was 20% and 19%, respectively, [12]. In France (Guerville) street canyons walls were covered with $TiO_2$ mortar; $NO_x$ measurements were taken continuously and recorded concentrations of about 40-80% lower than uncovered canyons [13].

Generally, most of the sols (aqueous suspensions of nanoparticles) coatings showed very high nitrogen oxide (NO) conversion (~90%), even when the coatings were extremely thin or diluted, independently on the deposition method (spraying or dip coating); Removal efficiency reached to 97% regardless of the initial NO concentration and independently on the number of layers applied [14]. The aim of this research work is to investigate the ability of the nano and micro aqueous solutions of $TiO_2$ for the removal of NO from surrounding air by applying two economic surface coating methods (spraying and dipping) that could be used even for previously constructed buildings. The performance of the coated cementitious specimens were assessed and then compared with the control, non-coated specimens.

## 2. Materials and Experimental Procedure

ASTMC305 standards [15] was used to prepare concrete substrates with cement to sand ratio of 1:2.75 and w/c of 0.484.All mortar specimens were casted in 9 cm diameter petri dish to form 6 mm thickness samples and let harden for 24 hr at room temperature then cured for 28 days at 100% relative humidity, then dried and stored in sealed bags.

Parts for reactor details were collected from local market and designed according to International Organization for Standardization (ISO 22197-1:2007) with some modification according to test requirements. The inlet NO gas concentrations applied on the coated samples was 1ppm.Tests parameters (humidity, temperature and light intensity) were the same for all samples. Details of the used experimental materials are presented in Table 1. Aqueous solution preparation: Two aqueous solutions were prepared by spreading 3g of nano and micro titanium dioxide in 750ml deionized water and 250 ml ethanol stirred for 30 min then ultrasonicated for 1 hr. Samples were coated by using spray pyrolysis equipment for 5 minutes (Figure 2).

Other samples were dipped in these solutions for 10 minutes, and then dripped for 3 minutes (Figure 3).

All samples were oven-dried at 105oC for 1 hour, and kept sealed until test. Reactor Setup: Rectangular chamber used with dimensions of about (30 cm x10 cm). All Tests were carried out at room temperature with applying a continuous airflow, gas flow used was about 1.6+0.2 l/min.

**Figure 2: spray pyrolysis equipment**

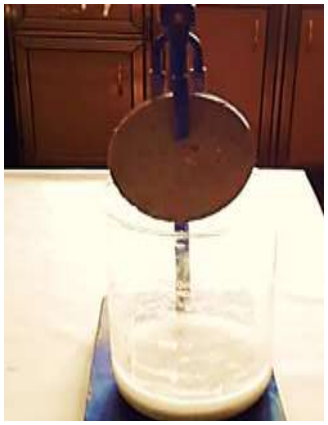

**Figure 3: dip method**

**Table 1: details and specifications of the material**

| Material | Specification | Origin | Comments |
|---|---|---|---|
| Cement | Type I ordinary portland cement | Local market | ----- |
| Sand | 600 μm | Local market | Graded according to ASTM C778 [16] |
| Micro size powder$TiO_2$ | 150-200 nm | Tianjin Zhi Yuan ReagentCo.,Ltd.-China | specific surface area = 6.9 $m^2/g$ |
| Nano size powder$TiO_2$ | PC105(20±5nm) | Cristal Active Millennium SAS- France | specific surface area = 85.6 $m^2/g$ |
| NO gas | 400ppm | mesa specialty gases and equipment USA, California | To be diluted with air cylinder (80% $N_2$, 20% $O_2$) |
| Gas detector | NO detection limits = 0 to 250 ppm $NO_2$detection limits =0 to 20 ppm | RAE system by Honeywell-USA, San Jose | ----- |

Two 6 W UV lamps have been used with intensity of 19 $W/m^2$ for each lamp and wave length range (300-400 nm). To control humidity inside the reactor a humidifier has been used with control Valves. Inlet NO gas concentration was calibrated to be 1 ppm (Figure 4).

