Nitric Oxide Reduction by Applying Various Coating Methods of TiO$_2$ on Cementitious Materials

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Abstract
Nitric oxide generated from various sources like car combustion is one of the most surrounding pollutants. Titanium dioxide considered an environmentally friendly active photocatalytics that can be used with building materials safely and effectively to react with nitric oxides in the presence of UV radiation from sunlight.

To study the possibility for the reduction of air pollutants two strategies were adopted. First one included mixing of micro particles of TiO$_2$ with cement paste in two percentages: 3% and 6%. In the second one mortar substrates were coated with micro TiO$_2$ (mT) aqueous solution by either dipping or spraying coating method. A laboratory test procedure was adopted to assess the performance of the prepared photoactive specimens. The specimens were subjected to NO gas and there efficiency in gas removal was monitored with time.

Results showed that coating strategy was more effective than mixing strategy in term of gaseous pollutants removal. The comparison between the two coating methods showed that the dipping method reached 98.08 % removal capacity and was better than spring method which reached 87.69 % only.

Keyword:
Cementitious; Coatings; mixtures; photocatalytic, microTiO$_2$

1. Introduction
Traffic and car combustion considered to be one of the most important sources for the generation of air pollutants. Photocatalytic materials can be used on the surfaces or mixed with building materials. In the presence of light and photocatalyst material, oxidation of the pollutants started and precipitated on the surface of the material, and then they are washed from the surface by rain. Heterogeneous photocatalysis using titanuim dioxide (TiO$_2$) as a catalyst is rapidly developed in the field of green environmental engineering (Beeldens, 2006).

The most notable characteristics for the wide use of titanium dioxide with cement-based materials are: 1) Safe; 2) High photocatalytic activity; 3) compatible with cementitious material; 4) react effectively even under weak UV radiation (Chen and C. sun Poon, 2009).
Furthermore, titanium dioxide have hydrophilic characteristics which enhance the self-cleaning performance for the surface (Hashimoto, Irie and Fujishima, 2007) and (Marco et al., 2013).

Using titanium dioxide with building materials lead to degradation of a broad range of pollutants, furthermore no chemical additives are required (Zhao and Yang, 2003). Titanium dioxide could be used either as a suspension or in the powder solid form, the photocatalytic activity may be reduced when TiO2 used in the solid state because it will be bounded by other materials while preparing a suspension of TiO2 was more efficient (Rachel, Subrahmanyam and Boule, 2002). In contrast, (Cassar, 2004) stated that the use of cement and TiO2 mixture contribute well towards NOx reduction.

Recently, the most applications for photocatalysis in construction buildings involve mixing of TiO2 inside concrete or mortars. The use of coatings are as well interesting because of the surface photocatalysis reaction, furthermore applying coating on the building surface lead to lower consumption of TiO2 (Martinez et al., 2011).

Both immobile and suspension forms results indicated that TiO2 loading technique and substrate characteristics considered a fundamental reasons in the activity of the TiO2 – cement mixtures (Ramirez et al., 2010).

(Folli et al., 2012) stated that the available surface area for the reaction is defined by TiO2 particle size and their agglomeration and dispersion in cement matrix. Big size pores formed due to high dispersion of the micro TiO2, nitrogen oxides which have small molecules size can be penetrated and degraded easily through formed pores.

(Lee, 2012) stated that the photocatalytic performance was not affected after exposure to various weather circumstances for the cement-TiO2 mixtures.

(Jayapalan et al., 2015) studied the reduction in the photocatalytic efficiency by the addition of different types of commercial TiO2 replaced by 5% cement paste. With continuous exposure for the pollutant gas, the rate of the photocatalysis could decrease, and saturation would eventually occur.

Aqueous coatings must be protective barrier against chemical attack, abrasion, in addition to aesthetics aspects (Balaguru and Chong, 2008).

Most rough surfaces could be altered to superhydrophilic by depositing submicroscopic particle coatings or by chemical treatment. Suspensions could be deposited on the substrates surfaces by using spray, sputtering, spin coatings and sol gel dip techniques (Chen, Kou and Poon, 2011) and (Drelich et al., 2011).

Some researchers showed that photocatalytic activity for the TiO2 films is more than other most active commercial TiO2 powder. Its stability and applicability make the thin-film configuration be adopted widely in the photo-oxidation of air pollutants (Zhao and Yang, 2003).

