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**Improvement of Photocatalytic Hydrophilic Concrete
Properties by Using TiO₂ for Enhancement of Air
Pollution Mitigation and Self –Cleaning Performance**

A Thesis

Submitted to the Department of Building and Construction Engineering of the
University of Technology
in Partial Fulfillment of the Requirements for the Degree of Doctor of
Philosophy in Sanitary and Environmental Engineering

By

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Supervised by

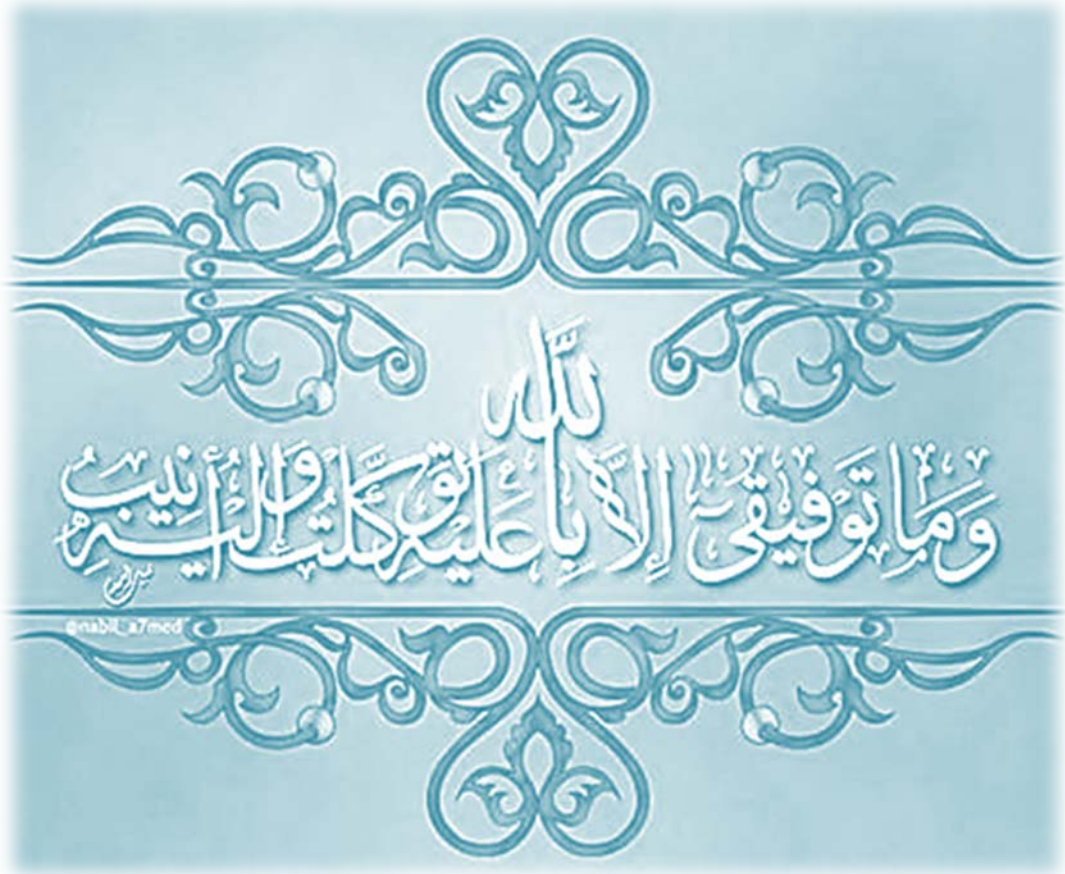
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Abstract

The use of the photocatalyst with building materials is considered one of the most recent methods being applied in the last decades as an environmentally friendly solution to remediate air pollutants generated from different sources like fuel combustion. In the presence of sun light, these pollutants can be transformed to more complex material forming photochemical smog and harmful ozone.

In this study, a side-by-side comparison was performed to examine the effects of nano-TiO₂ (nT) on the photocatalytic activity of Portland cement (PC) mixtures and its effectiveness was compared to similar replacement percentages of micro-TiO₂ (mT), both of which were 100% anatase. Cement paste specimens were prepared by progressive cement replacement with nT or mT. To simulate the natural atmospheric factors due to the difference in seasons, the Portland cement specimens were subjected to different moisture conditions, including normal conditions with 50% relative humidity (RH), saturated conditions with 100% RH, and dry conditions with 0% RH. Their photochemical reaction (i.e., pollutant gas removal ability) along with TiO₂ were evaluated and compared with the reference specimens. Another concrete mixture was prepared and some samples were coated with nano titanium aqueous solution and others were coated with micro titanium aqueous solution by using spray and dip coating methods. Pollutants removal tests were conducted via a laboratory photocatalytic reactor designed according to ISO 22197-1:2007; the pollutant used gases were NO and toluene. Furthermore, the self-cleaning ability for all types of samples was examined by applying a drop of methylene blue dye to the specimen surface; differences in dye discolouration with time under halogen lamp illuminations were noticed.

In order to investigate the levels of air pollution in the city of Baghdad, a pollution level measurement data were collected from two stations in Baghdad (Al-Wazeerya and Al- Andalus) for the period (2012-2014).

The results show that PC mixtures modified with nanotitanium dioxide were more effective in the dry conditions. In contrast, microtitanium mixtures appear to be favourable for wet conditions. Concerning coated samples, it appears that coating with micro titanium dioxide was less efficient in the removal of NO and toluene gases especially when spray method was used, the removal needs more time to be exhibited. Both dip and spray coatings have the same activity in the removal of NO gas when nano aqueous solution was used. The self –cleaning ability for the cementitious material was enhanced when using TiO₂ with different forms.

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ABBREVIATIONS

Symbol	Definition
ASTM	American Concrete Institute
BTEX	benzene, toluene, ethylbenzene and xylenes
CA	Contact Angle
CB	Conduction Band
CSH	Calcium silicate hydrate (main product of cement hydration which is primarily responsible for the strength in cement based materials).
DC	Dry Condition
eV	electron Volt
EPA	Environmental Protection Agency
ISO	International Organization for Standardization
JIS	Japanese Industrial Standards
mT	micro titanium
NC	normal condition
NMHC	Non Methane Hydrocarbons
NO	nitrogen oxide
NO ₂	nitrogen dioxide
NO _x	nitrogen oxides
nS	nano silica
nT	nano titanium
P25	a standard material of titanium dioxide with average paricle size of about 25nm produced by Evonic-Germany consist of anatase and rutile in a ratio of about 3:1
PC	Portland cement
PC105	Titanium dioxide produced by Cristal Active Millennium with a range size equals (20±5 nm) consists of anatase only
PM ₁₀	particulates matter with diameter of 10 micrometers or less
PE	photocatalytic efficiency
RH	relative humidity
RhB	rhodamine Blue dye
SC	saturated condition
TiO ₂	Titanium dioxide
UNI	Italian Organization for Standardization

UV	Ultra Violet
VB	valence band
VOC	volatile organic compound
w/c	water to cement ratio
W	Watt
WHO	World Health Organization

NOTATIONS

Symbol	Definition
γ_{lv}	Liquid-vapor interfacial tension
γ_{sl}	Solid-liquid interfacial tension
γ_{sv}	Solid-vapor interfacial tension
ρ	Water density, gm/cm ³
θ	Young's contact angle on a similar smooth surface
θ_c	Apparent contact angle
θ_w	Contact angle on the rough surface
f	Wetted surface solid fraction
f_1	Contact angles on phase 1
f_2	Contact angles on phase 2
g_1	Bulk density
g_2	Apparent density
r	Surface roughness factor

CHAPTER ONE

INTRODUCTION

Chapter One

Introduction

1.1 General

Air pollution is considered one of the most harmful environmental problems that affects on human health, causing deaths, illnesses, spending money in health care and loss of productivity every year(Boyd 2006).

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 titanium dioxide (TiO_2) as a catalyst is rapidly developed in the field of green environmental engineering (Beeldens 2006).

Photocatalytic chemistry was started at 1972 by Fujishima and Honda when used TiO_2 for water splitting (Fujishima & Honda 1972). The anatase type of TiO_2 is widely used because of its high photoactivity compared with other photoactive types. The most notable characteristics for the wide use of titanium dioxide as a photocatalytic with cement-based materials are (Chen & Poon 2009):

- (a) Safe, have chemical stability, and relatively inexpensive.
- (b) Higher photocatalytic activity than other photocatalysts metal oxides.
- (c) Titanium dioxide considered the most compatible material with cementitious material with no change has been shown in the performance.
- (d) Titanium dioxide react effectively even under weak UV radiation.

The use of photocatalysts in building material represents a promising solution for remediation of air pollution in urban areas, showing their effectiveness and a real eco-sustainable value (Marco et al. 2013). Using titanium dioxide (TiO_2) coatings and composites as an environmental application with building materials, is considered a good choice for the following reasons:

- 1- Self-cleaning ability due to chemical reactions that take place in the presence of sunlight, on the photocatalyst surface (Hashimoto et al. 2007) and (Marco et al. 2013).
- 2- Forming a hydrophilic catalyst surfaces which enhance the self-cleaning character, where dirt and stains that adsorbed by cementitious substances can be easily removed by rainwater causing a watersheet between the adsorbed inorganic dirt and TiO_2 surface (Hashimoto et al. 2007) and (Marco et al. 2013).
- 3- Mitigation of urban heat island effect, a phenomenon that raises temperature of urban areas about 2 to 4°C, could be gained by using white photocatalytic cement materials which reflect solar radiation, this could also save energy required for cooling buildings and improve air quality (Marco et al. 2013) and (Nuruzzaman 2015).
- 4- Reduce ozone formation especially during summer season which is the main reason for urban smog (Marco et al. 2013).
- 5- Decreasing photochemical pollution reactions thereby reduce production of noxious substances (Marco et al. 2013).
- 6- Environmental sustainability (Marco et al. 2013) and (Jayapalan 2013).

7- Promote other surface characteristics including antifouling, abrasion resistant, antibacterial, and oleophobic features (Marco et al. 2013).

The specification of cement matrix is compatible with TiO_2 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 Fig. (1.1) (Chen & Poon 2009).

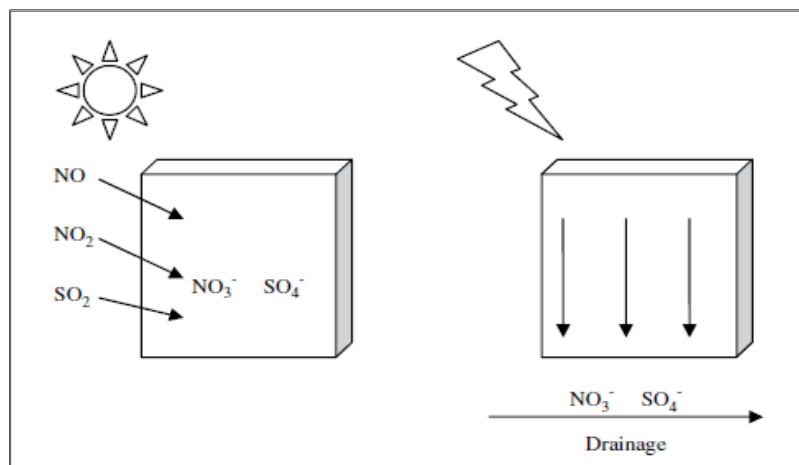


Figure 1.1- Removal of Pollutants by using photocatalytic in building materials. (Chen & Poon 2009)

1.2 Applications of TiO_2 into building materials

The utilization of the photocatalytic cementitious materials began from 1990 (Fujishima & Zhang 2006), and has been taken a great of interest as an application particularly from Europe and Japan (Beeldens 2006). The use of TiO_2 has been applied in the exterior structure materials and the interior finishing material, like mortar, paving blocks, tiles, glass, etc. the major uses of TiO_2 with building materials are shown in Table 1.1. In Japan- 2003, sales of the photoactive cementitious materials were 60 % of the total photocatalytic trade (Fujishima & Zhang 2006).

Table 1.1- Classification of building and construction materials using TiO₂ as based photocatalytic to improve environmental conditions (Fujishima & Zhang 2006)

Type	Material	Purpose
Exterior building materials	Tiles, glass, panels	Self-cleaning
Indoor furnishing materials	Tiles, wall paper, paints, finishing coatings, window blinds	Self- cleaning and anti- bacterial
Road materials	concrete pavement, sound-proof walls, Tunnel walls	Self- cleaning and air cleaning

The benefits of using TiO₂ with building materials are interesting for many industries as an application for sustainable technology and green buildings construction (Marco et al. 2013), in this type of constructions Italcementi Group implemented many projects (Fig. 1.2 a and b). Palazzo Italia (Italian Pavilion, Milan) received awards as the excellence winner in Concrete Construction program (American Concrete Institute 2017).

The application of photochemical reaction panels at the surfaces of car park buildings covered with white TiO₂ is investigated in European by Photocatalytic Innovative Coverings Application for Depollution Assessment (PICADA) project; results appeared a significant NO_x gases reduction. The removal percent of NO₂ and NO gases was 20% and 19%, respectively, (Maggos et al. 2007).

In France (Guerville) street canyons walls were covered with TiO₂ mortar; NO_x measurements were taken continuously and the recorded concentrations of about 40-80% lower than uncovered canyons (Maggos et al. 2008).

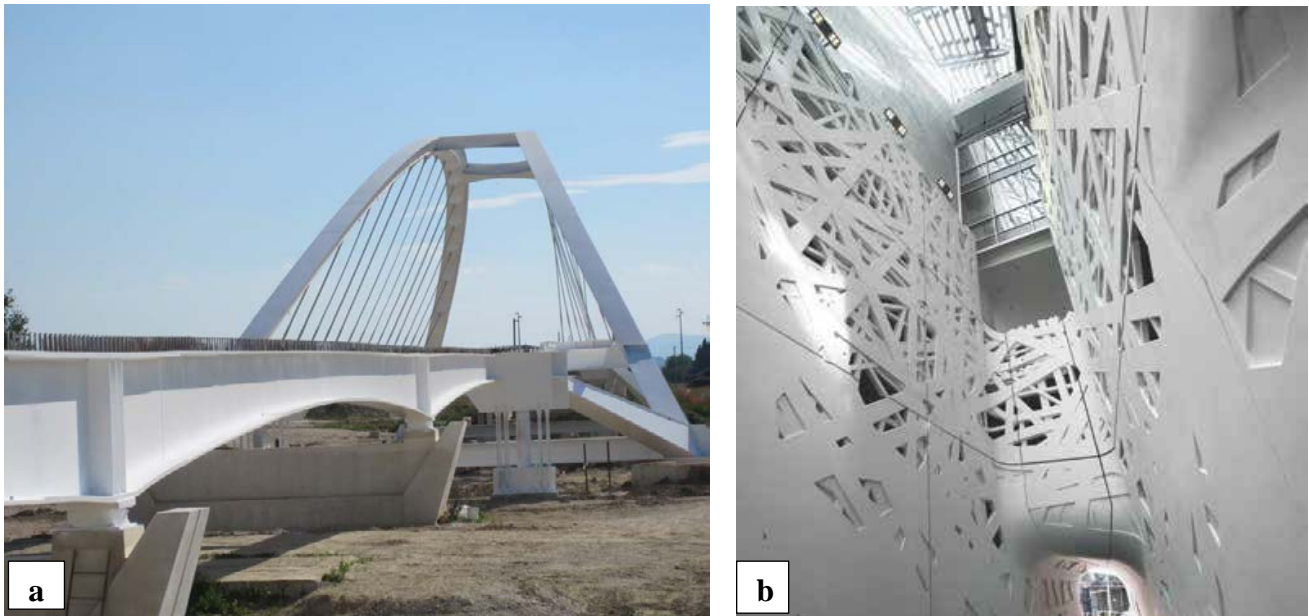


Figure 1.2- Projects implemented by Italcementi Group: a) Newly constructed bridge made by using photocatalytic cement piles. (Marco et al. 2013); b) Palazzo- Italia applied by using white cement - TiO_2 mixture (American Concrete Institute 2017)

One of the most effective ways to apply TiO_2 is by adding a thin coating to the weathering layer. Finishing sprayed coating for wide horizontal and vertical surfaces, like ceiling, walls, tunnel archs and multi-storey car parks were began to be used significantly (Marco et al. 2013).

If this layer is partly used, new titanium dioxide particles could be added to the surface (Beeldens 2006) and (Faraldos et al. 2016) .

Another environmentally friendly application is by using TiO_2 coatings and concrete lining for tunnels. This could be achieved by using artificial UV lamps as lighting source inside tunnels. There are many advantages which could be obtained by using such systems especially in the crowded traffic areas beside of lowering air pollutants concentrations: (Marco et al. 2013)

- 1- Visual comfort.

2- Reducing the maintenance and cleaning requirements, which considered a laborious mission in tunnels.

3- Lower maintenance leads to balance in energy consumption.

In Rome, Italy, NO_x levels were monitored by environmental campaigns in “Umberto I” tunnel, registrations were before and after the renewals work of the campaigns Fig. (1.3). NO_x removal was more than 50% at center of the tunnel, taking into account the actual concentrations data recorded officially in the monitoring station before the campaign. (Official Environmental Agency – ARPA) (Guerrini 2012).

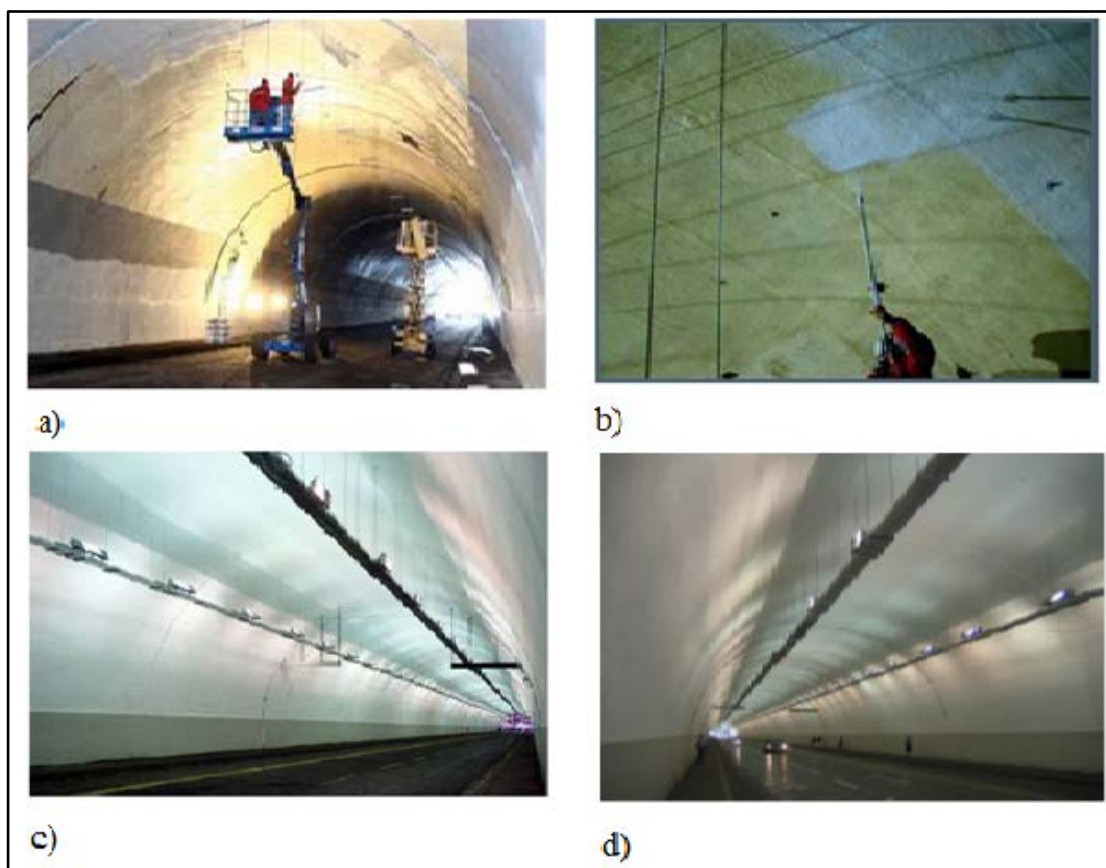


Figure 1.3- Rehabilitation steps in “Umberto I” tunnel -a and b during painting, c and d after finishing. (Guerrini 2012)

photocatalytic material could be used with architectural concrete or with white cement to enhance the aesthetic aspects for the building. Because of the photocatalytic reaction, the whiteness of the structure will continue for longer time (Maggos et al. 2007).

As an application of self- cleaning ability for buildings by using photocatalytic construction material and to maintain the aesthetic of the outlook appearance, a church in Rome (Dives in Misericordia) also in France - Chambéry the music hall were monitored. Only a slight difference in color were observed after 6 years of monitoring for the church, while the color remained almost constant after 5 years in Chambéry city hall (Guerrini et al. 2007).

Stadium roof of Dubai Sports City's Cricket is another applied project using TiO_2 photocatalytic Fig.(1.4) (Banerjee et al. 2015).

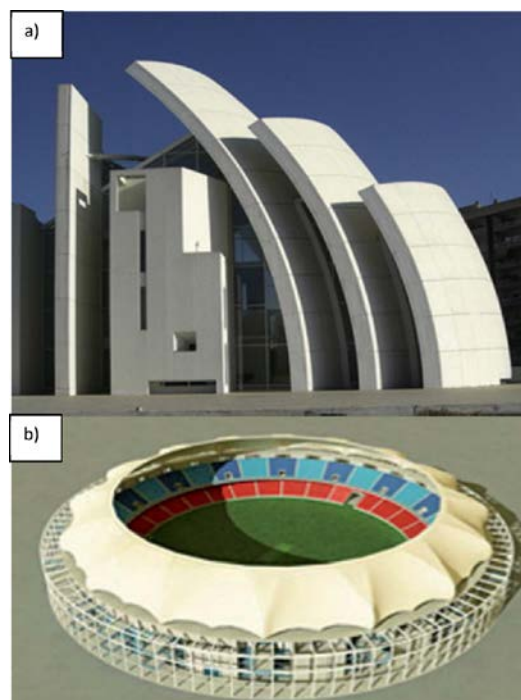


Figure 1.4- Application for self- cleaning buildings(a) Misericordia Church, (b) Dubai Stadium (Banerjee et al. 2015)

New method for energy saving is obtained by using TiO_2 photocatalyst for cooling buildings (Chen & Poon 2009) . To use this method water must be sprayed continuously at the building surfaces coated with a titanium dioxide layer; this could minimize the amount of water consumed to form a water film with thickness of about 0.1 mm that covers the whole building surfaces Fig. (1.5). The building is cooled by

the flux of latent heat after water evaporation. It was noticed that temperature drop was about 40–50 °C on the surfaces of a black roof tile on a summer clear day. This application can result to reduce the consumption of electricity used for air conditioning (Hashimoto et al. 2005).