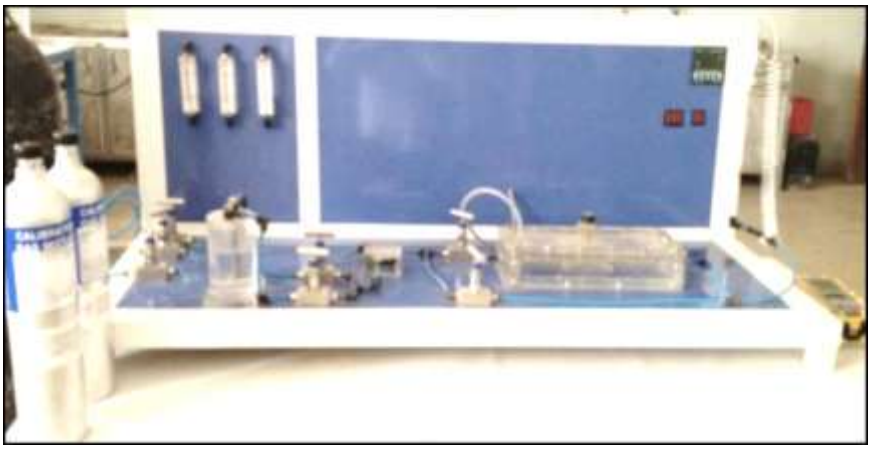

**Figure 4: Photo catalytic Reactor**

Represents the reactor used; the test procedure was as follows:

1. Calibration for the gas sensors must be done.
2. Putting the sample inside chamber and close tightly.
3. Inlet gas pollutant opened and calibrated until reached to the desired concentration.
4. Humidity was calibrated through control valves to obtain RH of about 50%.
5. Waiting for about 25 min to ensure chamber saturation and readings stabilization after this UV source is turned on.
6. The reaction continued until reaching a steady state.

**3.** After this UV is turned off, close the pollutant gas valve and again only air flow is ejected inside chamber

## 4. Results and Discussion

All samples were tested until reduction happened and need for minimum residence time after reaction stabilization of 30 min. Nitric oxide removal was very fast when micro-dipped substrates exposed to the pollutant gas. The removal was 98.08 %within 1.5 min. large amounts of NO2 generated make reaching to steady state reaction in a long time as shown in (Figure 5):

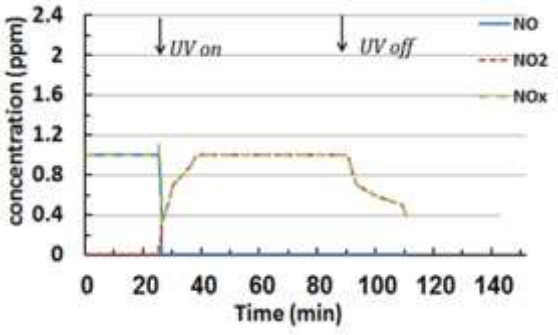


**Figure 5: Micro-dipped sample reduction for NO gas**

This could be explained due to the high amounts of TiO2 particles on the sample surface with little percent to be absorbed by substrate. Nano-dipped samples showed rapid removal for NO gas equals to 98.85% within 1 min, this could be explained due to the high activity for the nano-dipped samples with less generation of NO2 amounts (Figure 6):

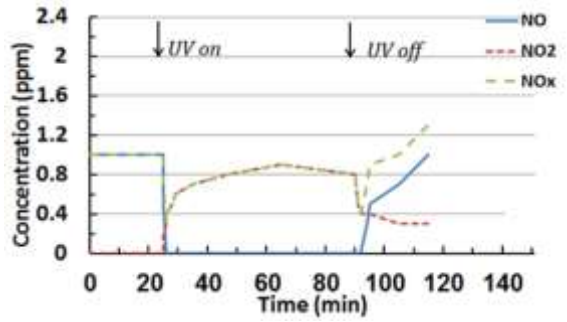


**Figure 6:Nano-dipped sample reduction for NO gas**

It is expected that nano particles which has more surface area than micro particles could be absorbed deeper into the substrate this gives more chance for the reaction to be happened on the surface. Generally, removal for the micro and nano dipped samples considered to be equal and no saturation with gas was happened for the both coated samples during the test period.

(5 min) micro-sprayed substrate showed a gradual NO removal of 87.69 % within 19 min as shown in (Figure 7).