(Guo, M. Z., Ling, T. C., and Poon, 2012) stated that dip-coated mortars displayed a highly improved photocatalytic activity and a much lower TiO2 dosage.

The aim of this research work is to evaluate the ability of micro scale TiO2 for the removal of nitric oxide from surrounding air by applying various forms of surface coating methods; mixing with the powder form of TiO2, spraying and dipping with aqueous solution of TiO2 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

The experimental programme is designed to assess the photocatalytic efficiency (PE) by comparing the performance of cement-based materials with various percentages and coatings of the commercially available photocatalytic TiO₂ particles.

2.1 Materials

Ordinary Portland cement (OPC) type I, which has a Bogue composition of 58.80% C₃S, 19.14% C₂S, 7.95% C₃A, and 9.42% C₄AF and complies with ASTM C150-15 and Iraqi specification No. 5/1984 (Iraqi Standard Specification, 1984), was used to prepare the samples.

Fine aggregate used in this work was the local natural sand from Al-Ekhaider.

The commercial titanium dioxide powder was anatase from Tianjin Zhi Yuan Reagent Co., Ltd.-Chinese market. The particale size equals to 150-200 nm and surface area 6.9 (m²/g).

The pollutant NO gas was from Mesa specialty gases and equipment, California, with concentration of 400 ppm, which was diluted using another air cylinder (80% N₂ and 20% O₂).

Gas detector device was from RAE system by Honeywell-USA, San Jose, were 0-250 ppm for nitric oxide, 0-20 ppm for NO₂. 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 as stated elsewhere (Hussein, Al Anbari and Hassan, 2017).

2.2 Cement paste substrates preparation

Two levels of TiO₂ replacements were used for the commercial TiO₂ product, 3% and 6%; a constant w/c ratio of 0.5 was used for all samples.

TiO₂ powder was initially dispersed in deionised water and mixed for 2 minute using a magnetic stirrer and another 2 minutes using a hand-held mixer. Then, cement was added, and the mixing was conducted according to ASTM C305 (ASTM C305, 2011), except that the duration of mixing time was increased to 3 minutes to ensure thorough mixing and dispersion of TiO₂ in the cement. To replicate conditions in field applications as closely as possible, no special procedures or chemicals were used for dispersion. The pastes were cast in 9-cm-diameter petri dishes to form 6-mm-thick samples, let harden for 24 h at room temperature, and cured for 28 days at 100% relative humidity. After 28 days of curing, the samples were conditioned in a 70°C oven until the weight stabilised and then stored under sealed conditions away from any light source until further testing.

2.3 Mortar substrates preparation

Sand was graded according to ASTM C778 (ASTM C778, 2002) by using sets of standard sieves and using the retained on sieve 0.6 mm. Sand was sieved by using 4 sets of
Mixing procedure was conducted according to ASTM C305 standards with cement to sand ratio of 1:2.75 and w/c of 0.484. Flow test was made to ensure workability for the mixture (ASTM:C1437-13, 2013). 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.

2.4 Aqueous solution preparation

Samples have been coated by using two methods (spray and dip coating). A suspension was prepared by spreading 3g TiO$_2$ micro (mT) powder in 250 ml ethanol and 750ml deionized water stirred for (30 min.) then ultrasonicated for 1 hour to obtain solution homogeneity.

In spray method, substrates were sprayed for 5 minutes by using spray pyrolysis equipment, (Fig. 1).

In dip coating method substrates were dipped in the same concentration of the aqueous solution for 10 minutes, and then dripped for 3 minutes (Fig. 2). Finally, for both methods samples were oven-dried at 105°C for 1 hour, and kept sealed till test.

2.5 Test procedure

Rectangular chamber used with dimensions of about (30 cm x10 cm), as shown in Fig. 3. All Tests were carried out at room temperature with applying a continuous air flow, gas flow used was about 1.6±0.2 l/min. 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) (Hussein, Al Anbari and Hassan, 2019). Test procedure was as follows:
1- Calibration for the gas detector must be checked.
2- Putting the sample inside chamber and close tightly.
3- A continuous air flow ejected inside the reactor to persuade cleaning with UV lamps turned off and dark conditions.
4- Inlet gas pollutant (NO) was opened and calibrated till reached the desired concentration 1ppm.
5- Waiting for about 25 min to ensure chamber saturation and readings stabilization after this UV source is turned on.
6- The reaction continued till reaching a steady state.
After this UV is turned off, close the pollutant gas valve and again only air flow is ejected inside chamber.