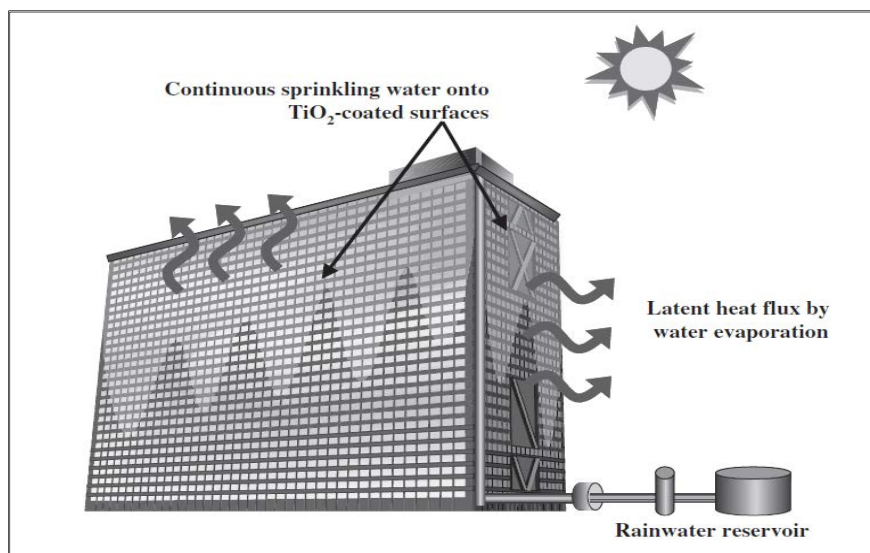


Figure 1.5- Cooling system for the building applied by using the collected rainwater and sun light radiation to save energy (Hashimoto et al. 2005)

1.3 Aim of the study

There are many benefits can be obtained through the use of the photocatalytic materials with building materials. Different methods are observed for applying TiO₂ as a photocatalyst; the choice of the appropriate method is decided according to the type and concentrations of the pollutants to be removed in addition to the surrounding weather conditions. The main concerns of this study are:

- 1- To investigate the possibility of utilizing titanium dioxide TiO₂ photocatalysis to provide an environmentally friendly solution using Self-cleaning concrete as an innovated building material by using different types and concentrations of TiO₂.

- 2- Evaluating the effects of using various percentage levels of nano-TiO₂ on the photocatalytic performance of the cement-based materials in comparison with similar added values of the commonly used micro-TiO₂.
- 3- Trying to use economic ways to apply photocatalytic different surface coating methods even for previously constructed buildings from materials that have become more widely recognized for green building constructions which enhance self-cleaning, combat pollution, save energy and reduce global warming.
- 4- Design and build up a laboratory reactor prototype according to Iraqi standards to evaluate self-cleaning performance in concrete for some air pollutants (NO and VOC) in sustainable way. These pollutants are considered the major gases of concern which effect adversely to the environment.

1.4 Thesis layout

The research work presented in this thesis is covered by five chapters:

- 1- Chapter One: represents the basic concept for the use of the photoactive cementitious materials with a review for the application of this technology in some countries; the objectives of the study are also presented in this chapter.
- 2- Chapter Two: introduces theoretical background with a review for the types of pollutants found in the ambient atmosphere and regulations for the acceptable limits; the basic theoretical idea for the activation of the photocatalytic material with chemical equations used are also introduced. A review for the most recent and important researches concerning the use of photocatalyst with building materials with different methods, reactor specifications and removal efficiency calculations are also illustrated in this chapter.

3- Chapter Four: the main steps for samples preparation, coating methods and details for the used reactor are illustrated in this chapter.

4- Chapter Five: the most important results obtained from the study are discussed in this chapter with comparison between methods enhanced with figures and images, data from the Ministry of Environment are also collected to study the level of pollution in Baghdad.

5- Chapter Six: conclusions obtained from tests results, with the most important recommendations for further studies and for the application of this technology in Baghdad are presented in this chapter.

CHAPTER TWO

THEORETICAL BACKGROUND

and

LITERATURE REVIEW

2.12 Using of nano-photocatalytic in building materials

There are two main ways to obtain nanoparticles, high milling or chemical synthesis (Miraldo et al. 2013). The ratio of surface area to volume for nanomaterial is high which leads to specific chemical reaction. Most studies use nano titanium oxide and nano silica, while a few studies use nano Fe_2O_3 Fig.(2.9) (Sanchez & Sobolev 2010).

(Chen 2010) stated that the addition of TiO_2 in the nano powder form significantly accelerate the hydration amount and promote rate of hydration at the early age. The spreading of TiO_2 particles in cement paste was confirmed to be not so homogeneous.

Understanding the effect of nano- TiO_2 on the cementitious material should be fully recognized. More studies are needed to relate water vapor transportation and pore size distribution of cementitious material. The addition of nano TiO_2 may effect on the pore structure and the hydration process, therefore water- transfer property may be influenced, thus affects the volume stability of the cementitious material (Zhang et al. 2015).

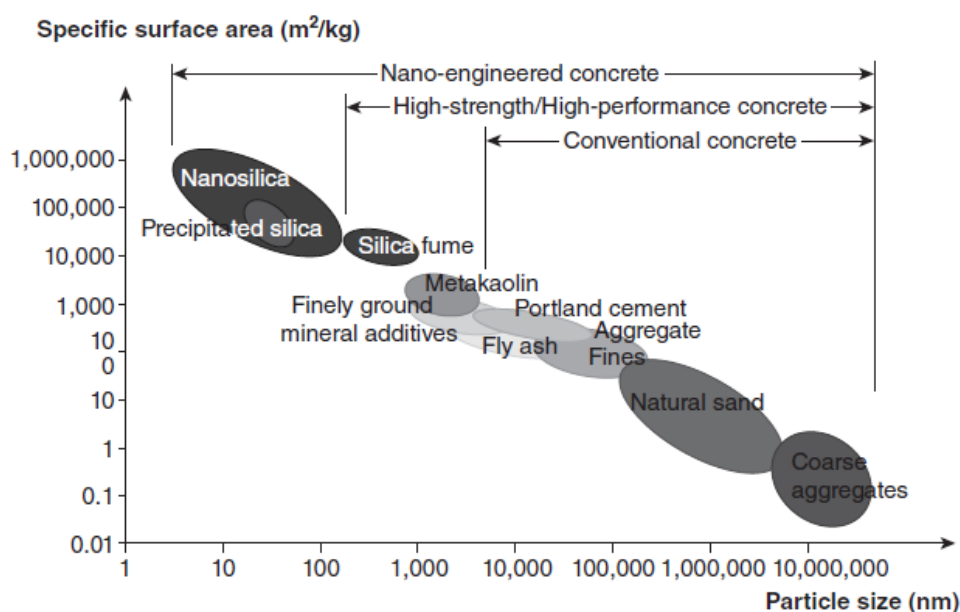


Figure 2.9- Comparing concrete materials with surface area and particle size (Sanchez & Sobolev 2010)

2.13 Mechanical properties

The addition of nanoparticles and the increase in the mechanical strength of cementitious material, help to produce of high performance concrete - HPC. The mechanism is explained as follows:(Miraldo et al. 2013)

- 1- Production of dense concrete due to filling voids in CSH (calcium silicate hydrate) structure.
- 2- Hydration development in Portland cement due to nanoparticles nucleation.
- 3- Production of CSH gel due to reaction of nanoparticles with $\text{Ca}(\text{OH})_2$ crystals; the nucleation of nanoparticles in cement paste reduces the crystal size of $\text{Ca}(\text{OH})_2$.

(Lackhoff et al. 2003) stated that the compressive strength was increased when TiO_2 mixed with the building materials.

(Chen 2010) concluded that pore size distribution and the total porosity of paste sample were decreased. Changes of microstructure and the hydration process acceleration was noticed as well as affected on mechanical and physical properties of the building materials. Initial and final setting times were reduced and further water was needed to sustain the consistency of the mixture. Mortar early age compressive strength was improved.

(Lee 2012) compared the addition of P25 and PC50 TiO_2 , the rate and the degree of hydration are improved, this results to reduce setting time than reference; concentrations of 5% and 10% PC50 samples had longer setting time than P25. Increasing in compressive strength with decreasing in microhardness was noted at lower water/cement ratio. The use of P25 TiO_2 nanoparticles dose not compromise compressive strength when added up to 10% replacement of cement at w/c equals to 0.5 and 0.6, while compressive strength increased in case of w/c = 0.4.

(Meng et al. 2012) attributed the enhancement in the mechanical properties of the cementitious materials to the decrease of hydration products of cement

induced by nano-TiO₂, a reduction in compressive strength was reported when nanoTiO₂ was added.

(Noorvand et al. 2013) study showed that the addition of 2 wt. % nano-TiO₂ resulted in compressive strength compared to the reference specimen value at 28 days.

(Essawy & Abd El.Aleem 2014) stated that when 5 wt. % nano-TiO₂ was added to cement mortar compressive strength increased by 5%.

(Zhang et al. 2015) investigated the addition of nano-TiO₂ (25 nm), pore refining effect and hydration rate acceleration result in increasing cement mortar compressive strength. The accelerated cement hydration rate for about 2 h in the addition of 5 wt. % nano-TiO₂, and a reduction of the pore size was also noted. Furthermore, pore refining effect and the contact angle decreasing for the cementitious material result in reducing the evaporation of water through drying. Refining pores and increasing hydrophilicity will be the reason in the reduction of drying shrinkage.

(Janus & Zajac 2016) concluded that photocatalytic activity is increased by increasing its weight percent added into cement, but if the adding amount is more than 5 % of the cement weight the compressive strength of the modified cement will be reduced.

2.14 Durability

(Chen et al. 2011) stated that the embedded nano particles become a nucleation sites for the hydration products (calcium hydroxide and calcium silicate hydrate) which are gradually bond together forming a solid supporting layer at the same time the photocatalytic may be deteriorated.

(Martinez et al. 2011) illustrated that the maximum amounts of the polymeric binder and the photocatalyst were difficult to be specified as the TiO₂ will be covered with the binder which reduces the durability and the photocatalytic efficiency of the material. Polymeric binders may be degraded

due to the oxidation process that occurs by the photocatalytic coatings. (Fujishima et al. 2008) stated that (chalking effect) may happen when the exterior TiO_2 coatings exposed to a strong sun light due to decomposition of the organic compound present in the paint.

(Lee 2012) stated that photocatalysis products like NO_x may decrease the activity of the photocatalytic material when they participate in formation of salts that resulted in the spalling or cracking of the construction materials. Furthermore, exposing to moisture and CO_2 from atmosphere effects the pore structure and the chemical composition of the cementitious material; this causes a decreasing in the degradation of the pollutants.

Adding nano TiO_2 to concrete structure contribute in the production of finer pores than adding other additives with higher surface area like nano SiO_2 , so resistance to chloride penetration will increase. It was also reported that refinement of pore structure increase with the content of nanoparticles in percents of (5% <3% <1%) while penetration of chloride decreases in the following percents (5% <3% <1%); this could be explained by the smaller particle diameter the higher water requirement, which causing pores formation (Miraldo et al. 2013).

2.15 Methods for applying titanium dioxide in building materials

Titanium dioxide is greatly used because of its superior characteristics; under certain operating conditions, a complete degradation of a broad range of pollutants can be achieved, furthermore no chemical additives are required (Zhao & Yang 2003).

There are various types of supporting materials that could be used for applying TiO_2 to reduce air pollutants. Interests are growing for using cementitious materials (e.g. mortar and concrete or cement paste) as supports because of their porous structures and high binding property (Chen et al. 2011).

Recently, the most applications for photocatalysis in construction buildings have involved mixing of TiO_2 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 TiO_2 (Martinez et al. 2011).

Titanium 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 NO_x reduction.

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). (Hüsken et al. 2009) reported that favorable NO_x degradation is obtained when photocatalytic concrete substrate is rough.

There are three main methods for concrete preparation with titanium dioxide as shown in Fig. (2.10) (Janus & Zajac 2016):

1- Coating concrete by thin layer of TiO_2 ; concrete surface can be covered with different types of slurries brushed onto the precast concrete.

- a) A homogeneous mixture of TiO_2 with water (TIW).
- b) A commercially water based TiO_2 (CWB).
- c) A transparent solution consists of a sealed mixture of TiO_2 with silicate and water based concrete (DIPM).
- d) Homogeneous thin slurry of TiO_2 mixed with low concentration of cement (CWLS).
- e) Commercial water based TiO_2 (PURETI) coated on the surface by using special equipment.

All slurries are prepared by using water; some organic solvents like ethanol are used to prepare photocatalyst dispersions.

2- A thick photo-active concrete laid over the cement based material.

In this type concrete consists of two layers, the bottom layer is the ordinary concrete and the upper layer consists of cement - TiO₂ mixture. Different amounts of titanium dioxide are added with cement mixtures in the top layer. Cement - TiO₂ mixtures with thickness of about 3 - 5 mm was tested, it was concluded that concrete carbonation depth can be reduced and corrosion performance was improved for the reinforcing bars.

3- Addition of TiO₂ with different percents in mass (cement replacement), concrete is replaced by TiO₂ as a part of its weight. The common commercial used types of TiO₂ are P25 (Evonic) and PC-105 (Millennium).

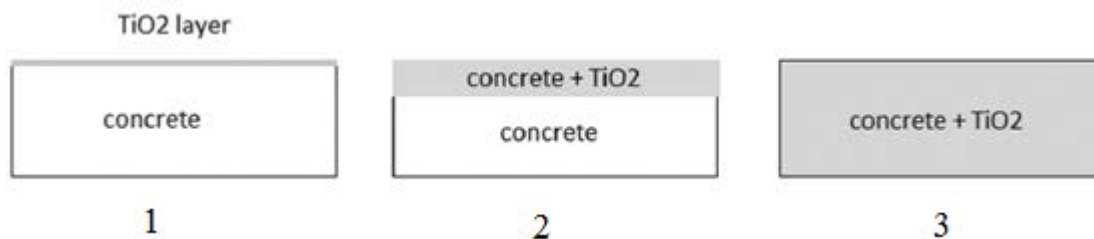


Figure 2.10- Main methods for applying photocatalytic with cement based materials (Janus & Zajac 2016)

2.16 Air pollutants removal by using Portland cement mixtures with TiO₂

(Strini et al. 2005) studied the removal of BTEX (as a volatile organic compound (VOC) pollutant combined from benzene, toluene, ethylbenzene and xylene) from ambient air using TiO₂ nanopowder mixed with white Portland cement. The removal efficiency ranged between 5% -54% with the highest photocatalytic activity was for o-xylene, ethylbenzene, toluene then benzene.

(Chen et al. 2011) evaluated the characteristics of TiO₂ mixed with concrete for the removal of NO_x and VOC in a specimens containing 0%, 5%,

10% TiO₂ replacements with cement and mixed with recycled glass instead of sand. Results showed effective removal for NO_x while toluene removal was not detected.

(Folli et al. 2012) studied the formed clusters structure and the colloids chemistry when 3.5 g of TiO₂ and 96.5g cement mixed at water: cement ratio (w/c) =0.4. The available surface area for the reaction is defined by TiO₂ particle size and their agglomeration and dispersion in cement matrix. Big particles size as RhB dye (rhodamine Blue dye) penetrate easily through the big formed pores due to high dispersion of the micro TiO₂ which offers a high surface area for the reaction and adsorption for dye molecules, as shown in Fig. (2.11). Conversely, nitrogen oxides gases can be penetrated and degraded easily through pores formed due to nano TiO₂ agglomerations, while dye particles hardly penetrate through nano TiO₂ agglomerations.

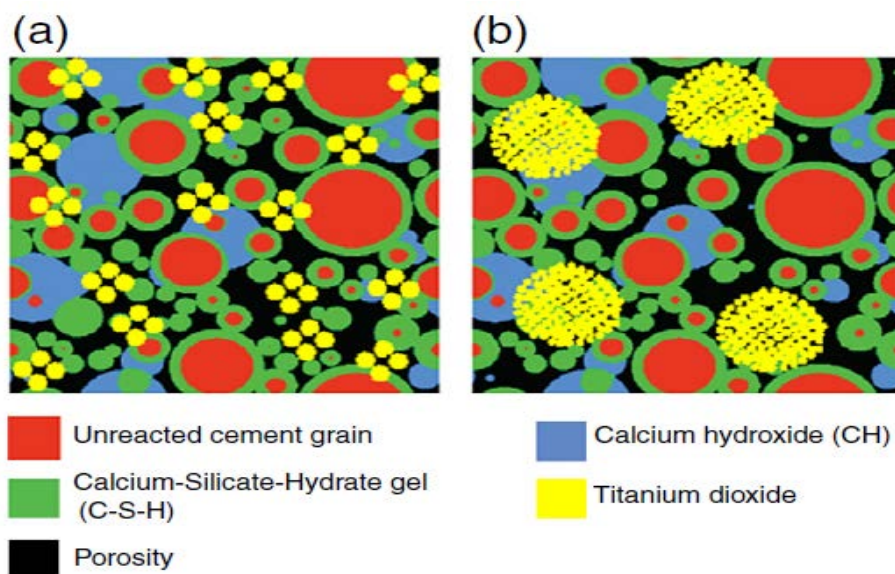


Figure 2.11 – Particles agglomeration and dispersion inside cement structure: (a) microTiO₂ ; (b) nano TiO₂ (Folli et al. 2012).

(Lee 2012) examined the addition of 5% TiO₂ replacement by cement mass with w/c = 0.4, 0.5, and 0.6 and concluded that cementitious material with

higher w/c have greater capacity for NO binding and this facilitate oxidation upon exposure to UV light. Photocatalytic efficiency for cement was tested after nitrogen oxides - wet - dry cycling, the gas concentrations was dropped incidentally when UV is switched on and returned quickly to its inlet value when UV is switched off, this indicates a good performance of the photocatalytic reactions after exposure to various circumstances.

(Jayapalan et al. 2015) studied the addition of different types of commercial TiO₂ replaced by 5% cement paste as shown in Table 2.5, as well as TiO₂- coated commercial ceramic tiles was tested for comparison. For T1 type results showed a decrease in the concentrations of NO and NO_x as soon as the UV light turned on, the concentrations of NO and NO_x decreased from 450 to 380ppb and from 450 to 395 ppb, respectively; NO₂ increased to 15 ppb because of the conversion of NO to NO₂. Final concentrations of gases after 5hr of exposure was approximately 305 ppb, 340 ppb, and 35 ppb for NO, NO_x, and NO₂, respectively, which equals to 24.4% decrease in the NO_x concentration. With continued exposure, the rate of the photocatalysis could decrease, and saturation would eventually occur. T3 was observed to be the most photocatalytically active among the TiO₂ samples tested.

Table 2.5 – Specifications of TiO₂ added in 5% to the cement paste (Jayapalan et al. 2015)

	Crystal size, nm	Agglomerate size, μm	Surface area, m²/g	structure
T1	20 to 30	1.5	45 to 55	100% Anatase
T2	15 to 25	1.2	75 to 95	100% Anatase
T3	21	0.58	50 ± 15	80% Anatase 20% Rutile
T4	30	1.5	52	100% Anatase
T5	67 to 75	1 to 2	8 to 12	100% Anatase

2.17 Air pollutants removal by applying TiO₂ as a coating layer

Coating material is a coherent layer formed by applying a single or multiple layer of the material to the substrate. This material may be in three types: powder, liquid or paste, which forms a decorative and protective coating. Coatings can be classified into four categories: (Dubbert et al. 2014)

1- Binders (or film formers): Most of them are based on organic polymers. They ensure the forming of a coherent film during drying - hardening process of the coating.

2- Pigments and extenders: pigments are insoluble coloured particles. Extenders are used when modifications are required to some physical properties.

3- Solvents: they are single liquids or mixture of liquids that dissolve other substances without reacting with them. Conventional formed lacquer contains organics like ethers, esters, or aliphatic hydrocarbons. Organic solvents are usually replaced by water. In most cases dispersion occurs rather than dissolved (dispersion lacquer).

4- Additives with different chemical composition: they are added to coatings in small quantities to modify their properties like weather and UV resistance, surface tension and flow behavior.

Nanostructure coatings and thin films are at the heart of the eco-efficient construction technologies because it may do a lot from a little (Granqvist 2013).

Coatings must be protective barrier against chemical attack, abrasion, in addition to aesthetics aspects. Most of coatings are in the micrometer size. New methods and materials are being investigated to develop nano size coatings that are durable. Experimental techniques are used to evaluate coatings performance. The main parameters should be taken into consideration are: durability under various conditions, friction and abrasion resistance, electrical characteristics, and high temperature resistance. Interface performance between film and substrate material takes an important part in the

durability of the whole system. Mechanical properties for some coating materials and substrate are known, but under mechanical force, magnetic force and hydrothermal force the interface performance is not well known; this leads to complexity of the analytical models. 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).

Another method used for photocatalytic coatings with nanoscale TiO_2 is via chemical vapour deposition CVD. This type of coating is used for various types of substrates. The choice of the manufacturing process depends on the specific application requirements of coatings (Dubbart et al. 2014).

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).

(Ramirez et al. 2010) used a dip coating method for substrates to investigate toluene removal efficiency which reached to 86%, the TiO_2 suspension was prepared by using ethanol in concentration equals to (0.05 g/mL).

(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.

