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AIR POLLUTANTS MITIGATION BY USING VARIOUS FORMS OF PHOTOCATALYTIC CEMENTITIOUS COATINGS MATERIALS

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ABSTRACT

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

To study the possibility for the reduction of air pollutants like nitric oxides, two types of substrates coatings were prepared. First, mixing nano particles of TiO2 with cement paste in two percents 3% and 6%. Second, mortar substrates coated with nano TiO2 aqueous solution. Two coating methods have been used dip and spray. 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 the effectivity of coating building materials with titanium dioxide, the removal of gaseous pollutants like nitric oxide reached to 98.85% when spary and dip methods are used. Mixing nano titanium with a percent of 3% was also efficient in the removal of nitric oxides, the removal reached to 97%. It was concluded that spray method was more practical to be used.

KEYWORD: Cementitious; Coatings; mixtures; photocatalytic, air pollutants

1. INTRODUCTION

Air pollution caused by traffic can be solved through treatment of the pollutants generated from the source as possible. 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 titanuin 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 & C. sun Poon 2009). In addition to the hydrophilic characteristics which enhance the self-cleaning performance for the surface (Hashimoto et al. 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 & Yang 2003).

Titanuim dioxide could be used either as a suspension or in the powder solid form , the photocatalytic activity may be reduced when TiO_2 used in the solid state because it will be bounded by other materials while preparing a suspension of TiO_2 was more efficient (Rachel et al. 2002). In contrast, (Cassar 2004) stated that the use of cement and TiO_2 mixture contribute well towards NOx reduction.

Recently, the most applications for photocatalysis in construction buildings involve mixing of TiO_2 inside concrete or mortars; the maximum amounts of the added polymeric binder were difficult to be specified as TiO_2 will be covered with binder which reduces its photocatalytic efficiency. 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 TiO_2 (Martinez et al. 2011).

Both immobile and suspension forms results indicated that TiO_2 loading technique and substrate characteristics considered a fundamental reasons in the activity of the TiO_2– cement mixtures (Ramirez et al. 2010).

Folli et al. 2012 stated that the available surface area for the reaction is defined by TiO_2 particle size and their agglomeration and dispersion in cement matrix. Nitrogen oxides which have small molecules size can be penetrated and degraded easily through pores formed due to nano TiO_2 agglomerations.

Lee, 2012 stated that the photocatalytic performance was not affected after exposure to various weather circumstances for the cement- TiO_2 mixtures; also pore solution take part in the pollutant binding amount through absorption in addition to the binding amounts on the hardened cement paste.

Jayapalan et al. 2015 studied the reduction in the photocatalytic efficiency by the addition of different types of commercial TiO_2 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. Applying nano size coatings that are durable, the main parameters should be taken into consideration are: durability under various conditions, friction and abrasion resistance, electrical characteristics, and high temperature resistance. Also nano coatings properties need more investigation; brittle coatings may fail by cracking and spalling rather than "wearing out" (Balaguru & Chong 2008).

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

Some researchers showed that photocatalytic activity for the TiO_2 films is more than other most active commercial TiO_2 powder. Its stability and applicability make the thin-film configuration be adopted widely in the photo-oxidation of air pollutants (Zhao & Yang 2003).

Guo et al., 2012 compared 5% nano- TiO_2 intermixed mortars with dip-coated mortars in nano-TiO_2 solution. Photocatalytic degradation of NO was evaluated to compare their air- purifying efficiencies; dip-coated mortars displayed a highly improved photocatalytic activity and a much lower TiO_2 dosage.

Hassan et al., 2012 compared removal efficiency for various types of coatings by using PC 105 ultrafine TiO_2, Results obtained appear that removal efficiency for 5% TiO_2 mixture and spraying water based TiO_2 were 26% and 25% respectively, the aqueous solution used with TiO_2 was effective because the product provides the most evenly concentrated coverage area.

The aim of this research work is to evaluate the ability of nano scale TiO_2 for the removal of nitric oxide from surrounding air due to increasing its amounts from combustion sources, this also lead to reduce the amounts of the photochemical smog and the harmful ozone which increased according to these reactions. Three forms of surface coating methods have been applied; mixing with the powder form of TiO_2, spraying and dipping with aqueous solution of TiO_2 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 TiO_2 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 nano-size PC105 (20±5 nm)-anatse with a specific surface area of 85.6 m^2/g from Cristal Active Millennium SAS- France.

The pollutant gases were from Mesa specialty gases and equipment, California. The concentrations were 400 ppm for both NO and toluene gases, which were diluted using another air cylinder (80% N_2 and 20% O_2).

Gas detector device was from RAE system by Honeywell-USA, San Jose, were 0-250 ppm for nitric oxide, 0-20 ppm for NO_2. 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 et al. 2017).

2.2. Cement paste substrates preparation

Two levels of TiO_2 replacements were used for the commercial TiO_2 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 TiO_2 in the cement. To replicate conditions in field applications as closely as possible, no special procedures or chemicals were used to disperse the nano TiO_2 particles. 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 sieves and standard sand gained by using the retained on sieve 600 µm according to ASTM C778.