The calculation details of the NOx removal have been described elsewhere (Chen and C.-S. Poon, 2009; Mills and Elouali, 2015) by calculating the area under curve.

3. Results and discussion
All tested samples were subjected to a relative humidity (RH) of 50%; the temperature and flow rate were almost constant.

3.1 The removal of NO and NOx using PC modified mixtures:
The reaction profiles and photocatalytic performance for NO and NOx removal and NO₂ generation are illustrated in Fig.4.
Although the removal efficiencies for both 3% and 6% mT appear to be equal, the NO\textsubscript{2} concentrations generated from the 3% mT during the reaction are greater than the amounts generated from the 6% mT sample with less removal for the NO\textsubscript{x} amounts. It is expected that mT replacement reduced the void percentages and water absorption of the mixtures, therefore, increasing percentage leads to reduce the reaction as a result this leads to reduce NO\textsubscript{2} generated from the 6% mT (Mahdi, Al Anbari and Hassan, 2018).

In the samples with 3% and 6% micro-replacements, the NO readings returned to 1 ppm because of the saturation with NO gas and reduced PC mixture efficiency in the removal with time as shown in Fig. 4, NO\textsubscript{2} values significantly increased at the end of the reaction for the 6% micro-replacement, which confirms that in this stage, the material was saturated and worked as a convertor instead of a remover, as stated by (Mills and Elouali, 2015).

### 3.2 The removal of NO and NO\textsubscript{x} using coated substrates by spray method:

Fig. 5 shows the reaction profiles for the micro sprayed sample, from figure it appears that 5 min- mT spray sample has NO removal efficiency and NO\textsubscript{2} generation percent equal to 87.69% and 66.31%, respectively; this result is expected because of the excess amounts of the sprayed solution that could be absorbed on the substrate surface, which results to more reaction and NO\textsubscript{2} generation. NO\textsubscript{x} removal was 21.38%.

![Figure 5- NO reaction profiles for the 5 min- micro TiO\textsubscript{2} spray coated substrate](image)

### 3.3 The removal of NO and NO\textsubscript{x} using coated substrates by dip method:

Nitric oxide removal was very fast when micro-dipped (mT dip) substrates exposed to the pollutant gas. The removal was 98.08% within 1.5 min. Large amounts of NO\textsubscript{2} generated due to the reaction as shown in Fig. 6; this could be explained due to the high amounts of TiO\textsubscript{2} particles on the substrate surface with little percent to be absorbed by the specimen. No saturation with gas was noticed for the coated samples during test period.
Figure 6- NO reaction profiles for the dip coated substrate

Generally, removals by using spray and dip methods considered to be more efficient for gas reduction, this can be explained due to the surface reaction that happened when the specimens coated with the same concentration of the liquid solution which forms a thin-film as stated by (Zhao and Yang, 2003). The durability of the material seems to be more for the mixed samples due to increase resistance to weather effect when TiO2 mixed with cement paste with reduction in the photoactivity as stated (Hassan et al., 2012). Table (1) summarize the obtained results for the NO and NOx removal and NO2 generation for the used methods.

Table(1)- Percentages of NO removed, NO2 generated and NOx removed for various photocatalytics cementitious materials

| Coating method          | NO removed (%) | NO2 generated (%) | NOx removed (%) |
|-------------------------|----------------|-------------------|-----------------|
| 3% micro TiO2 mixture   | 38.92          | 32.92             | 6               |
| 6% micro TiO2 mixture   | 39.06          | 27.38             | 11.69           |
| 5 min-micro TiO2 spray  | 87.69          | 66.31             | 21.38           |
| micro TiO2 - dip       | 98.08          | 92.46             | 5.62            |

4. Conclusions
In this study, various methods of coatings were adopted to assess pollutants removal performance of the produced cementitious specimens. Based on the experimental work results in this investigation, the following conclusions can be drawn:
1. PC modified mixtures with 3% and 6% mT mixtures have almost the same affectivity in the removal of nitric oxide pollution.
2. Spray and dip coating methods have more ability to reduce NO pollution than PC mixtures due to the exposed coating area to the polluted gas.
3. Spray method can be used effectively for the previously constructed buildings.
4. Dip method has more ability to reduce pollutants this could be explained to the thin film layer formed on the substrate surface.
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