Another method used for coating implemented by (Guo & Poon 2012), they sprayed concrete surface with a nano TiO₂ suspension prepared by dispersing the commercial (P25, Degussa- particle size of 20-50 nm) with methanol, the suspension concentration equals to (25 g/L); all samples were sprayed within 10 minutes after surface preparation; different types of substrates were prepared by using the recycled and reused glass with intermix material. It was concluded that NO photocatalytic removal efficiency is relatively high after 7 days curing, all the TiO₂ sprayed samples displayed higher photocatalytic NO removal activities than the TiO₂ intermixed samples. After 28 days curing, a little reduction in NO removal was detected, the sprayed TiO₂ particles on the surface display a satisfactory weathering resistance; this technique is easy to apply and brings down the cost. NO removal rates for the sprayed samples were about 6.31 and 6.38 mg.h⁻¹.m⁻².

(Hassan et al. 2012) compared removal efficiency for three types of coatings by using PC 105 ultrafine TiO₂ 95% pure anatase. Thin film of 10mm concrete surface with 3% and 5% TiO₂ mixtures, nano TiO₂ powder sprinkled to fresh concrete surface before hardening, and spraying water based TiO₂ on a hard concrete surface. Results obtained appear that removal efficiency for 5% TiO₂ mixture and spraying water based TiO₂ were 26% and 25% respectively. These applications were more effective in reducing nitrogen oxide from air flow containing NO with concentration of 410 ppb. Table 2.6 shows the TiO₂ coatings specifications.

(Faraldos et al. 2016) demonstrated NO removal efficiency for various types of coatings by using dip and spray methods. Coatings employed by using TiO₂ nanoparticles and compounds of SiO₂-TiO₂ sols showed to be very active in reducing NO concentration. Removal efficiency reached to 97% regardless of the number of layers applied or the used deposition method (dip or spray coating). Another type of samples coated with diluted (TiO₂ sols) showed removal more than 92% when the inlet NO concentration is 1.5ppm;

however, using a diluted solution contains TiO_2 of about 0.2% and increasing the inlet NO concentration to 15 ppm less removal was obtained reached to (63–73%). A Conclusion was made that even diluted or thin layers were sufficient to obtain self-cleaning performance for the building. Using high concentration of TiO_2 sols or multiple coating layers results in reducing the photocatalytic efficiency because of particles agglomerations that will obscure the bottom layer from illumination. The usual values of NO concentration in ambient atmosphere is about 0.01 ppm (10 ppb) which is much lower than the assumed values during the laboratory tests, therefore the diluted TiO_2 coatings will be sufficient to reduce NO concentration from air.

Table 2.6 - Details for coating methods used with concrete (Hassan et al. 2012)

Applied method	Specimen name	Surface area (g/m^2)	TiO_2 type
Reference	Reference	0	-
Concrete surface mixture	3% TiO_2	132	Anatase
	5% TiO_2	220	Anatase
Sprinkled on fresh concrete	3% Sp	132	Anatase
	5% Sp	220	Anatase
sprayed	PT	215	Anatase

Time scale for dip coating method is slow, also this method has a mechanical and environmental stability, while spray coating method is rapid, has moderate stability, fast and easy reparability (Liu et al. 2016).

The classic time scale for slow, moderate, and rapid techniques are 1 h or more, 1 to 5 minutes, and less than 30 second, respectively (Liu et al. 2016).

2.18 Factors affecting removal efficiency for NO and Toluene gases

The activity of the photocatalytic building materials for the degradation of NO_x and VOC pollutants is affected by various parameters.

There is a general coincidence about the effect of such environmental factors like illumination, speed of air flow, initial pollutant concentration (Martinez et al. 2011) and (Zhao & Yang 2003); Nevertheless there are various opinions about the effect of humidity on the photocatalytic efficiency (Martinez et al. 2011). The most important factors affecting on the removal efficiency are:

1- Light intensity: Many researchers studied the influence of light intensity on the photocatalyst oxidation process. Results indicated the functional dependence of the oxidation rate on UV-light intensity, photochemical reaction enhanced with increasing illumination because of increasing the number of the generated electrons (Zhao & Yang 2003) and (Sanabria 2011). Several authors pointed out that above a certain value of light intensity, the photocatalytic efficiency becomes independent of it (Sanabria 2011).

2- Air flow rate: Under a certain limit the speed of air entering the reactor may also affect the reaction rate. The photo-oxidation reaction is affected by mass transfer at low flow rate, but such effect will diminish as flow rate becomes larger (Zhao & Yang 2003).

The NO_x conversion amounts increased when the flow rate volume decreased because of the extended time required for the reaction of the pollutants. The conversion rate yields to 100% when the flow rate decreased to zero thus the apparatus become a batch reactor (Sanabria 2011).

(Folli et al. 2012) stated that at lower flow rate the better removal obtained for NO at 90 min residence time. Increasing flow rate reduce conversion rate. Generally mortars containing nano-TiO₂ performs better than micro-TiO₂ in the removal with different flow rates.

3- Initial concentration: reaction rates varies according to the inlet pollutants concentrations (Zhao & Yang 2003).

(Sanabria 2011) stated that better removal rates are obtained for nitrogen oxides when initial concentrations are increased.

Also many researches on organic compounds pollutants demonstrated that increasing inlet pollutant concentration lead to increase the reaction rate. Reaction rate can be determined by measuring the amounts of the adsorbed contaminants through the substrate surface (Zhao & Yang 2003) and (Chen 2010).

(Chen 2010) gave a general description for the pollutants concentrations that is reaction rates increased with increasing pollutants concentration until it reaches a certain limit the photocatalytic begin to loss its activity.

4- Relative humidity: Its effects seems to be dependent on both experiment conditions and photocatalytic material (Martinez et al. 2011).

The reaction efficiency depends on the active locations in the photocatalytic-concrete surface. Different behavior of NO and toluene was described on the same substrate matrix. The acidic feature for the NO_x gas increase its adsorption and attraction by the alkaline hydrated cement paste radicals (HO_x) (Chen et al. 2011).

(Lee 2012) illustrated the ability of NO_x binding with cementitious material; NO₂ had greater potential to be bound than NO. NO_x bound in cement paste slightly higher for wet samples than dry samples, pore solution takes part in binding amounts of NO and NO₂ through absorption but these amounts were negligible compared to the gas bound on hardened cement paste.

(Bayar 2013) stated that in case of zero relative humidity the oxygen from air and the substrate water content will be the responsible parameters for the oxidation process; increasing air humidity allows hydroxyl radicals for NO oxidation. The photocatalytic efficiency is improved by increasing water content.

(Devahasdin et al. 2003) indicated that increasing relative humidity (RH) from (0-50%) cause an increase in NO oxidation rate, when RH is more than 50% NO conversion becomes constant. (Yu & Brouwers 2009) stated that NO_x conversion increases by increasing relative humidity in the range of RH (10-70%).(Hüsken et al. 2009), (Hunger et al. 2010) and (de Melo & Trichês 2012) concluded that the photocatalytic activity decreases linearly as relative humidity increased.

(Sanabria 2011) stated that varying relative humidity between 40 to 70% did not induce any significant variation on the NO degradation rate.

(Martinez et al. 2011) reported that the relation between humidity and inlet NO concentration is not clear. No significant effect of the humidity was observed when the initial NO concentrations were 400 and 1000 ppb. When the NO concentrations increased to 2000 ppb and humidity decreased, a significant decrease in the degradation rate was observed. The effect of the substrate material and humidity was also studied; the photocatalytic efficiency could be developed by using substrates with high adsorption capacities. Small amounts of NO₂ generated because of the adsorption ability of the mortar substrates, while in glass substrate high amounts of NO₂ were generated which cause decreasing in NO_x removal efficiency. The lower adsorption capacity for the glass substrate leads to increase competition between humidity and pollutant gas on the active substrate sites. The activity for both substrates is decreased by increasing the initial pollutant concentration.

Regarding toluene, the adsorption capacity by the cementitious material may possibly be low due to the bounded water molecules in the hydration products which restrain the reaction with the active radicals. Mixing nano TiO₂ with the cementitious materials may results to different photocatalytic efficiency according to the type of the gaseou pollutant (Chen et al. 2011).

The w/c ratio should be carefully selected because it affects the penetration of pollutants, the availability of the hydroxyl groups created by the dissociative

chemisorption of water (Zhao & Yang 2003), and the photocatalytic activity (nature and number of active sites). (Zhao & Yang 2003) found that the photochemical degradation of some chemical compounds like toluene and formaldehyde was seriously delayed because of the lack of water vapour in the matrix pores, although excessive water cause decreasing in the reaction rate due to occupation for the active sites by water.

Furthermore, another studies noted that the photocatalytic efficiency for the degradation of VOCs depended on both air humidity and initial pollutant concentration (Martinez et al. 2011) .

(Demeestere et al. 2008) studied the removal of toluene from air; they reported that high relative humidity and high inlet concentration led to low toluene removal performance, however better performance occurred at increased residence time.

(Chen et al. 2011) studied TiO₂ modified concrete surface layer, they confirmed that photocatalytic degradation of toluene was not noticed, although NO removed effectively in the same process. There is no inhibition effect noticed between NO and toluene when different toluene concentrations were used.

2.19 Self- cleaning performance

Self-cleaning ability for the surface can be defined as the effect of both deposits degradation and surface superhydrophilicity which may happen at the same time. Both mechanisms are important and have a synergetic effect in the photocatalytic reaction (Chen & Poon 2009).

To enhance the aesthetic appearance and the self-cleaning performance for the buildings using photocatalysis, degradation for the stains and dirt with different types of illuminations was tested. (Chen et al. 2011) stated that UV and strong halogen light irradiation show fast discolorations for the applied rhodamine B dye on the mortar surface than weak illuminations. When the

added dose of TiO_2 was increased from 2% to 5% no difference in the discoloration was noticed, the process is controlled by photon absorption rather than surface chemistry kinetics.

(Folli et al. 2012) stated that using micro TiO_2 performs better or at least the same as nano TiO_2 because of the pores formed by particles agglomerations. When micro TiO_2 added to the cement paste, particles agglomerations will be available for the adsorption and reaction due to the high dispersion for the formed agglomerates as described previously in Fig. (2.11)

(Faraldos et al. 2016) reported that the porosity and pore pH/humidity in concrete pores could cause hydrolysis and improve the discolouration ability of the cementitious substrate, particularly in the presence of nano TiO_2 as a photocatalyst.

2.20 Photocatalytic sustainability

TiO_2 could be used safely in urban areas because of its high oxidation ability to convert NO_x to harmless nitrates (Dalton et al. 2002). It is considered a passive technology work by using UV light only; also it could be regenerated by washing with rainwater without be consumed, so material feeding is not always needed (Sanabria 2011).

The use of nano sized binders with cement mixtures may contribute in reducing CO_2 emissions produced during amending cement compositions by reducing clinker temperature (Lee 2012).

To obtain effective improvement for air quality this technology should be used to large scale area, taking into consideration applying this technology economically with less cost in return to pollutants removal. Mixing TiO_2 with cement mixtures increases the applied cost in addition to the adverse effect to the mechanical properties when the photocatalytic dosage added more than a certain limit, therefore; cost for the applied dose must be studied extensively (Faraldos et al. 2016).

The cost of the commercial photocatalytic cement produced by Italcement Group ranged 8-10 times the cost of the ordinary cement (Janus & Zajac 2016). The average cost for the nano TiO₂ was approximately 9.07\$ per lb (24.99\$/kg) in 2010 (Burton 2011). This cost decreased to 20\$ per kg in 2011 (Hassan et al. 2012) and around 15\$ per kg in 2013, if the cost of a concrete surface with 254mm thickness assumed to be 250\$ per m³ the added cost for the use of TiO₂ will be 4.68\$ per m³ (Jayapalan 2013). It is expected that the manufacturing cost for TiO₂ will significantly be reduced if the photoactive construction industry with better removal efficiency is achieved (Hassan et al. 2012) and (Jayapalan 2013).

2.21 Reactor specifications

The air purifying properties of products containing photocatalytic materials can be evaluated by different test methods. One of the most common methods for testing the performance of these products is based on the degradation of NO and/or NO₂ under defined conditions in a plug flow reactor (Sanabria 2011).

Experimental and modeling methods have been conducted to understand the mechanisms of photocatalytic oxidation reaction as well as to optimize the reactor design. The types of reactors adopted extensively include annular reactors, monolith reactors, and fluidized-bed reactors (Zhao & Yang 2003).

The controlled weather conditions during the laboratory test give an overestimation of the photocatalytic capacity for purification, this may be because of the increasing the contact between the photoactive surface and pollutant (Martinez et al. 2011).

Methods for test are conducted according to national and international standards. Although these standards aim is to provide constant and repeatable measurements, their boundary conditions differ from one to other (Sanabria 2011). A comparison of the reactor specifications used by international

standards ISO 22197-1 (2007), Japanese standards JIS R 1701-1 (2004) and the Italian standards UNI 11247 (2010) are shown in Table 2.7.

Table 2.7- Comparison of boundary conditions and parameters used for testing NO_x conversion for the three standards (Jayapalan et al. 2015)

		ISO 22197-1	JIS R 1701-1	UNI 11247
Testing parameters	Test gas	NO	NO	NO and NO ₂
	Test gas concentration, ppb	1000 ppb	1000 ppb	400 ppb NO + 150 ppb NO ₂
	Gas flow rate, L/min	3	3	3
	Test duration, hours	5	5	1
	UV intensity, W/m ²	10	10	20
Sample parameters	Sample area, cm ²	49.25	49.25	65
	Sample curing	-	-	-
	Surface preparation	-	-	-

JIS R 1701-1 is considered one of earliest methods which were developed by the Japanese Standards Association in 2004; it was specifically addressed for ceramics. In this test procedure a continuous reactant gas passes over the sample surface (dynamic method) and the gas concentration is continuously measured by using chemiluminescent NO_x analyzer. Samples dimensions are 49.5 ± 0.5 mm wide and 99.5 ± 0.5 mm long. The gas is passing through a gap over the sample surface of 5mm thickness. A UV light source is used with 300 to 400 nm wavelength and 10W/m^2 irradiance. NO gas with 1ppm concentration is used at flow rate of 3.0 L/min and relative humidity 50%. The samples are stabilized under the reactant gas before UV is turned on, after gas stabilization samples exposed to the UV light source for 5 hours (Jayapalan et al. 2015).

ISO 22197-1 standards was developed in 2007 by ISO based on the JIS R 701- 1 standard and follows the same procedure given in the Japanese standards (Jayapalan et al. 2015).

UNI 11247 was developed in 2010 by the Italian standards organization UNI. This test is similar to the JIS R 1701-1 and ISO 22197-1 tests, and is also a dynamic method with a continuous flow of NO_x gases. The concentration of gases is different from the previous tests, and uses 0.55 ppm of total NO_x gas,

which is a mixture of 0.15 ppm of NO₂ and 0.40 ppm of NO gas. The irradiance is doubled from the ISO and JIS tests to 20 W/m², and the samples are tested for 1 hour (Jayapalan et al. 2015) in a round vessel of 3L capacity and the gap which the gas is passing through is 1mm thickness (Sanabria 2011). The other parameters used are similar the ISO and JIS tests described previously. The use of a combination of NO and NO₂ in the UNI 11247 test could simulate real-world conditions, but during photocatalysis, there could be a conversion of NO to NO₂ and vice versa. These reactions and conversions cannot be studied accurately using the UNI 11247 test (Jayapalan et al. 2015).

It's important to know that this reactor can be used to measure the removal efficiency for different types of pollutants. Static test is also used by some researchers in which a certain amount of the reactant gas is recirculates inside a close reaction chamber; concentration of gas is measured before and after the experiment. This method do not represent a real world condition where gas would move over the surfaces because of the air circulation (Jayapalan et al. 2015).

2.22 Reaction efficiency calculations

Various experimentally measured or derived parameters can be used to characterize the activity of photocatalytic materials. For example, the initial decrease in the concentration of NO_x or the maximum difference between inlet and outlet concentration can be used as a measure of photocatalytic activity (Jayapalan et al. 2015).

The values of the NO removed, NO₂ generated, and NO_x removed can be calculated by measuring the area under the curve according to the following equations (Mills & Elouali 2015):

$$NO\ removed(\%) = \int_{t_0}^t \frac{[NO]_{in} - [NO]_{exit}}{[NO]_{in}} dt \times 100\% \quad (2.17)$$

$$NO_2 \text{ generated } (\%) = \int_{t_0}^t \frac{[NO_2]_{exit}}{[NO]_{in}} dt \times 100\% \quad (2.18)$$

$$NO_x \text{ removed } (\%) = \int_{t_0}^t \frac{[NO]_{in} - [NO]_{exit} - [NO_2]_{exit}}{[NO]_{in}} dt \times 100\% \quad (2.19)$$

Where $[NO]_{in}$ and $[NO]_{exit}$ are the levels of NO gas stream measured before and during UV irradiation. The stated equations can be used for different types of substrates.

2.23 Concluding remarks

According to the reviewed researches concerning the use of the photocatalytic with building materials, the following points can be considered the most influenceable parameters on the photoactive concrete:

- 1- Different particles size of TiO_2 (micro and nano) replacements with cement paste.
- 2- Different percentages of TiO_2 replacements with cement in the concrete mixtures.
- 3- Various weather conditions like humidity, air flow and light intensity may affect the pollutants removal efficiency.
- 4- Photocatalytic has the ability of reducing the most surrounding gaseous pollutants like NO_x and volatile organic compounds which have harmful environmental effects.
- 5- There are many practical methods that can be used for applying TiO_2 with cementitious materials or even with previously constructed buildings, like spray and other coating methods or forming a thin layer of the TiO_2 - cement mixture.

6- Applying TiO_2 with building material gives the surface a hydrophilic performance which helps in self- cleaning capability for the buildings and the aesthetic appearance.

Because of the stated points, this thesis is concerned to study the most argument points of the previous researches by conducting methods for applying TiO_2 with cementitious materials. The pollutants concentrations were measured by using a new type of reactor, taking into consideration the parameters that may affect the pollutants removal efficiency.

CHAPTER THREE

EXPERIMENTAL PROGRAM

Chapter Three

Experimental Program

3.1 General

To achieve the aim of this work; experimental program is designed to assess the photocatalytic efficiency (PE) by preparing different types of substrates and comparing their performance with each other. Various percentages and sizes of commercially available photocatalytic TiO₂ particles are used. The main experimental work steps are as follows:

- 1) Two types of substrates were prepared; cement paste substrates mixed with TiO₂ particles and mortar substrates coated with TiO₂ aqueous solution.
- 2) Mechanical properties were tested for the modified cement mixtures; this includes setting time and compressive strength.
- 3) Reactor was designed to investigate the gaseous pollutants removal efficiency.
- 4) To evaluate the effect of humidity on the removal efficiency; samples were tested at three conditions, normal condition (NC), saturated condition (SC) and oven dry condition (DC).
- 5) Self- cleaning performance for all substrates have been tested to evaluate the photocatalytic efficiency for the different types of substrates; this test was done by applying methylene blue drop on the substrates surface, the contact angles for the substrates were also measured.

Experimental procedure details and the material used specifications are also illustrated. Flow chart for the experimental program is shown in Fig. (3.1).

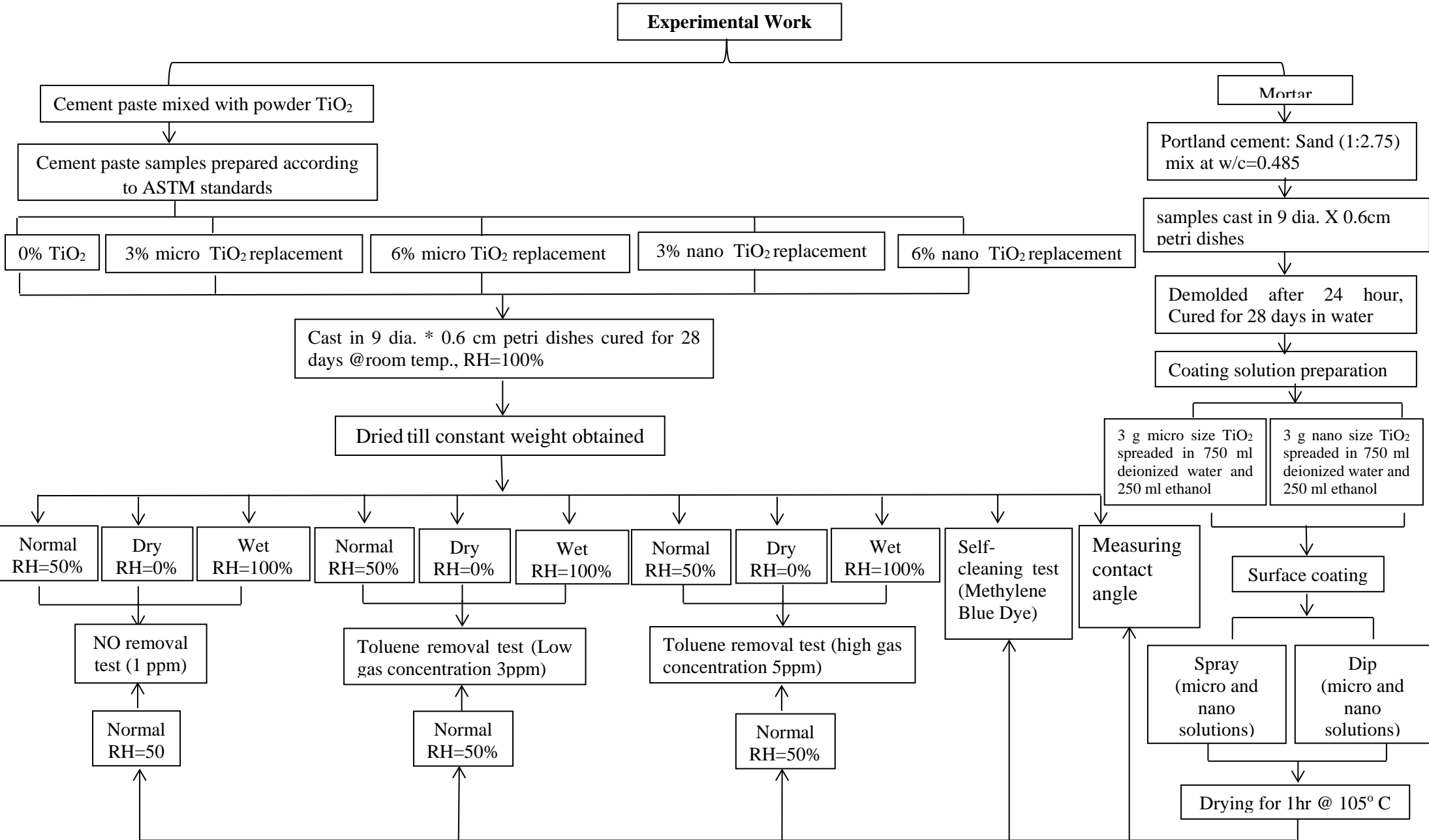


Figure 3.1- Experimental Program Flow Chart

3.2 Materials

3.2.1 Cement

The type of cement used for the preparation of substrates is the ordinary Portland cement (OPC) type I, called Karasta. The chemical composition for the cement complies with ASTM C150-15 and Iraqi specification No. 5/1984 (Iraqi Standard Specification 1984) as shown in Table 3.1.