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 nano 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^{o}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). To control humidity inside the reactor a humidifier has been used with control valves.

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. Humidity was calibrated through control valves to obtain RH of about 50%.
6. Waiting for about 25 min to ensure chamber saturation and readings stabilization after this UV source is turned on.
7. The reaction continued till reaching a steady state.
8. 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 & C.-S. Poon 2009; Mills & Elouali 2015) by calculating the area under curve.

Fig. 1. Spray pyrolysis equipment for spraying nano TiO_2 aqueous solutions.

Fig. 2. Dipping method.

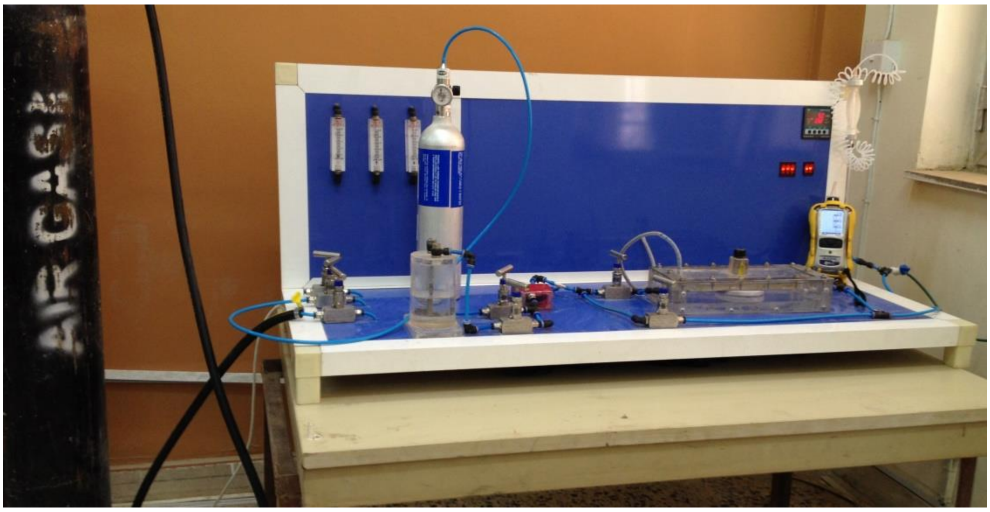

Fig. 3. Lab. Photocatalytic Reactor.

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 for the NO and NOx removal and NO2 generation are illustrated in Fig. 4.

The PC specimens with nano- TiO_2 replacements appear to have a high removal for the nitric oxides reached to 97% for the 3% nT and 94% for the 6% nT. The fast reduction in NO concentration shown in Fig. 4 (a) for the 3% nano- TiO_2 samples can be explained by the fast adsorption of gas molecules by the hardened cement paste in addition to the photochemical reaction as stated by Lee 2012.

Although the NOx removal efficiencies were almost equal for 3% and 6% nT, the reaction efficiencies indicate that the removal capacity improvements expected with 6% nT replacement were not clearly evident compared to the 3% nT replacement, high concentrations of the added TiO_2 seems to be bounded with cement particles as stated by Martinez et al., 2011. No saturation with gas was noticed for the substrates and the reaction continued till the UV was turned off.

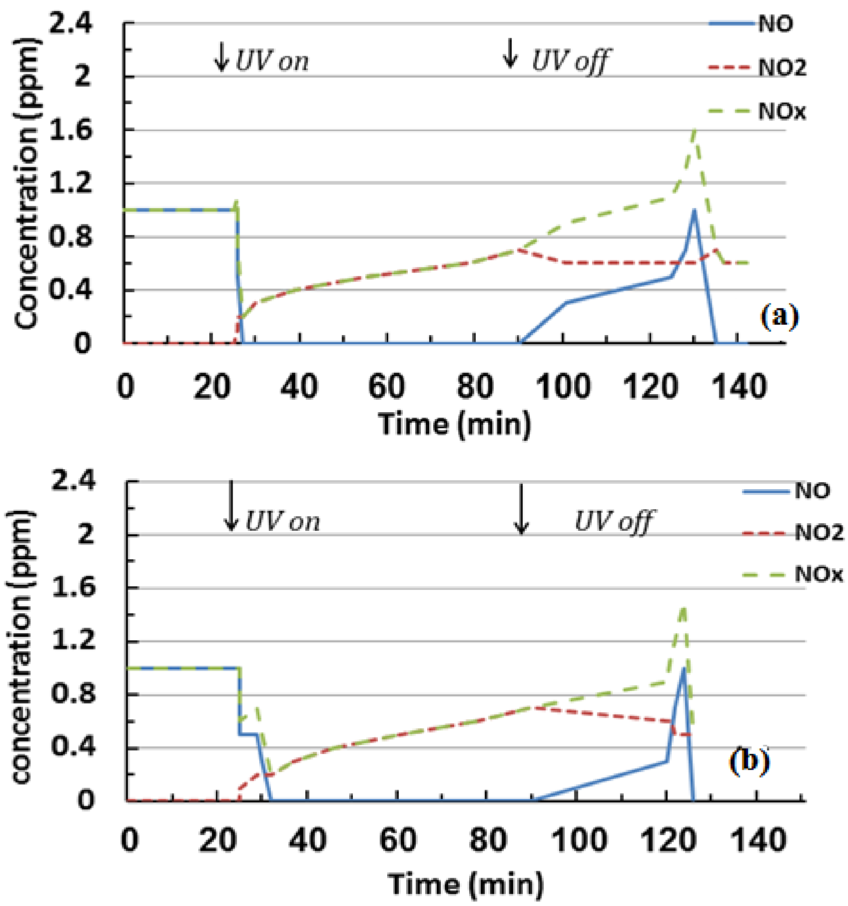

Fig. 4. NO reaction profiles for TiO_2 -modified PC mixtures: a) 3% nT; b) 6% nT.