The removal efficiency of NO gas was about 98.85 % within 1 min for (5 min) nano- sprayed samples, as shown in Figure 8.

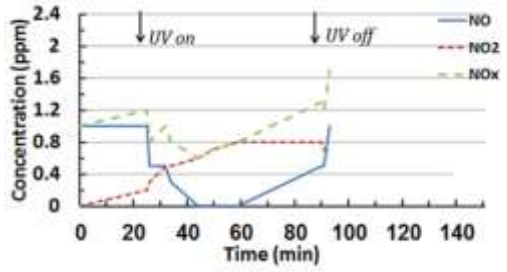


**Figure 7: (5 min) micro-sprayed samples reduction for NO gas**

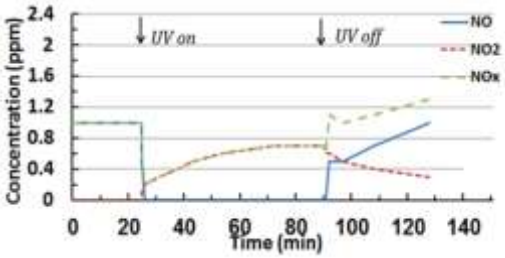


**Figure 8: (5 min) nano-sprayed samples reduction for NO gas**

Nano-sprayed samples absorbed deeply through the substrate surface pores this lead to increase the reaction for the 5 min nano-sprayed samples due to continuity of the reaction , while micro sprayed samples have greater particle size which lead to high agglomeration on the substrate surface.

compares between the time required for NO reduction and NO2 generation due to the reaction, from figure it appears that maximum time required for reduction of NO concentrations was in5 min micro-sprayed samples due to the low surface area and low binding capacity for the micro solution to the substrate surface especially when sprayed over it, while dipping the sample into the micro solution gives more ability for the particles to be attracted over the sample surface Figure 9.

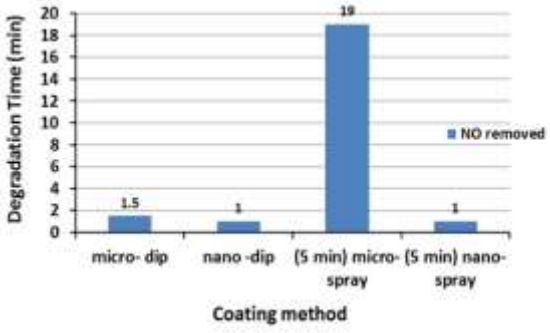


**Figure 9: comparison between coating methods and time elapsed for NO reduction and NO2generated**

**Table 2: summarize the obtained results for the removal of nitric oxides and the generated NO2.**

| Coating method | NO removed (%) | $NO_2$ generated (%) | $NO_x$ removed (%) |
|---|---|---|---|
| mT- dip | 98.08 | 92.46 | 5.62 |
| nT- dip | 98.85 | 77.31 | 21.54 |
| 5 min-mT spray | 87.69 | 66.31 | 21.38 |
| 5 min-nT spray | 98.85 | 52.38 | 46.46 |

## 5. Conclusion

In this study, economic simple methods of spray and dip coating were adopted to assess the reduction of air pollution by improving the performance of the cementitious specimens. Based on the experimental work results in this research, the following conclusions can be drawn:

1. Coating cementitious materials with an aqueous solution contain micro or nano titanium dioxide was effective in reducing NO concentration.

2. Coatings with micro titanium dioxide were less efficient in the removal especially in spray method the removal need more time to be exhibited.

3. Both dip and spray coatings have the same activity in the removal when nano aqueous solution was used, the removal efficiency reached to 98.85%.

4. When the micro aqueous solution was used in dip method the gas removal efficiency reached to 98.08%, while gas removal efficiency reached to 87.69% when spray method was used.

## 6. Recommendations

1. Using other concentrations of the aqueous solution less than 3g/L.

2. Using another method of coating like brushing the cementitious substrates to form thin film of the aqueous solution.

3. Studying the ability of adding aqueous solution with paints used in painting buildings.

Painting various types of substrates and studying its ability in the adsorption of the aqueous solution.

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