Table 3.1- Chemical composition of the ordinary Portland cement *

Oxides	OPC % by weight	Limits of Iraqi specifications No.5/1984
SiO ₂	21.93	-
Al ₂ O ₃	4.98	-
CaO	66.11	-
Fe ₂ O ₃	3.10	-
MgO	2.00	< 5
SO ₃	2.25	< 2.8
Loss on ignition	2.39	< 4
Insoluble material	1.29	< 1.5
Lime saturation factor	0.93	0.66-1.02

* Tests results were adopted in the lab of Central Organization for Standardization and Quality Control

3.2.2 Fine aggregate

Fine aggregate used in this work is the local natural sand from Al-Ekhaider. Sand was graded according to ASTM C778 (ASTM C778 2002) by using sets of sieves shown in Table 3.2, standard sand gained by using the retained on sieve 0.6 mm. The sieve analysis with the physical and chemical properties of sand are shown in Tables 3.2 and 3.3 respectively, which were within the Iraqi limits No. 45/1984 (Iraqi Standard Specification , 1984)

Table 3.2- Grades of sieves used for fine aggregate

Sieve size (mm)	Passing by weight %	Iraqi specification (No.45/1984)
9.5	100	100
4.75	99.5	90-100
2.36	93.0	85-100
1.18	84.1	75-100
0.6	72.9	60-79

Table 3.3- Physical and chemical properties for the used sand*

Physical and chemical properties	Test results	Iraqi specification (No.45/1984)
Specific gravity	2.6	-
Bulk Density(kg/m ³)	1729	-
Absorption%	2	-
Sulfate content%	0.343	Less than 0.5%

* Tested at the National Center for Construction Lab. and Researches

3.2.3 Titanium dioxide

Two grain sizes of commercial titanium dioxide powder were used: the micro-size (mT) from Tianjin Zhi Yuan Reagent Co., Ltd.-Chinese market, and the nano-size (nT) PC105 from Cristal Active Millennium SAS- France. Table 3.4 represents specifications for the titanium dioxide.

Table 3.4- Titanium dioxide specifications

Photocatalytic Type	Particle Size (nm)	Specific Surface Area (m ² /g)
mT- Anatase	150-200*	6.9*
nT- Anatase	20±5**	85.6**

*Tested at the Ministry of Science and Technology

** According to the manufacturer certification

3.2.4 Deionized water

Deionized water with conductivity equals to zero was used for the mixing of the PC modified mixture samples; also it was used for the preparation of the titanium dioxide aqueous solution.

3.2.5 Pollutant gases

The pollutant gases were supplied from Mesa Specialty Gases and Equipment, California. The concentrations were 400 ppm for both NO and toluene gases, balanced with nitrogen according to the manufacturer certification, Fig. (3.2). Air cylinder (80% N₂ and 20% O₂) was used to dilute pollutant gases, which was supplied by Gulf Cryo Company for Filling and Manufacturing Industrial Gases L.T.D, Baghdad.



Figure 3.2- 116 Liters Nitric Oxide cylinder (left) and 37 Liters Toluene cylinder (right)

3.3 Substrates preparation

Two types of substrates have been prepared to apply TiO₂ with; the first is by mixing titanium dioxide powders with cement paste, the second is by coating substrates (mortar) surface with titanium dioxide aqueous solution.

3.3.1 Cement paste preparation

Three sets of cement paste were prepared: one for the commercial micro-TiO₂, one for the commercial nano-TiO₂ and one as a reference sample. Two levels of TiO₂ replacements were used for each commercial TiO₂ product of 3% and 6%; a constant w/c ratio of 0.5 was used for all samples, Table 3.5 shows summary for the cement paste sets.

Each TiO₂ powder was initially dispersed in deionised water and mixed for 2 minutes by 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 to disperse the micro- or nano-TiO₂ particles. The pastes were casted 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, Fig. (3.3) shows cement paste substrates.

Table 3.5 – Cement paste sets

Specimen Type	TiO ₂ replacement percentage from cement weight	w/c
Set I- Reference	0	0.5
Set II- mT	3%	0.5
	6%	
Set III- nT	3%	0.5
	6%	



Figure 3.3 - Cement paste substrates

3.3.2 Mortar preparation

Concrete substrates were prepared according to ASTM C305 standards (ASTM C305 2011). Cement to sand ratio was 1:2.75 and w/c of 0.484. Flow test was made to ensure workability for the mixture (ASTM:C1437-13 2013) and found to be approximately equals to 110% which was compatible with ASTM standards, Fig. (3.4).

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 like cement paste substrates, Fig. (3.5) shows mortar substrates.



Figure 3.4 - Flow test



Figure 3.5 - Mortar substrates

3.3.3 Aqueous solution preparation:

Mortar samples have been coated by using two methods (spray and dip coating). Two types of titanium powder were used nano and micro, aqueous solutions for both types prepared on the same concentration. A suspension was prepared by spreading 3g of TiO_2 powder in 250 ml ethanol and 750ml deionized water stirred for (30 min) then ultrasonicated for 1 hour to obtain

solution homogeneity (Ramirez et al. 2010), Fig (3.6) shows the ultrasonic water bath, Table 3.6 illustrates coating methods schedule.

In spray method, substrates were sprayed for 1 minute and others for 5 minutes by using spray pyrolysis equipment illustrated in Fig. 3.7 (a).

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. 3.7 (b). Finally, for both methods samples were oven-dried at 105°C for 1 hour, and kept sealed till test. Fig. (3.8) shows mortar substrates after coating.



Figure 3.6- Ultrasonic water bath

Table 3.6- Coating method schedule

Coating type	Coating duration	Aqueous solution concentration	
mT spray	1 min	3g micro TiO ₂	750 ml deionized water+ 250 ml ethanol
mT spray	5 min		
nT spray	1 min	3g nano TiO ₂	750 ml deionized water+ 250 ml ethanol
nT spray	5 min		
mT dip	10 min dip 3 min drip	3g micro TiO ₂	750 ml deionized water+ 250 ml ethanol
nT dip	10 min dip 3 min drip	3g nano TiO ₂	750 ml deionized water+ 250 ml ethanol

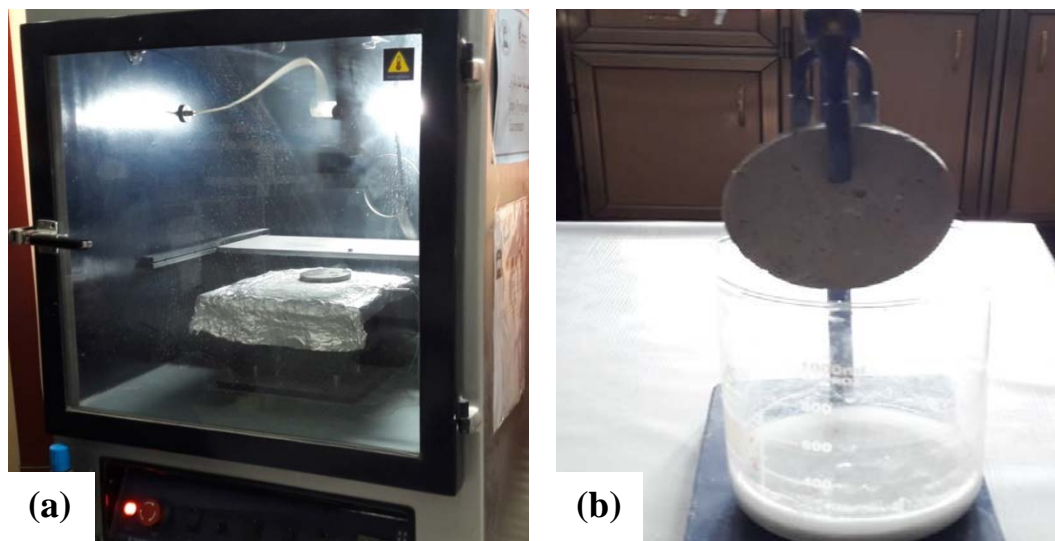


Figure 3.7- Coating micro and nano TiO_2 aqueous solutions by: (a) Spray pyrolysis equipment; (b) Dipping method

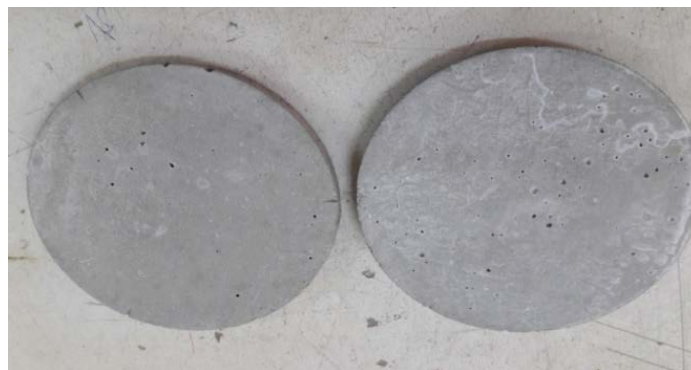


Figure 3.8- Samples after spraying and drying (left) and after dipping and drying (right)

3.4 Substrates distribution

The prepared substrates/ specimens were distributed according to the required tests to be conducted. Table 3.7 summarizes the required samples for each test.

Table 3.7- Tests and number of samples required

Substrate type	Setting time	Compressive strength	NO removal	Toluene removal	Self -cleaning		Adsorption and voids ratio
					Dye test	Contact angle	
Reference	2 vicate cone	3 cubs	3 discs	3 discs	3 discs	2 discs	3 discs
3% mT	2 vicate cone	3 cubs	6 discs	6 discs	3 discs	2 discs	3 discs
6% mT	2 vicate cone	3 cubs	6 discs	6 discs	3 discs	2 discs	3 discs
3% nT	2 vicate cone	3 cubs	6 discs	6 discs	3 discs	2 discs	3 discs
6% nT	2 vicate cone	3 cubs	6 discs	6 discs	3 discs	2 discs	3 discs
Reference	-	-	2 disc	2 disc	3 discs	2 discs	3 discs
1 min-mT spray	-	-	2 discs	2 discs	3 discs	2 discs	3 discs
5 min- mT	-	-	2 discs	2 discs	3 discs	2 discs	3 discs
spray	-	-	2 discs	2 discs	3 discs	2 discs	3 discs
1 min- nT spray	-	-	2 discs	2 discs	3 discs	2 discs	3 discs
5 min- nT spray	-	-	2 discs	2 discs	3 discs	2 discs	3 discs
mT dip	-	-	2 discs	2 discs	3 discs	2 discs	3 discs
nT dip							

3.5 Setting time test

Setting time has been tested for the PC modified mixtures in order to study the effect of replacing cement with the micro and nano titanium dioxide with different percents and compared them with the reference samples. The same w/c =0.5 used for all mixtures. The test has been conducted by using vicat apparatus shown in Fig.(3.9) according to the ASTM standards (ASTM C191 2008).



Figure 3.9 - Setting time test by using vicat apparatus

3.6 Compressive strength measurement

Compressive strength has been conducted in order to study the effect of adding micro and nano material with different presents to the cement paste mixtures. Cubs of (5cm x5cm) were casted and cured for 7 days and 28 days; the average of three cubs have been considered to study the effect of the adding percent and compared with reference cubs as shown in Fig. (3.10). Fig. (3.11) represents the compressive strength apparatus.

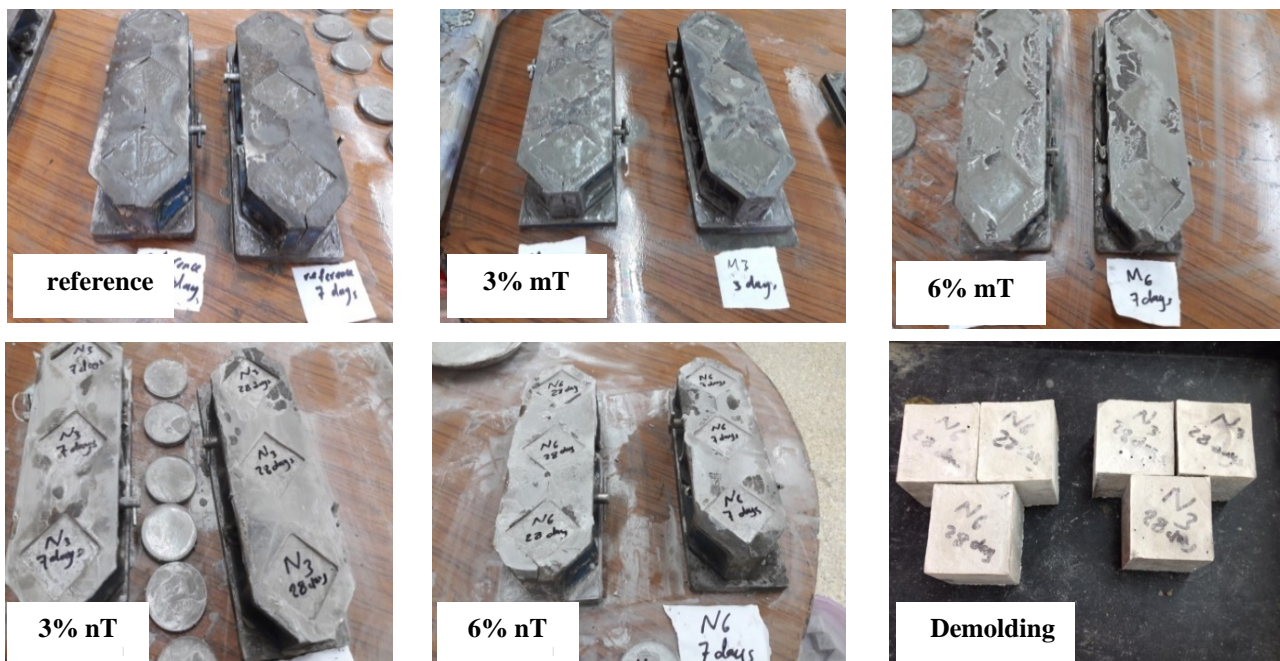


Figure 3.10- PC modified mixtures cubs casting with micro and nano TiO_2 percentages



Figure 3.11- Compressive strength apparatus

3.7 Substrates conditioning

Most cementitious finishing layers are frequently exposed to various atmospheric variables that mainly depend on the geographical zone or the season. In Middle East countries, such as Iraq, Jordan, Iran and Saudi Arabia, summer temperatures can reach 50° C, where even the shaded areas are warm and dry; these conditions continue for several months during the year. Consequently, photocatalytic cementitious materials may show different performances because of the notably low air humidities or high temperatures during the life cycle in such hot regions.

To assess the atmosphere effects on the photocatalytic efficiency of TiO₂-modified PC composites, the prepared specimens were conditioned before the photocatalytic efficiency (PE) test as follows:

- Normal conditions (NC): place the test specimens for four days in an ambient temperature of 23±2 °C and 50% relative humidity (RH) so

that all faces are sufficiently aerated. For this purpose, the specimens were tested in March.

- Saturated conditions (SC): immerse the test specimens in water for 48 h at 20 ± 2 °C. For this purpose, the specimens were tested in February. The specimens were tested upon removal from water and in a saturated surface dry condition (SSD).
- Oven-drying conditions (DC): dry out the test specimen in an oven at 102 °C until the difference between two consecutive weighings does not exceed 0.1% of the mass at 2 h intervals. Then, test the specimens in an ambient temperature of 40 ± 2 °C. For this purpose, the specimens were tested in July.

3.8 Reactor setup

The design for the NO_x photodegradation chamber and accessory components were according to ISO 22197-1:2007 standard (ISO 22197-1 2007). The inlet nitric oxide concentration and the diluted gas stream were modified to satisfy the research purposes and test requirements. The photodegradation chamber had a rectangular shape with dimensions of 30 cm x10 cm and was made of non-absorbing plastic, cross section for the reaction chamber is shown in Fig. (3.12).

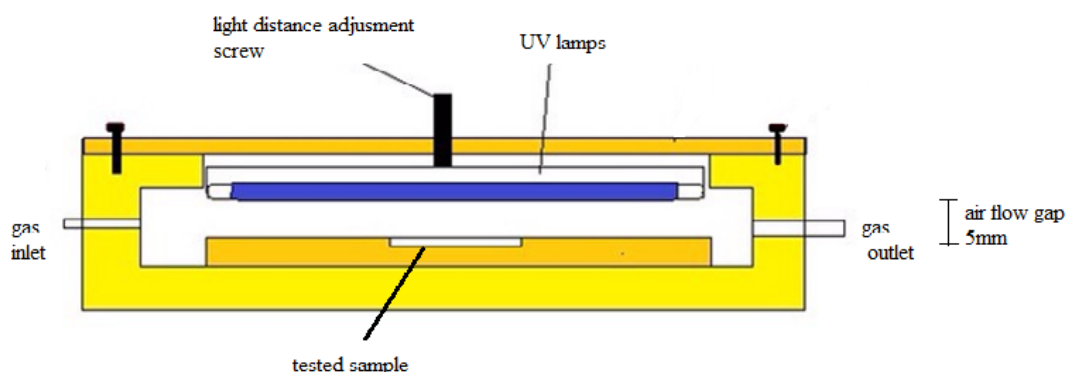


Figure 3.12- A cross-sectional view of the photoreaction chamber

The system was completely sealed to prevent inadvertent leakage of the NO gas/air mixture. The gas detector device was from RAE Systems by Honeywell-USA, San Jose. The detection limits were 0-250 ppm for nitric oxide, 0-20 ppm for NO₂ and 1-1000 ppm for VOCs. This device is simpler than the gas analyser used elsewhere (Sanabria 2011) and (Folli et al. 2012) and is intended to facilitate the experimental setup with lower costs but sufficient accuracy as shown in Fig. (3.13). The used laboratory reactor and schematic diagram of the experimental setup are represented in Figs. (3.14) and (3.15), respectively.

All tests were performed at room temperature with applying a continuous air flow at approximately 1.6 ± 0.2 l/min. Two 6-W UV lamps were used with an intensity of 19 W/m^2 per lamp and a wavelength range of 300-400 nm. The gas detector must be calibrated before each test. A piece of PC sample was placed inside the chamber, which was then tightly closed. Continuous air flow was ejected inside the reactor for approximately 1 h to clean the reactor, particularly the VOCs, with the UV lamps turned off to maintain dark conditions. The inlet for gas pollutant was opened and calibrated till the desired concentration (1 ppm for the NO test); for the toluene removal test, two concentrations were selected (3 ppm and 5 ppm). For both tests (NO and toluene removal) the humidity of the reactor was calibrated through control valves by using a humidifier to obtain the desired RH. In all test conditions, a waiting period of 25 min was maintained before the UV source was turned on to ensure chamber saturation and reading stabilisation. Upon starting, the reaction continued for approximately 62 ± 2 min. Then, UV was turned off, the pollutant gas valve was closed, and only air flow was ejected into the chamber.