3.2. The removal of NO and NOx using coated substrates by spray method:

Fig. 5 shows the reaction profiles for the nano sprayed samples; from figure, it appears that 5 min nT-spray samples seem to have a high percent of NO removal efficiency reached to (98.85 %), NOx removal reached to (46.46%) and NO_2 generated equals to (52.38%). No saturation with gas was happened during the test period. The high efficiency can be explained due to the surface reaction happened by the aqueous solution layer on the substrate surface which gives a high coverage area on the substrate surface as stated by Hassan et al., 2012 .

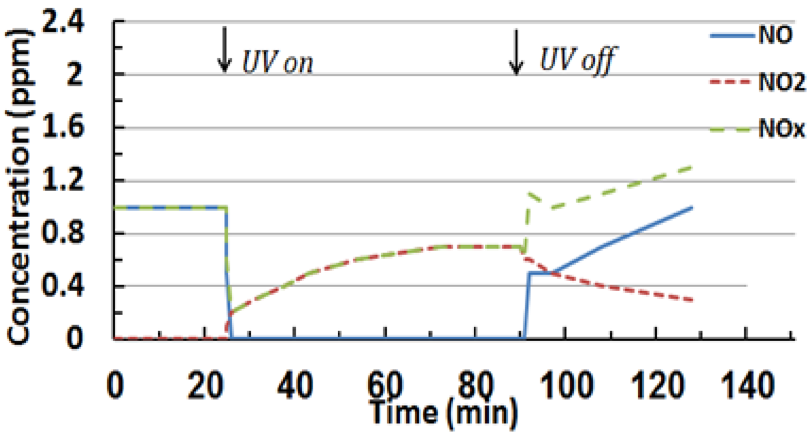

Fig. 5. NO reaction profiles for the 5 min- nT spray coated substrate.

3.3. The removal of NO and NOx using coated substrates by dip method:

Nano-dipped (nT dip) samples showed rapid removal for NO gas equals to 98.85%, this could be explained due to the high activity for the nano-dipped samples with high generation of NO_2 amounts as shown in Fig. 6, it is expected that nano particles which has high surface area could be absorbed deeper into the substrate this gives more chance for the reaction to be happened on the surface and increasing the rate of NO_2 generation, this affectivity for the dipping method was mentioned by Guo et al., 2012. No saturation with gas was happened for the both coated samples during test period.

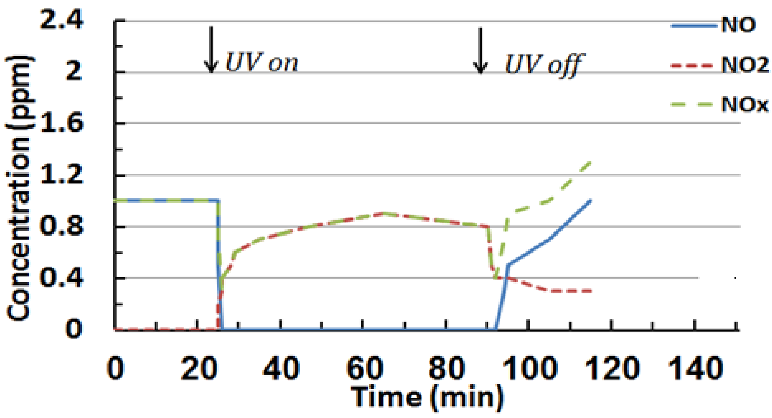

Fig. 6. NO reaction profiles for the dip coated substrate.

Generally, removals by using spray and dip methods considered to be equal and having the same activity for the 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 & Yang 2003 . Although little differences in the removal are shown between these methods due to the high photocatalytic activity for this type of the anatse TiO_2, the durability of the material seems to be more for the mixed samples due to increase resistance to weathering effect as stated by Hassan et al., 2012. Table 1 summarize the obtained results for the NO and NOx removal and NO_2 generation.

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

Coating method	NO removed (%)	NO_2 generated (%)	NO_x removed (%)
3% nT mixture	97.31	43.77	53.54
6% nT mixture	94.46	40.15	54.31
5 min- nT spray	98.85	52.38	46.46
nT- dip	98.85	77.31	21.54

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% nT have NO and NOx removal efficiency more than 6% nT mixtures.
2. Spray and dip coating methods have the same NO removal efficiency.
3. Spray method can be used effectively for the previously constructed buildings with moderate reactions for the NO_2 generation.

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