Figure 3.13- Gas detector

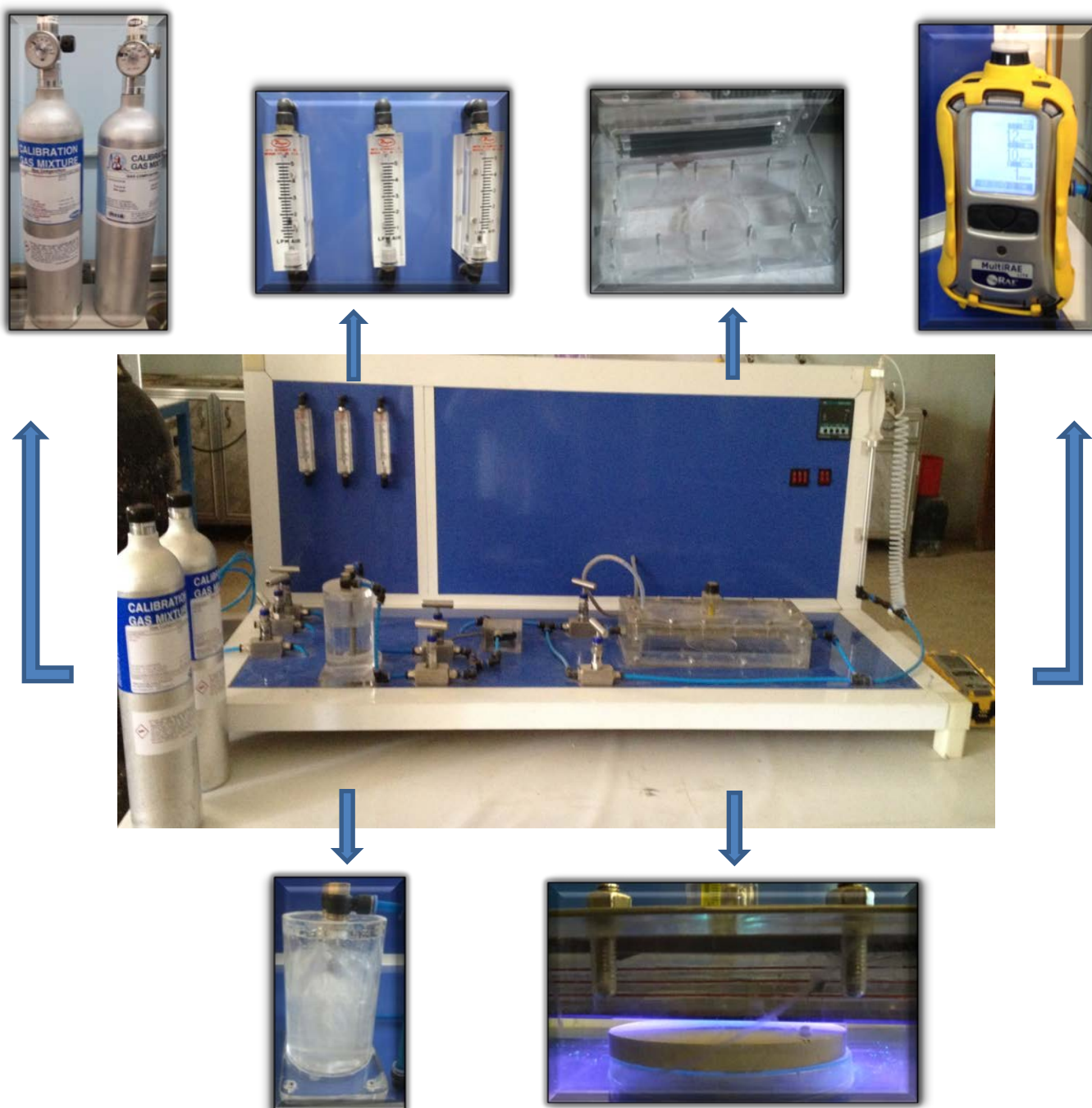


Figure 3.14- Lab. photocatalytic reactor details

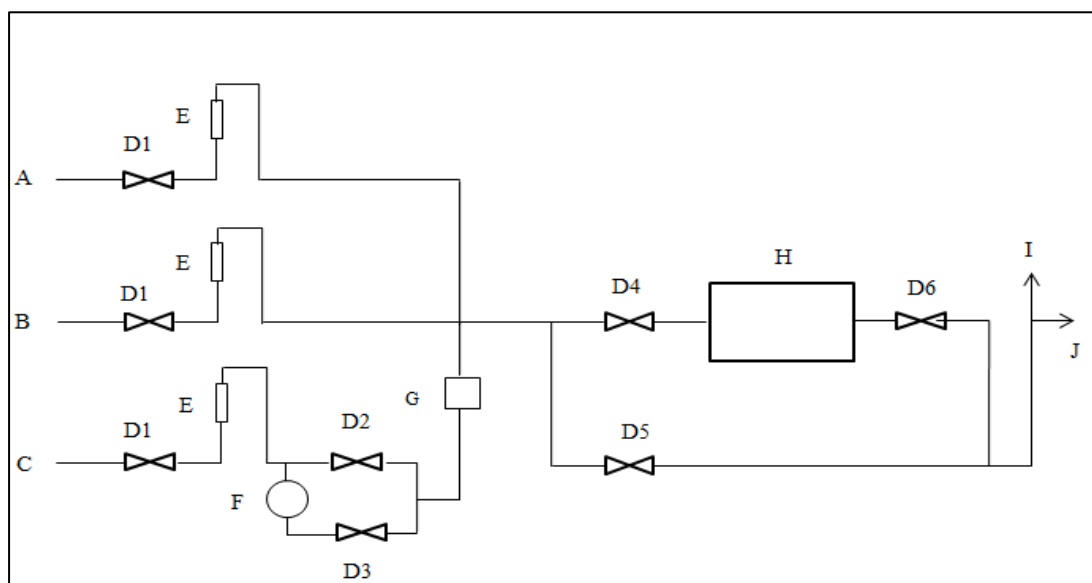


Figure 3.15- Reactor schematic diagram (A,B: pollutant gases entrances; C: calibrating air gas entrance; D (1,2,3,4,5,6): control valves; E: flow meter; F: humidifier; G: temperature and humidity sensor; H: reaction chamber; I: gas sensor; J: vent)

3.9 Self- cleaning test procedure

Self-cleaning performance can be observed by two major tests: dye degradation and contact angle measurement.

3.9.1 Dye degradation test

A surface observation to assess the photocatalytic capability for degradation was conducted by depositing a drop of methylene blue dye solution onto the surface of the PC samples (dye aqueous solution was prepared in a concentration of 1 g/L (Folli et al. 2012)). Samples were exposed to a halogen lamp of 2000 W (21000 Lux). The disappearance of the surface colour and variation of the stain area under illumination were monitored to determine the photocatalytic capacity. Photographs were taken before and after 10 h of exposure to recognise the potential development of stains with time. The degradation of the deposited dye was compared after 10

hours of illumination in order to investigate the ability for the degradation progress.

3.9.2 Contact angle measurement

In order to investigate surface hydrophilicity for the mixed, coated and reference samples, contact angle has been tested by applying a water droplet at different spots on the sample surface and measuring the contact angle at the interfacial zone which the liquid meets the solid surface. Spreading water droplet at the sample surface means that contact angle equals to zero and the surface is classified as a superhydrophilic.

Fig. (3.16) represents (Contact Angle Meter, CAM 110-Tiwan); a water droplet is infused on the surface of the substrate by using (5 μL) micro-injector syringe pointed over the sample surface at a distance of 1cm from the surface. An image of the water droplet is captured by using a high resolution camera which is built in the system, and then analyzed by using image analysis software. Fig. (3.17) shows sample during test.

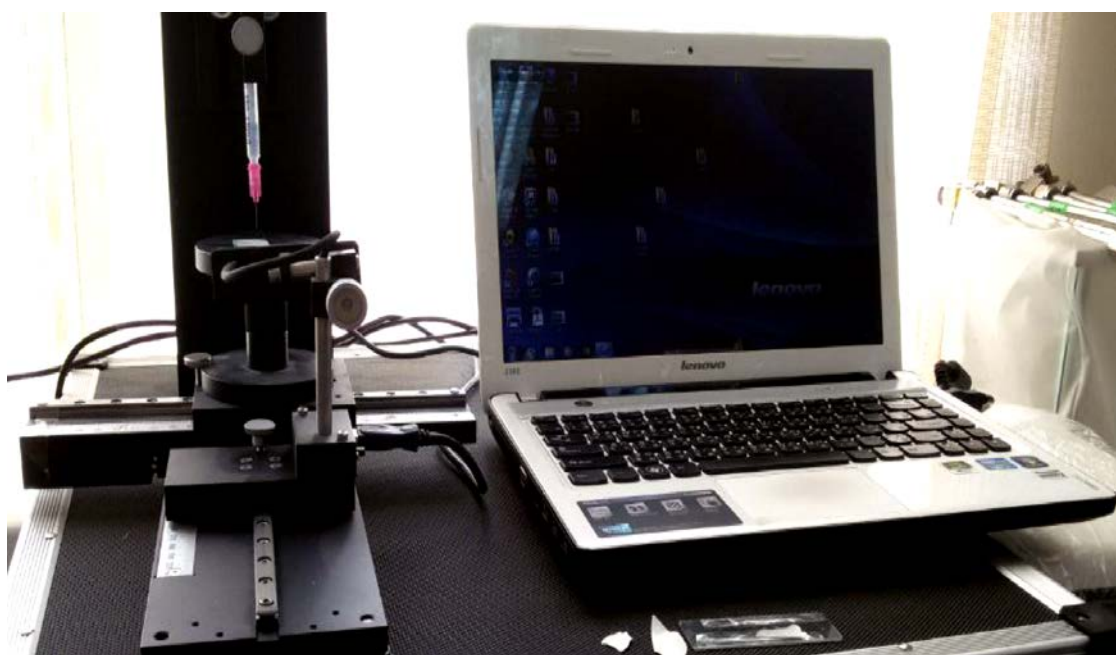


Figure 3.16- Contact angle apparatus

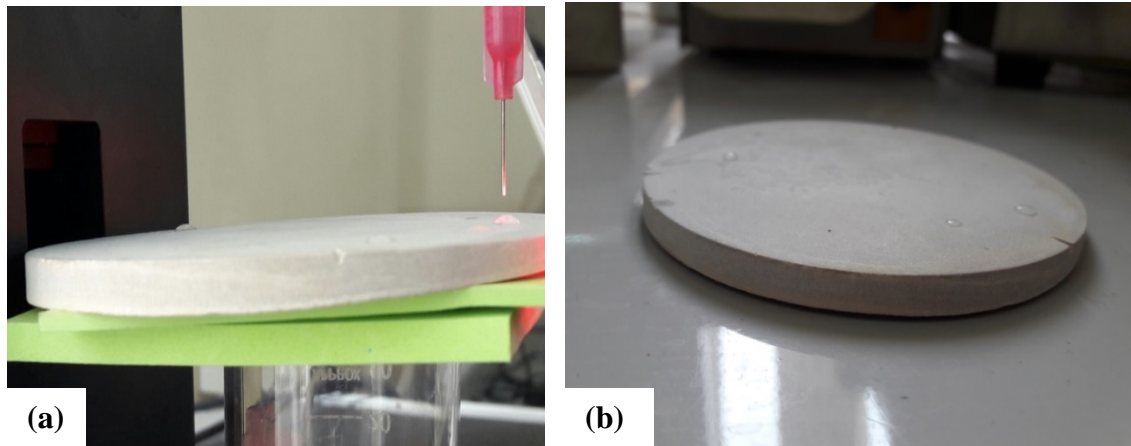


Figure 3.17- substrate during contact angle test :(a) Applying water drop, (b) drop disappearance

3.10 Absorption and voids ratio determination

To study the effect of the replacement of different titanium dioxide percents to the voids ratio inside cementitious substrates and its absorption percent, absorption and voids ratios standard test method have been conducted according to the ASTM standards C 642 – 97 (ASTM C 642 1997).

The average of three samples have been considered for each percent of the micro and nano titanium dioxide replacement and compared with cement paste reference samples, also reference mortar has been tested in order to optimize the coatings absorption ability on the substrates surface.

The standard test procedure is summarized in the following way:

- 1- Dry mass is determined by drying samples for 24 hours at 100°C until constant weight is obtained. This represents weight A.
- 2- After final drying, cooling, samples were immersed for about 48 hours in water. Specimen surface moisture was wiped; this represents surface dry mass B.
- 3- After the above processed steps; samples were put in a suitable vessel, covered with water, and then boiled for about 5 hours. Samples were cooled naturally for about 14 hours. This represents weight C.

4- After immersing and boiling; samples were suspended in water to determine apparent mass under water. This represents mass D.

Absorption and voids ratio can be calculated from the following equations:

$$\text{Absorption \%} = \left[\left(\frac{B-A}{A} \right) \right] * 100 \quad (3.1)$$

$$\text{Voids \%} = \frac{g_2 - g_1}{g_2} * 100 \quad (3.2)$$

g_1 and g_2 represent bulk and apparent densities respectively, which are calculated from the following equations:

$$\text{Bulk density } (g_1) = \left[\frac{A}{C-D} \right] \cdot \rho \quad (3.3)$$

$$\text{Apparent density } (g_2) = \left[\frac{A}{(A-D)} \right] \cdot \rho \quad (3.4)$$

ρ = water density, gm/cm³

CHAPTER FOUR

RESULTS AND DISCUSSION

Chapter Four

Results and Discussion

4.1 General

This chapter is divided into three sections; in the first section, the early age properties for the PC modified mixtures have been studied, these include setting time and compressive strength. In the second and third sections, the photocatalytic efficiency for the cementitious specimens has been evaluated by using two techniques: mixing with TiO₂ or coating with TiO₂. Several variable parameters were discussed including: TiO₂ based supplementary cementitious replacement levels (3%, and 6%), particle size (nano and micro size), and various types of polluted gases.

Furthermore, to investigate the levels of the pollution in the city of Baghdad, a pollution level measurement data collected from the Ministry of Environment were analyzed and evaluated. The evaluated polluted gases include: NO and NMHC (non- methane hydrocarbons) and the generated gases NO₂ and O₃. The data were collected from two stations in Baghdad: Al-Wazeerya and Al- Andalus for the period 2012 to 2014. This phase of study is aimed to evaluate the pollution levels in Baghdad and then to determine the feasibility of using TiO₂ with building materials.

The natural atmospheric effects on the NO_x and VOC removal ability of PC samples are evaluated. Toluene was selected to represent the VOC species because of its abundance in the urban atmosphere (Chen et al. 2011). A comparison was made to examine the effects of nano TiO₂ (nT) on the photocatalytic activity for both techniques implemented to utilize the TiO₂ with cementitious materials. Its effectiveness was also compared to the similar replacement percentages of micro TiO₂ (mT), both of which were 100% anatase.

4.2 Early age properties

4.2.1 Setting time:

The time available for mixing the cement and placing it in position is an initial setting time of cement; while the time taken by cement to gain its entire strength is the final setting time of cement

Setting time results for the TiO₂ modified PC specimens were illustrated in the Table 4.1 and plotted in Fig. (4.1).

Table 4.1- TiO₂ modified PC specimens setting times compared with reference and Iraqi standards

Sample Type	Initial Setting Time (min)	Final Setting Time (min)
Iraqi specifications (No.5/1984)	≥45	≤600
Reference	115	250
3% mT	160	220
6% mT	175	230
3% nT	127	165
6% nT	94	143

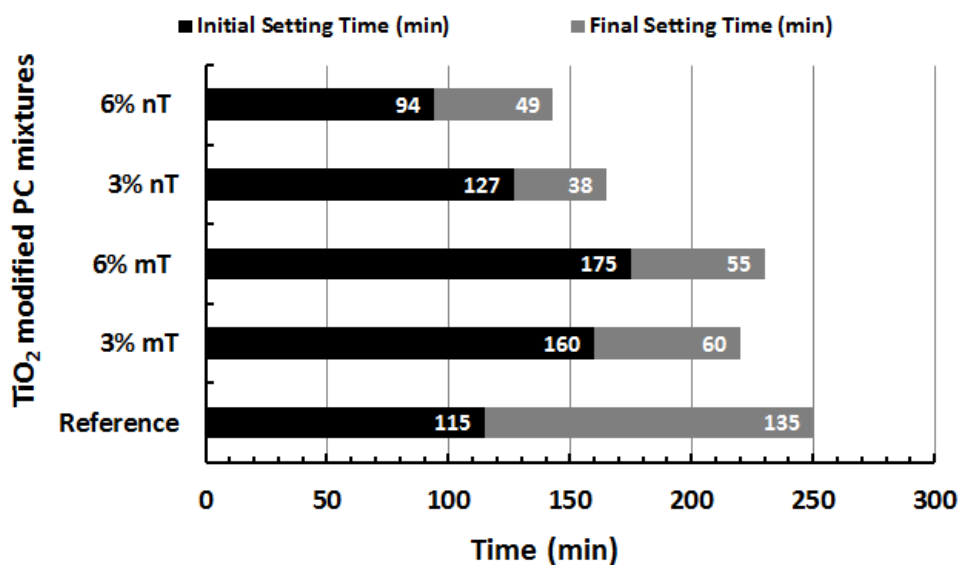


Figure 4.1- Setting times for the PC modified mixtures

For both PC specimens modified whether with micro or nano TiO₂ particles, their initial setting time was longer than the reference. The only exception was the specimens made with 6% nT. Increasing initial setting time could be explained due to the particles size dispersion and surface area where large particles size for the mT and nT agglomerations might not contribute in the formation of nucleation which increases the hydration process time. Increasing nT concentration to 6% leads to reduce initial setting time due to the available nucleation sites which accelerates the hydration process.

Generally, final setting time for all the PC modified mixtures show shorter setting times than reference; this indicates that adding TiO₂ to the cement matrix accelerates the degree of hydration as stated by (Lee 2012). Increasing mT concentration to 6% leads to increase final setting time as compared to the 3% mT due to the large particle size which reduces hydration process. While increasing nT concentration to 6% reduces final setting time due to small particle size with high surface area which affects on the formed microstructure by providing heterogeneous nucleation sites and this is coincide with the conclusion obtained by (Jayapalan 2013) .

4.2.2 Compressive strength

Compressive strength results for the TiO₂ modified PC specimens were illustrated in Fig. (4.2). Cement replacements with 3% mT and 3% nT increased the compressive strength at age of 7 days ,the results were almost compared to the reference values as stated by (Noorvand et al. 2013). Increasing micro and nanoTiO₂ concentration to 6% leads to decrease compressive strength at age of 7 days. At age of 28 day compressive strength decreased as compared to the reference specimens as stated by (Meng et al. 2012) except 6% nT where readings show a little increment in compressive strength. Increasing nT percent to 6% work as a filler which increases binding between TiO₂ and cement particles.

Small particle size helps to form nucleation sites where the formed fabric microstructure helps to increase the compressive strength.

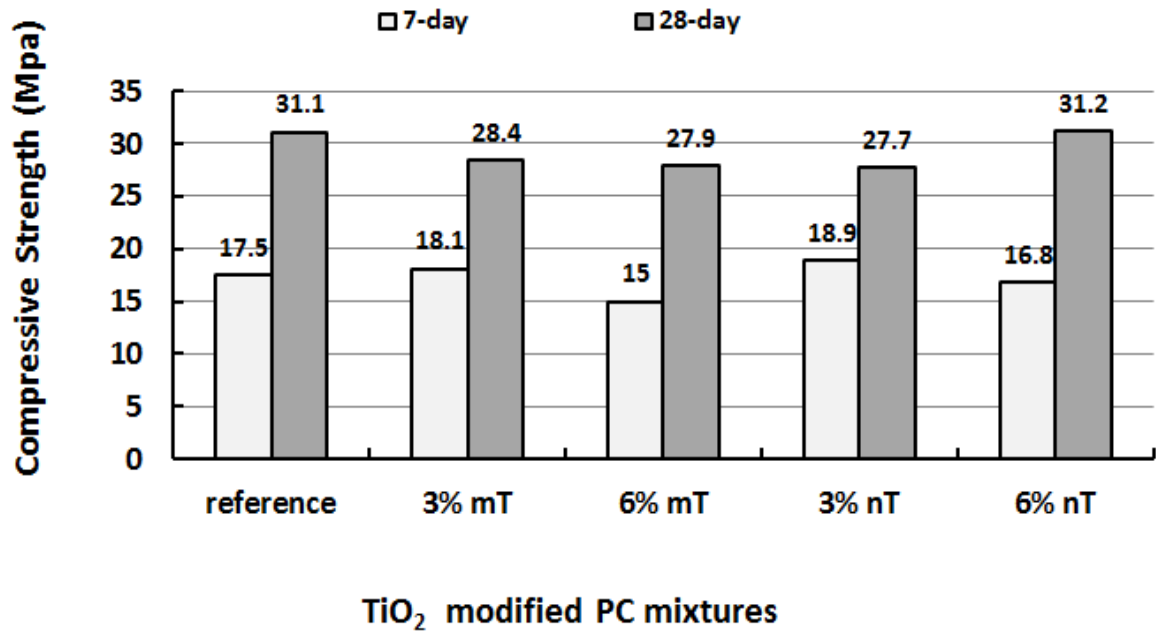


Figure 4.2- Compressive strength for the PC modified mixtures

Figure (4.3) represents the improvement percentages in compressive strength for the specimens, this was demonstrated by calculating the 28/7 ratio for the used replacements. From figure, it appears that 6% mT and 6% nT have high percentage of improvement in compressive strength after 28 days of curing equals to 186%. While 3% nT shows the least percent of improvement 147%. Large particle size for the 6% mT and the complex microstructure for the 6% nT give low compressive strength at age of 7 days which need more curing period to improve its binding ability at the age of 28 day.

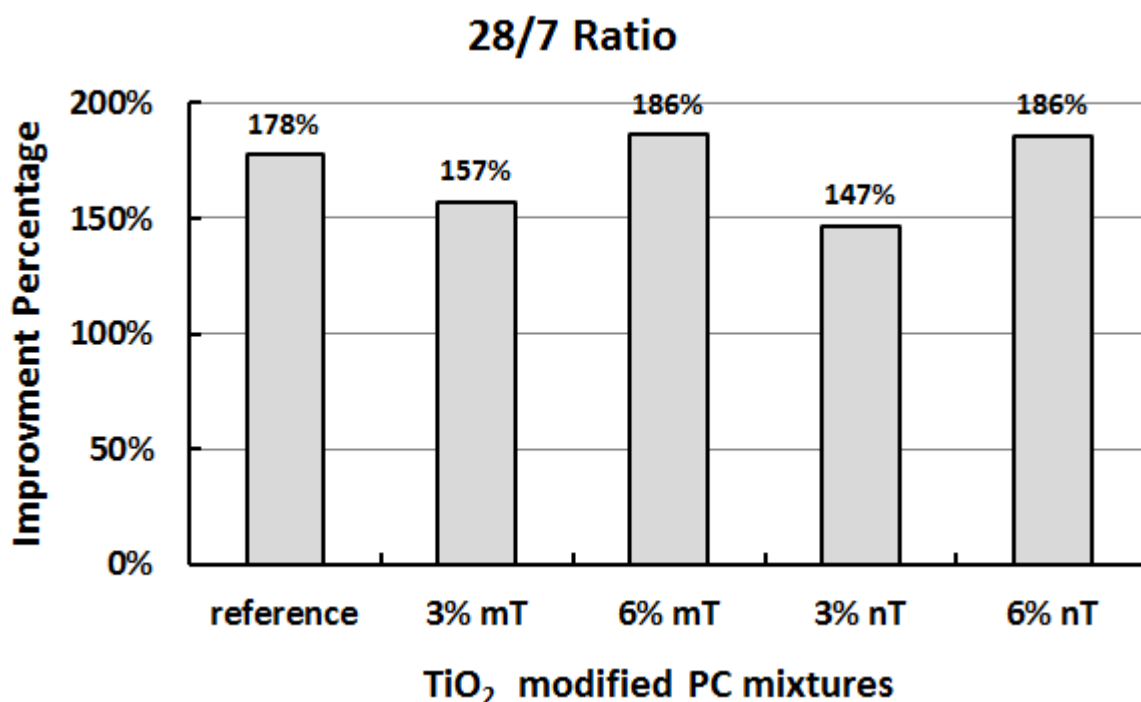


Figure 4.3- Improving ratio for the PC modified mixtures

4.3 Photocatalytic removal capacity of TiO₂ modified PC samples

The NO/NO₂ reaction profiles and toluene removal plots for the PC modified mixtures are illustrated in the Figs. (4.4) to (4.12) for all conditions, removal efficiencies are calculated according to the equations mentioned previously by (Mills & Elouali 2015)

4.3.1 Normal conditions: In this case, the samples were subjected to a relative humidity (RH) of 50%; the temperature and flow rate were almost constant. The reaction profiles and photocatalytic performance for NO and NO_x removal and NO₂ generation are illustrated in Figs. 4.4 and 4.5, respectively.

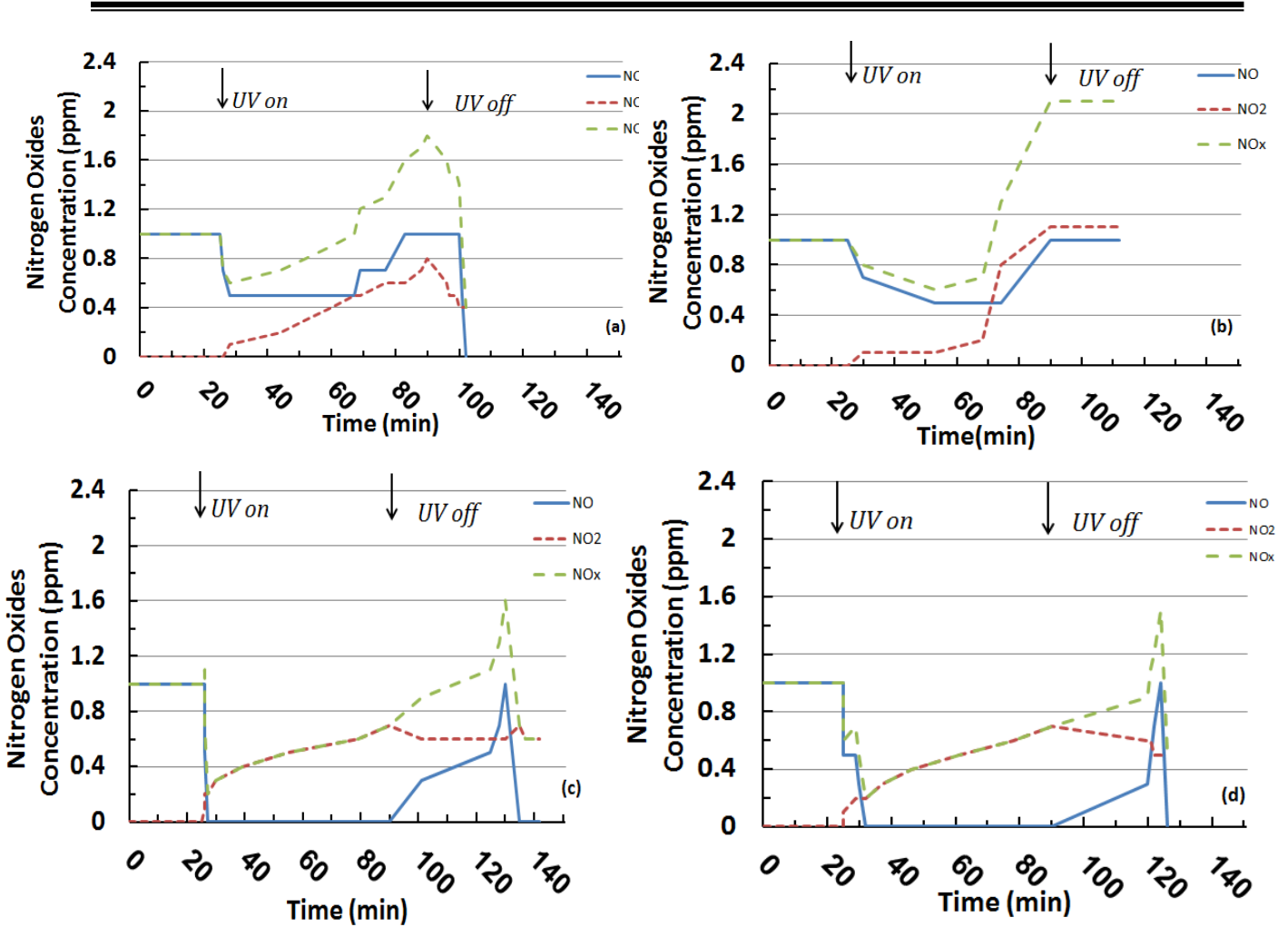


Figure 4.4-NO reaction profiles for TiO₂ -modified PC in normal conditions: a) 3% mT; b) 6% mT; c) 3% nT; d) 6% nT

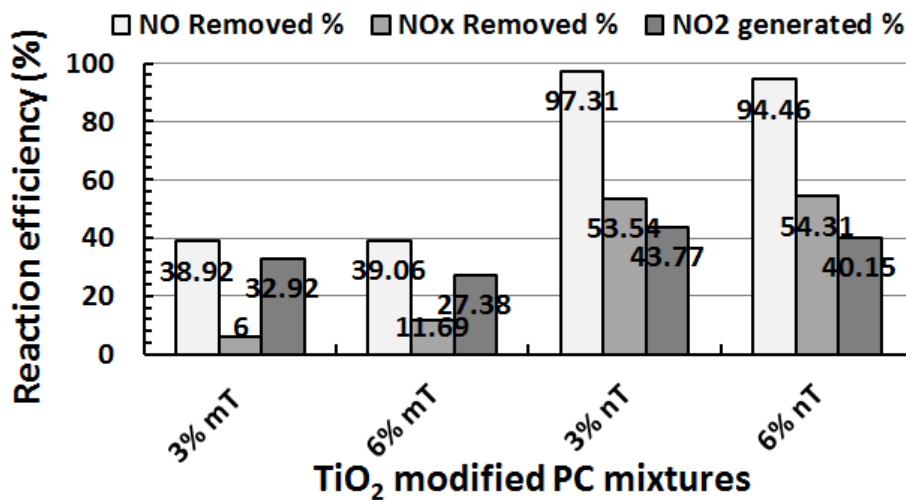


Figure 4.5-Reaction efficiency for TiO₂ -modified PC mixtures in normal conditions

Although the removal efficiencies for both 3% and 6% mT appear equal, the NO₂ 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_x amounts. The PC specimens with nano-replacements appear to behave better than the micro-replacement, with good NO_x removal. The fast reduction (Fig. 4.4c) in 3% nano-TiO₂ samples can be explained by the fast adsorption of gas molecules by the hardened cement paste in addition to the photochemical reaction, even though the adsorption is of small amounts, as stated by (Lee 2012). The reaction efficiencies indicate that the removal capacity improvements expected with 6% nT replacement were not clearly evident as compared to the 3% nT replacement. The PC specimens with the 6% nT replacement had 3% less NO removal and 1.5 % more NO_x removal than the PC specimens with 3% nT. This result contradicts with the hypothesis that higher TiO₂ concentrations will lead to better photocatalytic reaction effects, as reported by other researchers (Jayapalan et al. 2015). To explain the results, the water absorption on the control and TiO₂-modified PC specimens was tested on three additional discs of each PC mixture according to ASTM C642 (ASTM C 642 1997) to measure the variations in porosity because of the mT or nT replacement. The results are presented in Fig. (4.6).

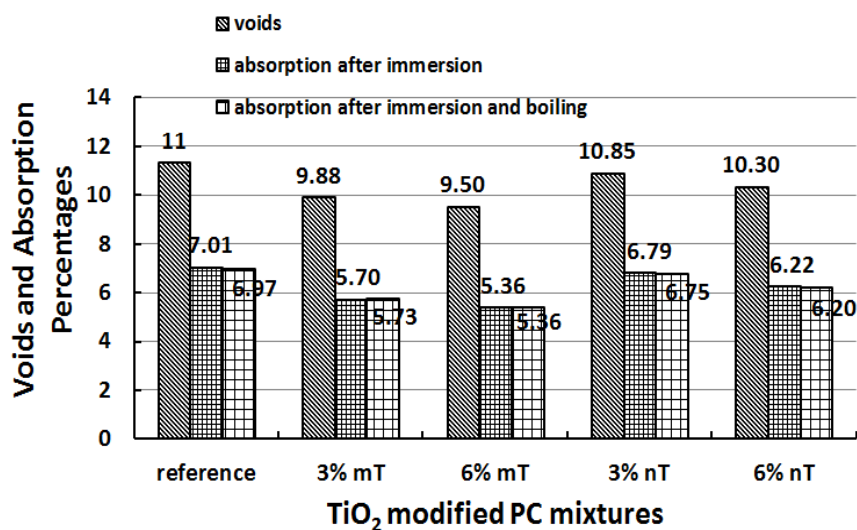


Figure 4.6- Absorption of TiO₂ -modified PC specimens with 0%, 3%, and 6% replacements

The absorption test reveals that the PC specimens modified with TiO₂ had lower absorption values than the control specimens. The nT replacement in this study actually increased the void percentages and water absorption of the mixtures compared to their counterparts of mT mixture. Higher replacement levels further reduced the voids and absorption results. The observed photocatalytic reaction behaviour may be related to this increase in the voids and absorption by using nT. This behaviour can be explained by the high concentration of TiO₂ particles bounded with cement paste, which formed a dense solid mass layer, as stated by (Chen et al. 2011). The reaction is on the surface instead of being in the inner part of the particles.

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.(4.4), NO₂ values significantly increased at the end of the reaction for the 6% micro-replacement (Figs. 4.4a and b) , which confirms that in this stage, the material was saturated and worked as a convertor instead of a remover, as stated by (Mills & Elouali 2015); the nano-replacements continued until UV was turned off without saturation, as shown in Figs 4.4c and d.

Regarding the toluene removal, no removal was noted for the low gas concentration (3ppm) in the photocatalytic toluene degradation experiment. Fig.(4.7) shows toluene removal at concentration of (5ppm).

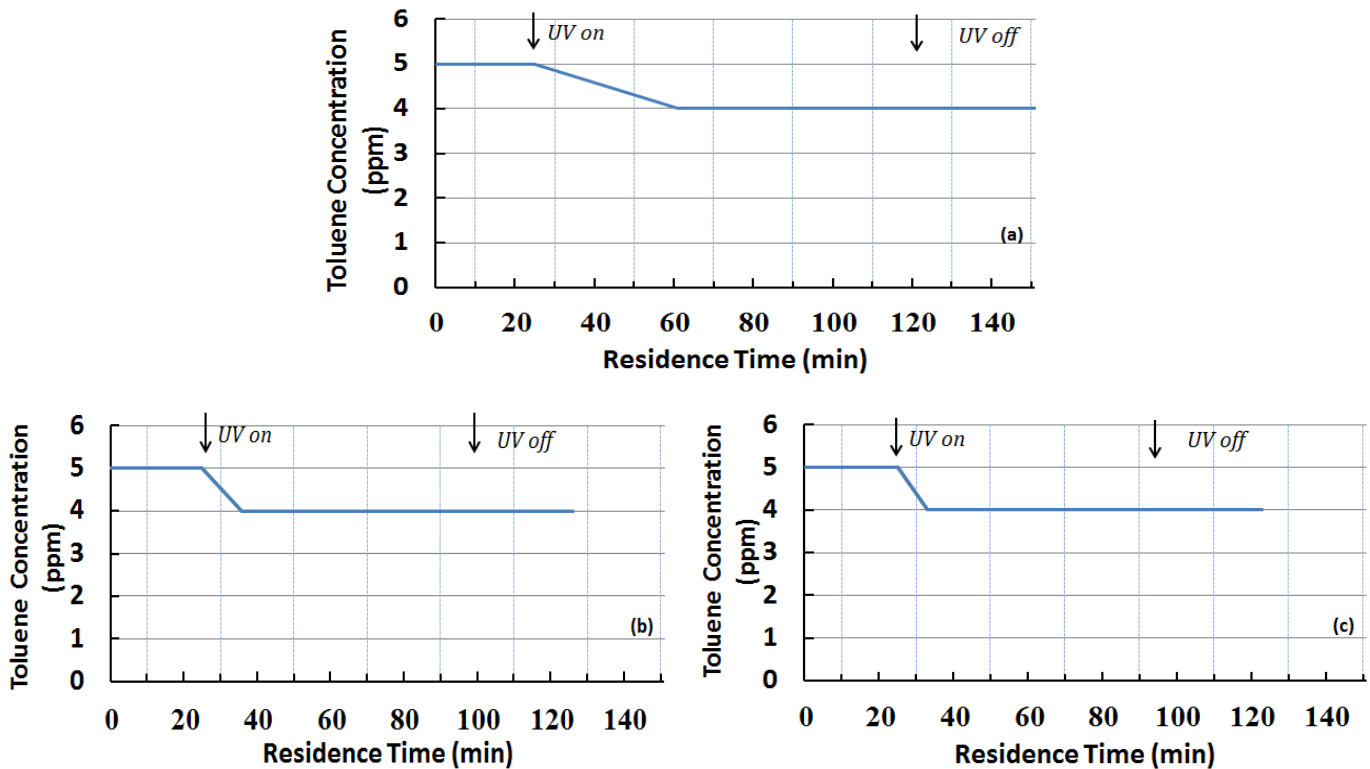


Figure 4.7- High concentration toluene removal profile for TiO_2 -modified PC in normal conditions: a) 6% mT; b) 3% nT; c) 6% nT

Increasing the toluene gas concentration to 5 ppm resulted in a removal of 12.5%, 16.9% and 17.6% for the PC specimens that contained 6% mT, 3% nT, and 6% nT, respectively. Fig. 4.7a shows that more time was required for the removal by the 6% mT specimens and approximately the same time was required for the toluene removal by the 3% nT and 6% nT specimens Figs. 4.7b and c respectively.

4.3.2 Saturated conditions: Fig. (4.8) represents reaction profiles for the PC modified specimens when they are fully saturated with water.

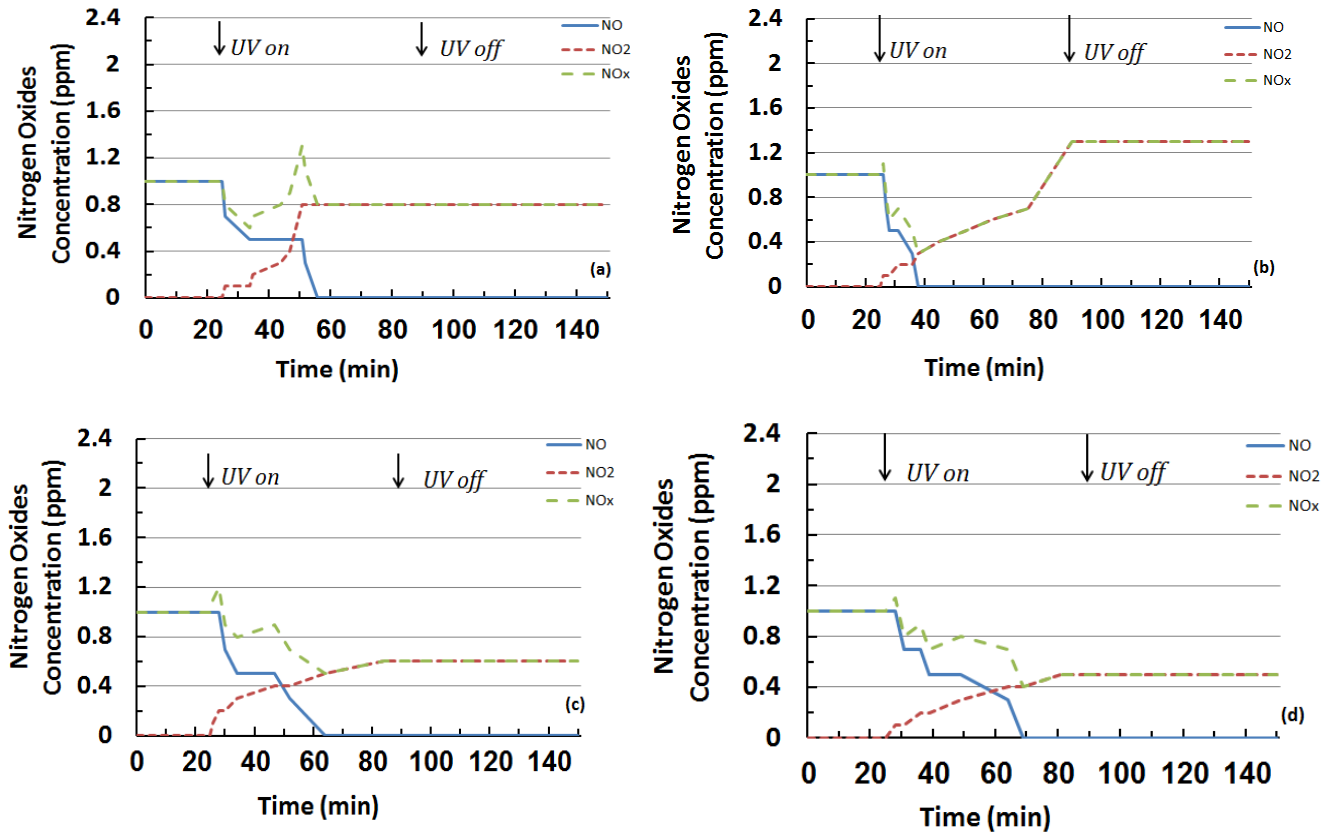


Figure 4.8-NO reaction profiles for TiO₂-modified PC in saturated conditions: a) 3% mT; b) 6% mT; c) 3% nT; d) 6% nT

When the PC specimens are completely wet, the removal of NO concentrations was much higher for the 3% mT and 6% mT samples than for their nano-counterparts, with increasing amounts of NO₂ generation due to the reaction. In addition, the removal for the 3% nT and 6% nT samples was low with less generation of NO₂ concentrations as shown in Fig. (4.9).

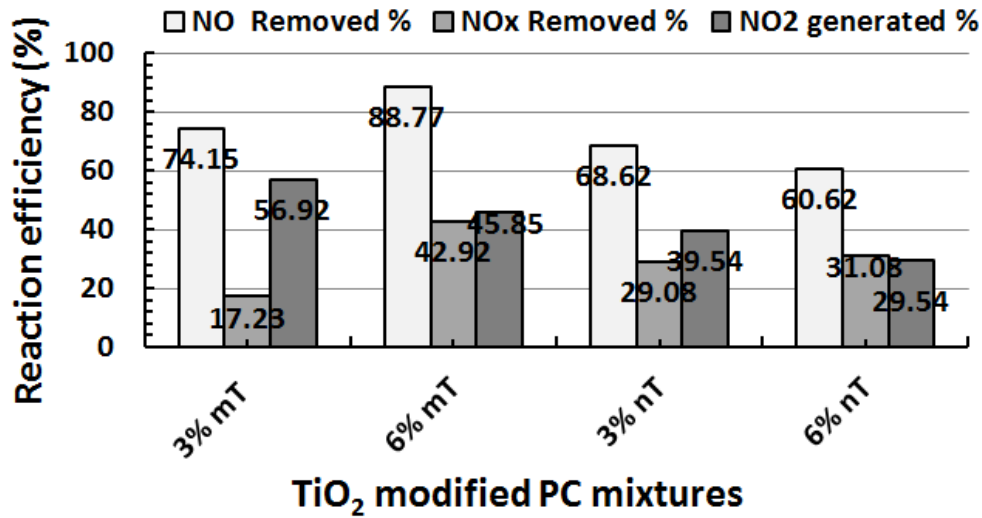


Figure 4.9-Reaction efficiency for TiO₂ -modified PC mixtures in saturated conditions

The decrease in removal capacity for the nano-TiO₂-modified PC samples in the saturated conditions can be explained by the ultrafine TiO₂ particles being bounded with water. A high TiO₂ replacement level (i.e., 6%) with a large particle size (i.e., micro-size) improves the reaction in wet conditions as compared to similar replacement levels with nano-size TiO₂. The PC specimens with 3 and 6% mT replacements had 7.5, and 31.5% more NO removal, respectively, than the identical replacements levels of nT (Fig. 4.9).

Fig. (4.8) shows that the saturated samples require more time to be recover to their inlet NO concentrations when UV is turned off. Thus, the reaction is with water-bound molecules instead of adsorption with cement-based material, and this reaction requires more time to recover than the dry samples, as stated by (Lee 2012).

There was no removal by the saturated samples for toluene gas at low or high inlet concentrations, which may be because of the low adsorption capacity of the physically and chemically bounded water in the hydrated cementitious material, as stated by (Chen et al. 2011). In general, the presence of excessive water

competes with pollutants, which reduces the photochemical reaction for the PC mixture.

4.3.3 Dry conditions: The effect of dry conditions on the photocatalytic reactions and removal efficiencies based on NO and NO_x removal and NO₂ generation during the test period is shown in Figs. 4.10 and 4.11.

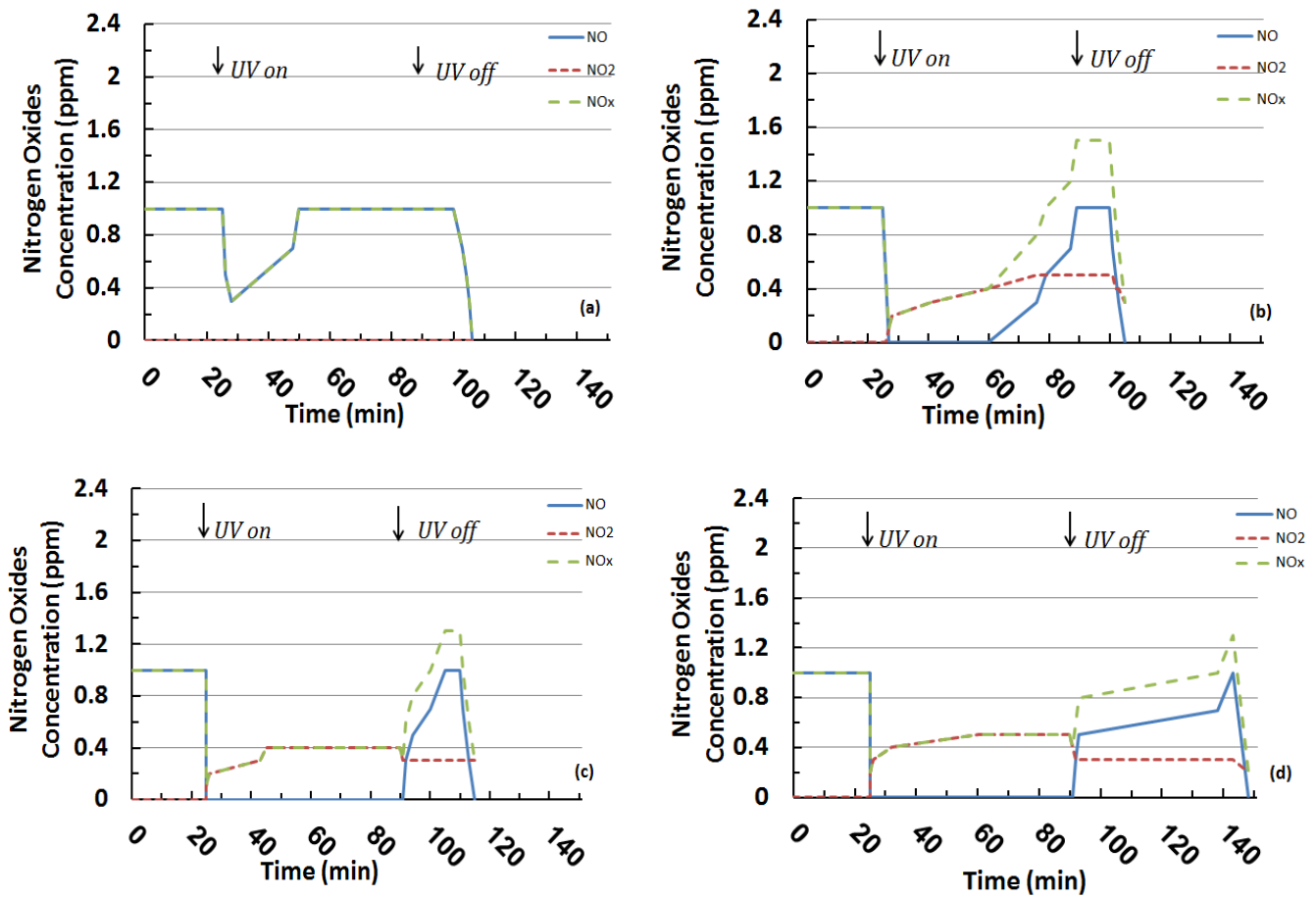


Figure 4.10-NO reaction profiles for TiO₂-modified PC in dry conditions: a) 3% mT; b) 6% mT; c) 3% nT; d) 6% nT

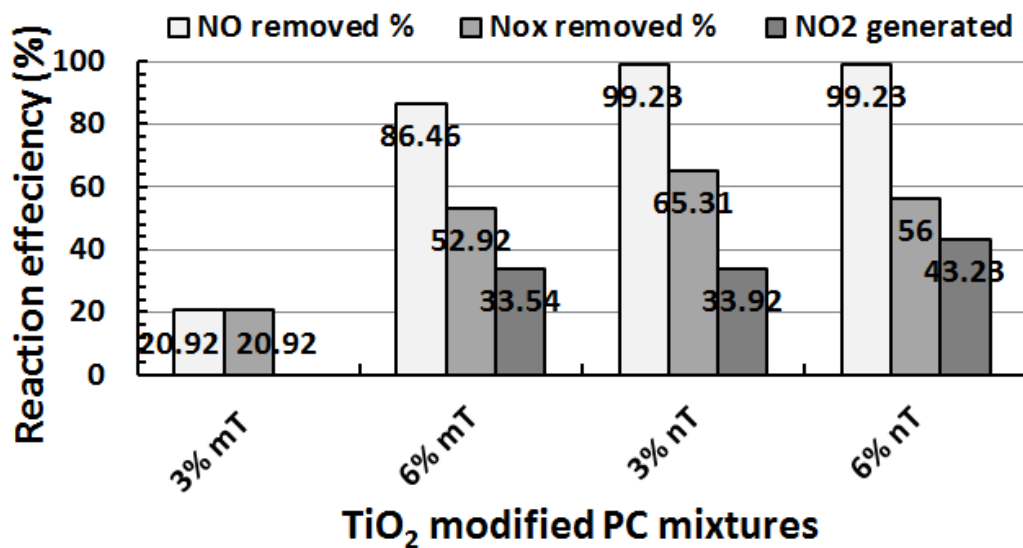


Figure 4.11-Reaction efficiency for TiO₂ modified PC mixtures in dry conditions

As observed, a sharp reduction in NO concentrations appeared when UV was turned on for all studied specimens. This fast reduction shows that the behaviour of TiO₂ in the removal is enhanced without water molecule competition, and the oxidation occurred because of the reaction with oxygen molecules in the air, as stated by (Bayar 2013), by generating the superoxide radicals. Furthermore, the PC specimens with 6% mT were more efficient in the removal than the 3% mT one, and the PC mixture was saturated with pollutant gas before the reaction ended for both 3% mT and 6% mT replacements, as shown in Figs 4.10 a and b, respectively.

The use of nT significantly improved the NO removal efficiency, as represented by an increase of specimen bar removal percentages in Fig. 4.11. The PC specimens with 3 and 6% nT replacement had 375% and 14.5% more NO removal, respectively, than the same replacements levels of mT. In the case of NO_x removal, the identical replacements had 212.2% and 5.8% more removal than the mT specimens, respectively. The removal efficiency of the PC specimens with nT replacement shows that the nT-containing specimens

exhibited notably similar levels of removal efficiency, which indicates that higher levels of nT replacement are not essentially proportionally valuable.

More NO_2 was generated by the 6% nT specimens, as shown in Fig. 4.11, which indicates that a higher concentration of nT replacements leads to more reaction under dry conditions.

The toluene test results show a lack of removal efficiency for all TiO_2 -modified PC mixtures except the mixtures modified with 6% nT, also specimen was tested at (5 ppm) gas concentration as shown in Fig. (4.12), the removal was 13.79%. Fig. 4.12 confirms the reduced reaction with water molecules of the gas, which was easily returned to its inlet concentration when UV was turned off.

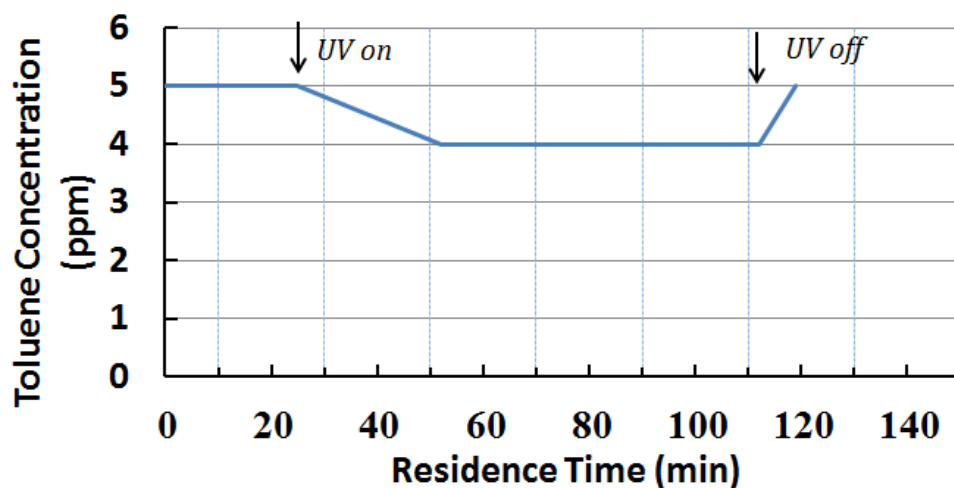


Figure 4.12- High concentration toluene removal profile for 6% nano TiO_2 -modified PC in dry conditions

NO and toluene removal efficiencies on TiO_2 -modified PC samples under UV irradiation subjected to different weather conditions are summarized in Tables 4.2 and 4.3 respectively.

Table 4.2- Percentages of NO removed, NO₂ generated and NO_x removed for TiO₂ modified PC photocatalysts under various weather conditions

Material	NO removed (%)			NO ₂ generated (%)			NO _x removed (%)		
	NC	SC	DC	NC	SC	DC	NC	SC	DC
3% mT	38.92	74.15	20.92	32.92	56.92	0	6	17.23	20.92
6% mT	39.06	88.77	86.46	27.38	45.85	33.54	11.69	42.92	52.92
3% nT	97.31	68.62	99.23	43.77	39.54	33.92	53.54	29.08	65.31
6% nT	94.46	60.62	99.23	40.15	29.54	43.23	54.31	31.08	56

Table 4.3- Percentages of toluene removed for TiO₂ modified PC photocatalysts under various weather conditions

Material	Toluene removed for 5ppm inlet concentration (%)			Toluene removed for 3ppm inlet concentration (%)		
	NC	SC	DC	NC	SC	DC
3% mT	0	0	0	0	0	0
6% mT	12.5	0	0	0	0	0
3% nT	16.9	0	0	0	0	0
6% nT	17.6	0	13.79	0	0	0

4.4 Photocatalytic removal capacity for the coated samples

Test parameters (i.e., humidity, temperature and light intensity) were the same for all tested samples for both spraying and dipping methods. Results were compared to gas removal for two spraying times 1 min and 5 min by the mT solution, the same procedure was repeated for other samples sprayed by the nT solution.

4.4.1 Spraying method

4.4.1.1 NO removal efficiency

Fig. (4.13) shows the reaction profiles for the micro and nano sprayed samples, from figure it appears that 5 min- mT spray samples have NO removal efficiency and NO₂ generation percent equal to 87.69% and 66.31%, respectively, which is more than 1 min- mT spray samples; this result is expected because of the excess amounts of the sprayed solution that could be absorbed by the substrate surface, which resulted to more reaction and NO₂ generation. NO_x

removal seems to be close to each other. 1 min and 5 min nT-spray samples appear to have an equal percent of NO removal efficiency (98.85 %). Less amounts of NO₂ generated from 1 min- nT sprayed samples and more NO_x removal than 5 min- nT sprayed samples.

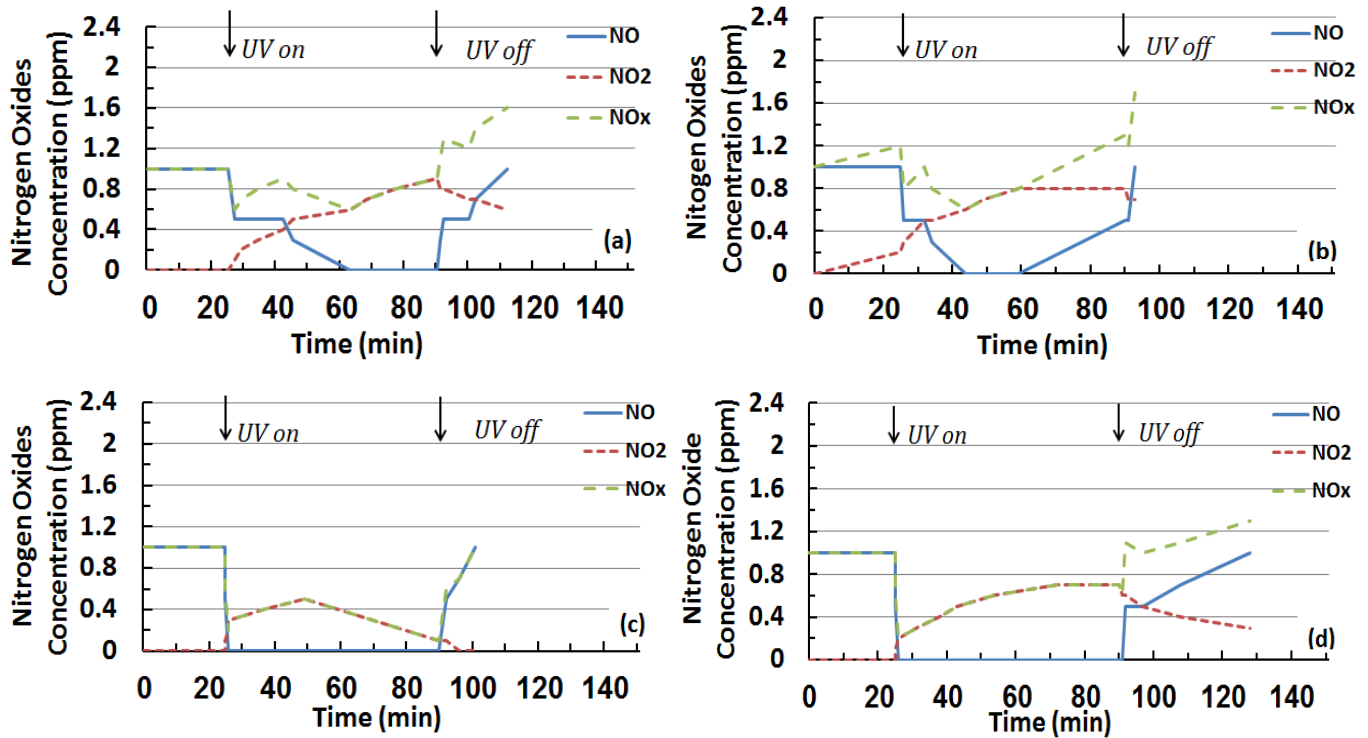


Figure 4.13- NO reaction profiles for the spray coated substrates: a) 1 min- mT spray; b) 5 min- mT spray; c) 1 min- nT spray; d) 5 min- nT spray

For the above stated tests; no saturation with gas was happened during the test period.

Using 1 min- nT spray coating increases NO and NO_x removal efficiency by 32.2 % and 136 %, respectively as compared with 1 min- mT spray coatings, with less NO₂ generation by 14.6 %. While using 5 min- nT spray coating increases NO and NO_x removal efficiency by 12.7 % and 117.3 %, respectively; with less NO₂ generation equals to 21% as compared to its identical amounts of mT coatings as shown in Fig. (4.14).

Increasing spraying time for the mT solution coating to 5 min enhanced NO removal by 17.3 %, while nT solution has the same NO removal which is 98.85 % when spraying time increased to 5 min as shown in Fig. (4.14). It could be concluded that nT behaved well as compared to mT, increasing spraying time did not have a significant effect on the removal efficiency and the use of 1 min micro and nano spray coating could be used effectively.

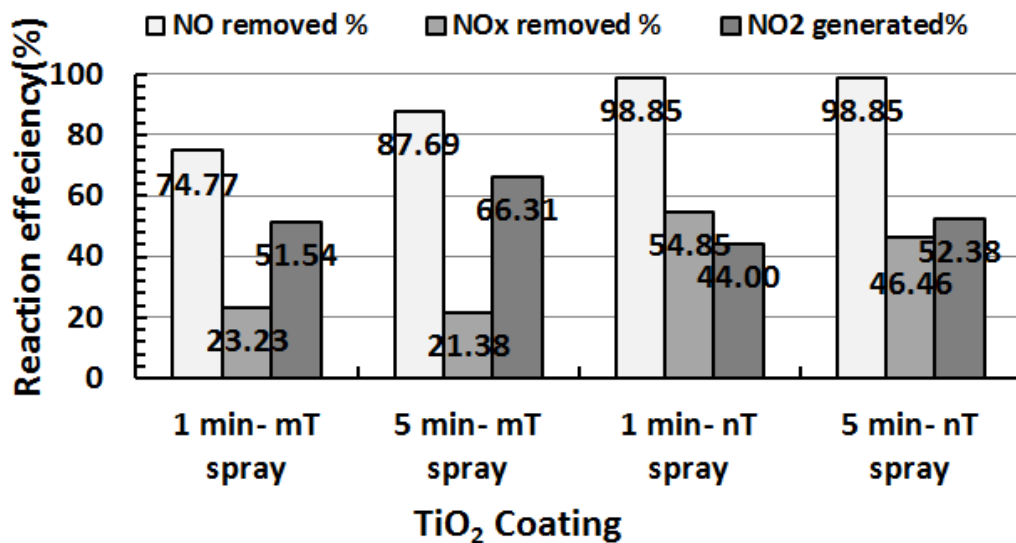


Figure 4.14-Reaction efficiency for TiO₂ spray coatings

4.4.1.2 Toluene removal efficiency

Tests were made to evaluate the suitability of the coated samples for toluene (as a VOC substance) mitigation at 3 ppm and 5 ppm concentrations with maintaining other test parameters constant. Minimum residence time of 60 min was used for all samples to investigate toluene concentration reduction. If reduction happened for a sample another 60 min was added to note if there is any more reaction happened. The removal for toluene was 1 ppm from the inert concentration (5ppm to 4 ppm or 3ppm to 2 ppm) with differences in the time required for the reduction. The tests were conducted for the two gas concentrations as follows:

1. Low VOC concentration reduction results by using spraying method:

Ejecting low gas concentration equals to 3ppm for the 1 min- mT and 5 min- mT sprayed samples showed no gas removal as shown in Fig. (4.15 a).

1 min- nT sprayed samples showed gas removal equals to 19.05%, while 5 min- nT sprayed samples showed reduction equals to 20.62%, as shown in Figs. 4.15 b and c. The little variance in the removal between 1 min and 5 min spraying times for the nT material could be explained due to the multiple layers that could be absorbed by cement surface when sprayed for 5 min which reduces the removal efficiency due to the clogging or shielding from illumination by large agglomeration of titanium particles for the coating layers as stated by (Faraldos et al. 2016) in addition to the saturation with gas.

It could be concluded that applying thin-film coating would be enough for photocatalytic reaction as stated by (Zhao & Yang 2003) and this could be obtained by 1 min spraying time.

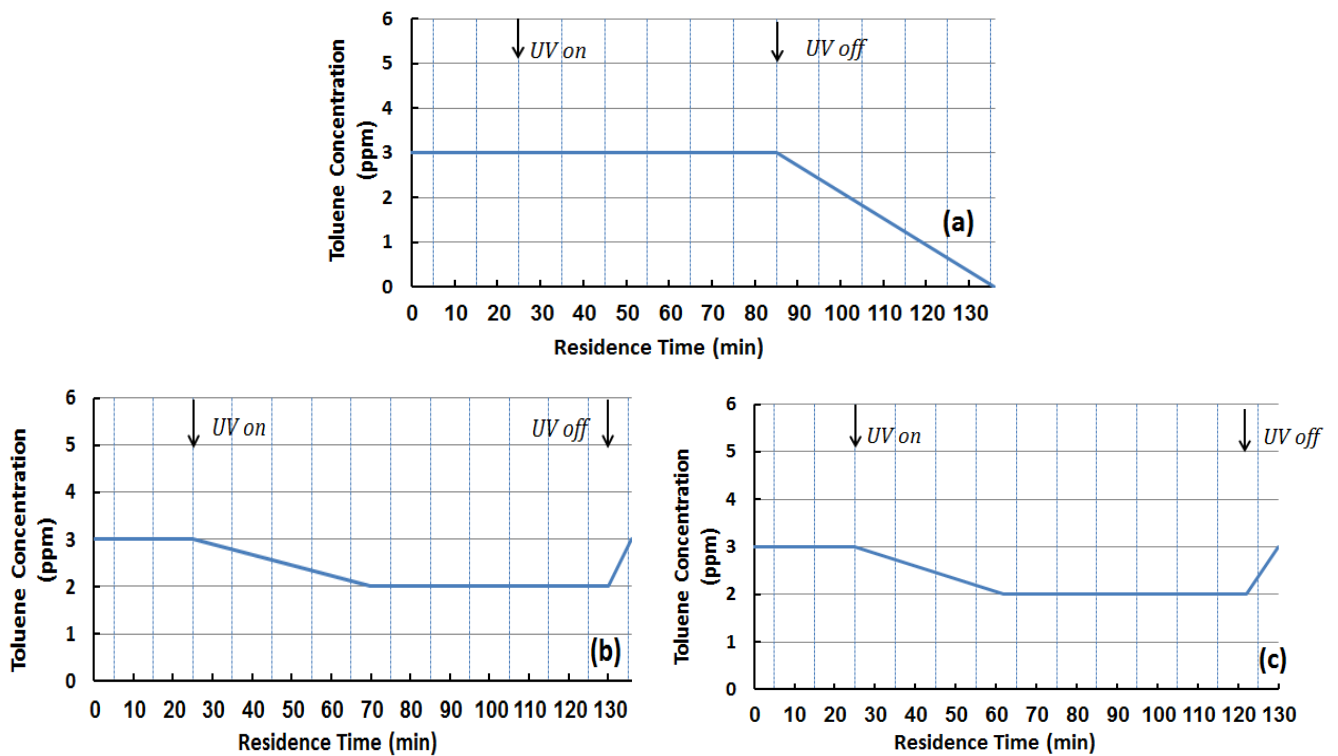


Figure 4.15- Low concentration toluene removal profile for the spray coated substrates:

a) 1 min and 5 min- mT spray; b) 1 min- nT spray; c) 5 min- nT spray

2. High VOC concentration reduction results by using spraying method:

1min- mT sprayed samples showed no gas removal for toluene concentration, while 5 min- mT sprayed samples; the removal was 10.16% as shown in Fig. 4.16 a and b.

1 min- nT-sprayed samples showed removal efficiency of 13.95 % within 26 min, while the removal for the 5 min- nT sprayed samples was 15.79 % with less time required for the removal (16 min) as shown in the Fig. 4.16 c and d. These results are expected due to high reactivity of nano coated samples especially for the greater spraying time (5 min) which reduce the time required for the removal.

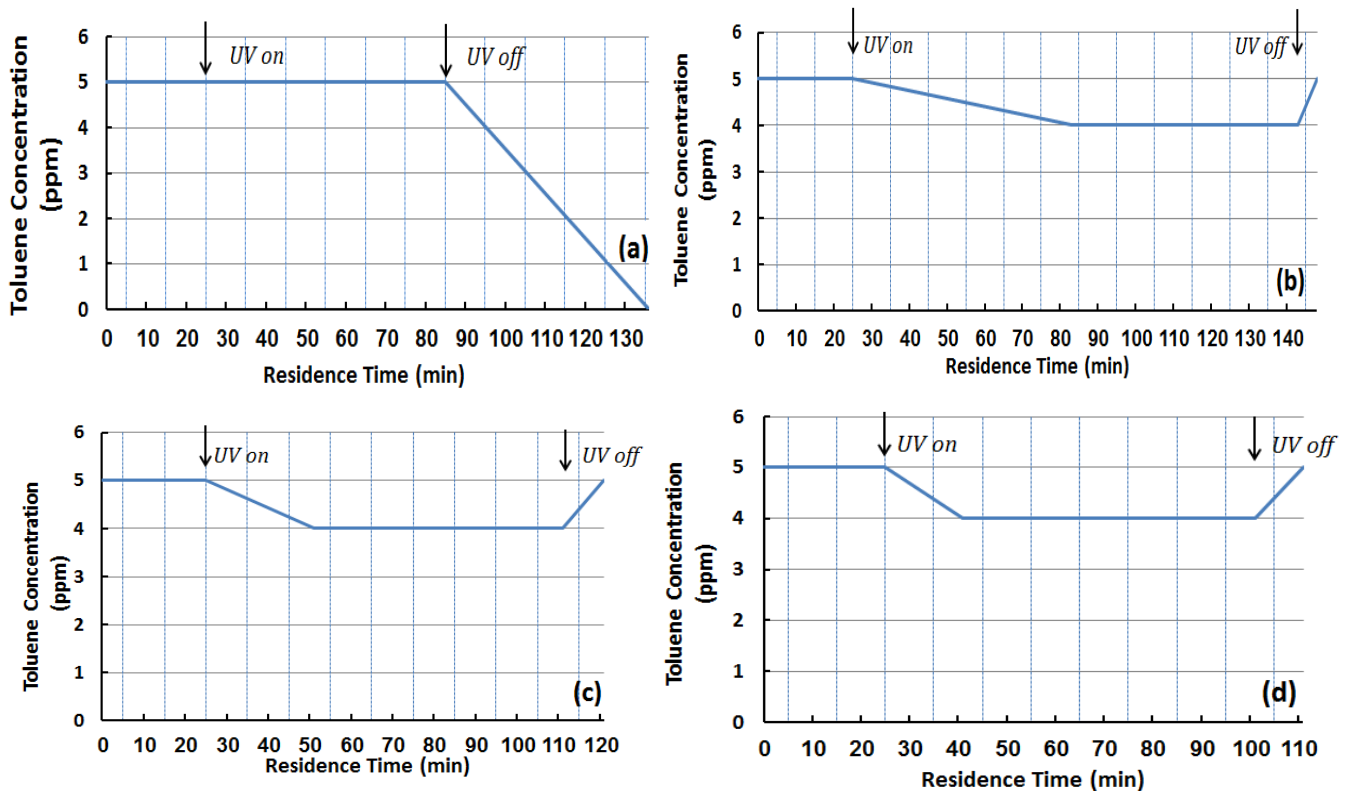


Figure 4.16- High concentration toluene removal profile for the spray coated substrates:

a) 1 min- mT spray; b) 5 min- mT spray; c) 1 min- nT spray; d) 5 min- nT spray

4.4.2 Dipping method

The same test conditions in spraying method was applied on the previously micro and nano dipped samples and tested for NO and toluene removal.

4.4.2.1 NO removal efficiency

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 NO₂ generated due to the reaction as shown in Fig. (4.17 a); this could be explained due to the high amounts of TiO₂ particles on the substrate surface with little percent to be absorbed by the specimen.

Nano-dipped (nT dip) 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 as shown in Fig. (4.17 b), 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 is considered to be equal and no saturation with gas that was happened for the both coated samples during test period.

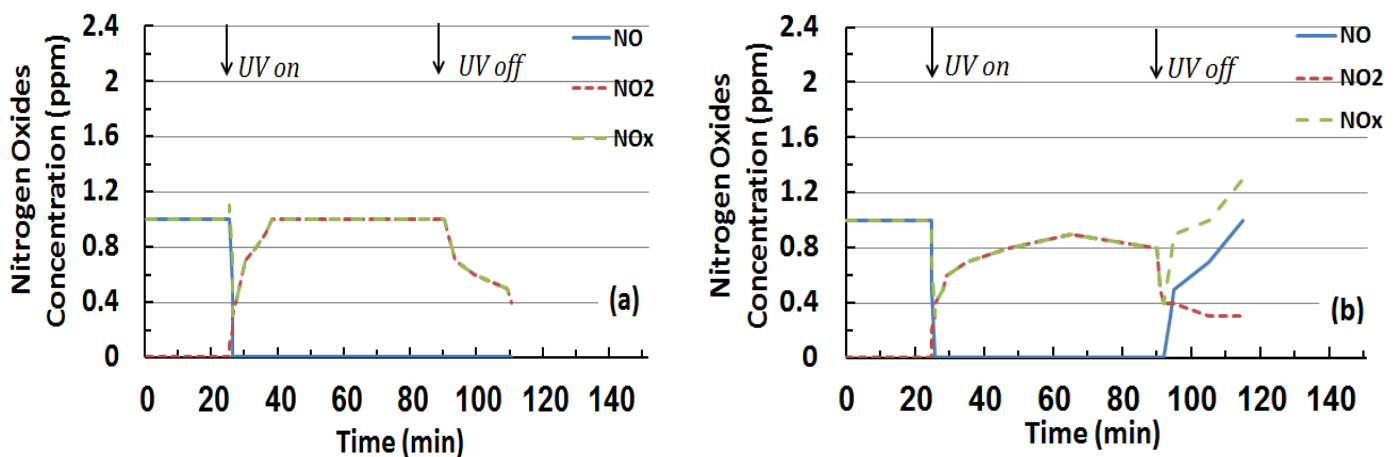


Figure 4.17- NO reaction profiles for the dip coated substrates: a) mT dip; b) nT dip

Although equal amounts for the NO were removed by the micro and nano dipped samples, nT-dipped samples show high NO_x removal and less NO₂ generation as compared to the mT-dipped samples by percents equal to 283.3 % and 16.39% , respectively, as shown in Fig. (4.18).

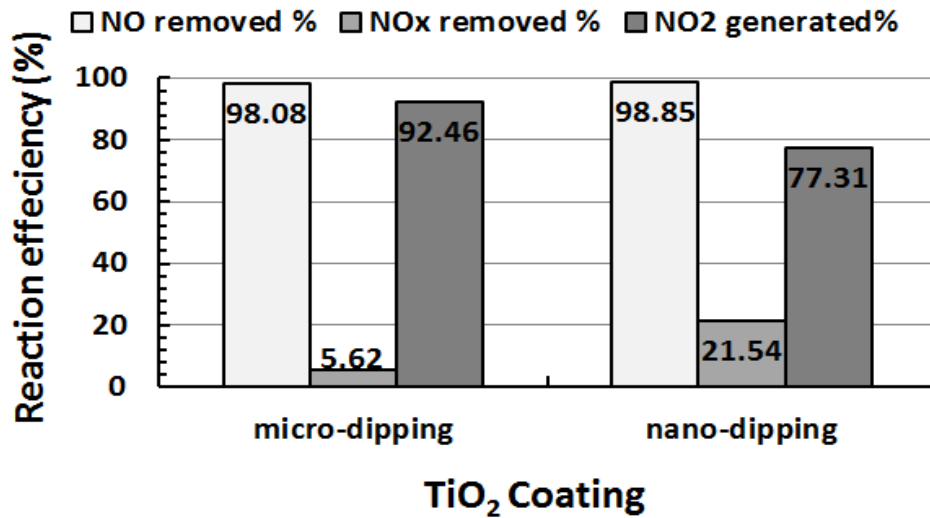


Figure 4.18-Reaction efficiency for TiO₂ dip coatings

4.4.2.2 Toluene removal efficiency

The same test procedure applied in the spray method for toluene removal was adopted in the dipping method for the removal of both toluene concentrations 3 ppm and 5 ppm. The tests were conducted for the two gas concentrations as follows:

1- Low VOC concentration reduction results by using dipping method:

There was no removal efficiency observed for toluene concentration from micro-dipped samples as shown in Fig. (4.19 a), while nano-dipped samples showed removal efficiency of almost 20.62% within 37 min, Fig. (4.19 b).

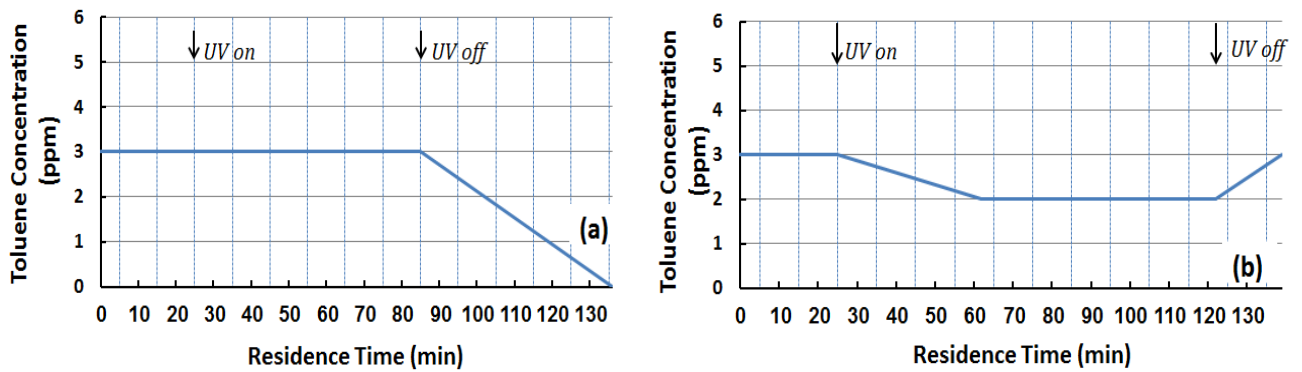


Figure 4.19- Low concentration toluene removal profiles for the dip coated substrates: a) mT-dip ; b) nT-dip

2- High VOC concentration reduction results by using dipping method:

Removal efficiency was 13.48 % for micro-dipped samples after 29 min from reaction and 15% within 20 min for nano-dipped samples which indicates increasing susceptibility for the high gas concentrations rather than low gas concentrations as stated by (Martinez et al. 2011) especially for the micro-dipped samples; Fig. 4.20 a and b shows the obtained results for micro and nano-dipped samples, respectively. From the above results; it could be concluded that the same range of the removal could be happened but within different times, that is depending on the type of the material used. Nano coated samples required shorter time than micro coated sample. This result is expected due to the high surface area for the nano coated samples, which results in reducing time required for the reduction especially for high gas concentrations as stated by (Demeestere et al. 2008) and (Martinez et al. 2011).

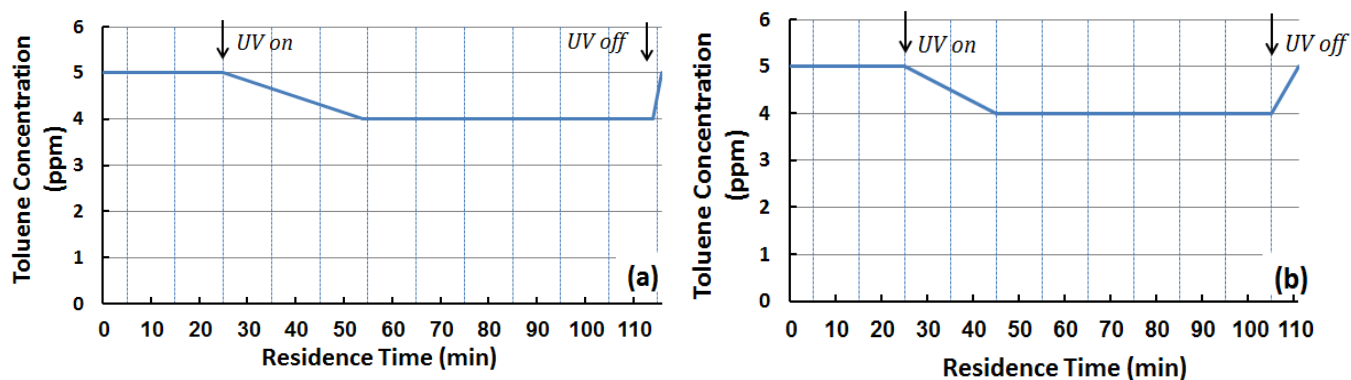


Figure 4.20- High concentration toluene removal profiles for the dip coated substrates: a) mT-dip; b) mT-dip

Tables 4.4 and 4.5 summarize the obtained results for the removal of nitric oxides and toluene, respectively.

Table 4.4- Percentages of NO removed, NO₂ generated and NO_x removed for TiO₂ coated substrates

Coating method	NO removed (%)	NO ₂ generated (%)	NO _x removed (%)
1 min- mT spray	74.77	51.54	23.23
5 min- mT spray	87.69	66.31	21.38
1 min- nT spray	98.85	44	54.85
5 min- nT spray	98.85	52.38	46.46
mT- dip	98.08	92.46	5.62
nT- dip	98.85	77.31	21.54

Table 4.5- Percentages of toluene removed for TiO₂ coated substrates

Coating method	Toluene removed for 3ppm inlet concentration (%)	Toluene removed for 5ppm inlet concentration (%)
1 min- mT spray	0	0
5 min- mT spray	0	10.17
1 min- nT spray	19.05	13.95
5 min- nT spray	20.62	15.79
mT- dip	0	13.48
nT- dip	20.62	15

Fig. 4.21 represents the time required for toluene degradation by substrates for the stated coating methods, the figure shows that the removal of high gas concentrations by mT-solution seems to be better when dipping method was used, while 5 min-nT spray and nT-dipping have almost the same time for the removal due to the large amount of the solution applied onto the substrates surface.

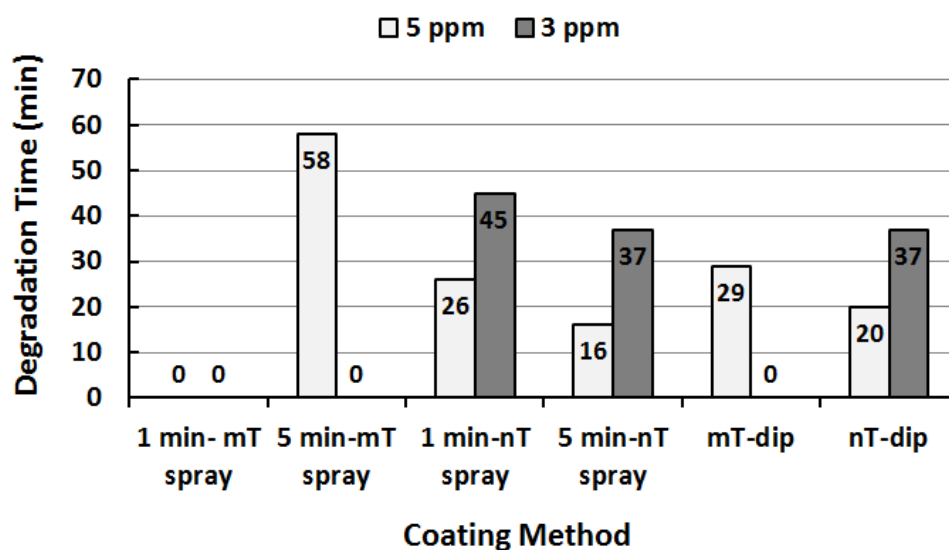


Figure 4.21- Time required for toluene degradation by coated substrates

4.5 Washing coated samples

In order to determine the amount of coatings consistency and adhering ability on the substrates surface, selective samples which show higher removal efficiency have been tested for gas removal and then washed and the test was repeated for three successive times. Two main characteristics were expected to be the main parameters for the consistency of the coatings on the substrates surface; chemical propriety like Van der Waals and ionic bonds and physical propriety like adsorption of the liquid particles through specimen. Tables 4.6 and 4.7 show the reaction efficiency obtained by nano-sprayed and nano-dipped samples after a periodic washing for the removal of nitric oxides and toluene, respectively.

Table 4.6- Average nitrogen oxides reaction efficiency after 3 successive washing for the coated samples

Coating Method	NO removal %		NO ₂ generation %		NO _x removal %	
	Before washing	After washing	Before washing	After washing	Before washing	After washing
5 min- nT spray	98.85	95.18	52.38	38.41	46.46	56.77
nT- dip	98.85	98.59	77.31	65.44	21.54	33.15

Table 4.7- Average toluene removal efficiency after 3 successive washing for the coated samples

Coating Method	Toluene (5 ppm) %	
	Before washing	After washing
5 min- nT spray	15.79	12.85
nT- dip	15	16.60

For the selective nT coatings; it appears that nano-dipped samples were not affected by washing and the samples have almost the same NO and toluene removal efficiency. Nano-sprayed samples show reduction in NO removal by percent equals to 3.72 %, and toluene removal reduced by percent equals to 18.6 % after washing.

4.6 Self-cleaning performance

4.6.1 Dye degradation

A methylene blue test was implemented in this study to observe the potential photo degradation and degree of discoloration of the blue colour, which can be related to the photocatalytic oxidative behaviour for the mixed and coated specimens. Furthermore, the hydrophilicity of the specimens can be evaluated by comparing the spot of the TiO₂-modified PC specimens with the control. A wider

area indicates higher hydrophilicity for the same deposited methylene blue solution volume. Figs. 4.22, 4.23 and 4.24 show the amount of dye degradation after 10 h of exposure to halogen illumination for the mixed, 5 min- sprayed and dipped specimens, respectively. Even the PC specimens without TiO₂ (i.e., the reference) had a degradation in colour, which highlights the importance of using a reference specimen to avoid misinterpretation (Folli et al. 2012).

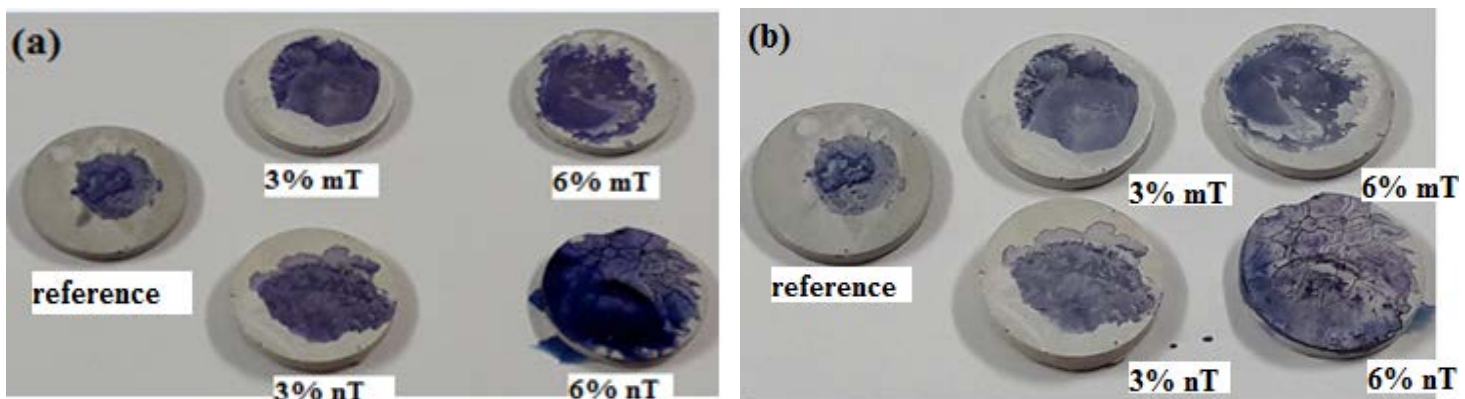


Figure 4.22- micro and nano mixed TiO₂ percentages (a) samples before exposure to halogen light, (b) samples after 10 h exposure to halogen light

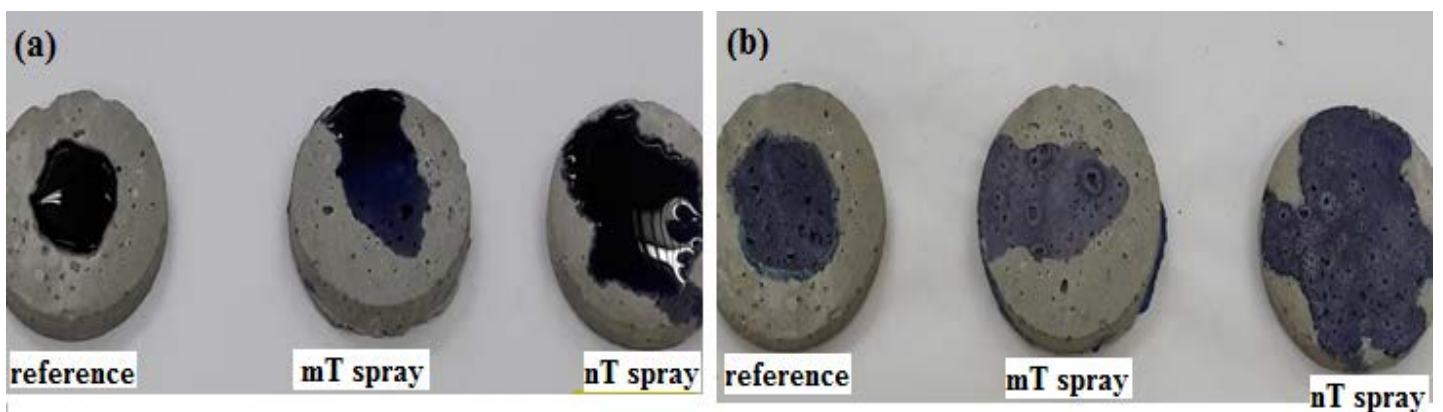


Figure 4.23- micro and nano spray coatings: (a) samples before exposure to halogen light; (b) samples after 10 h exposure to halogen light

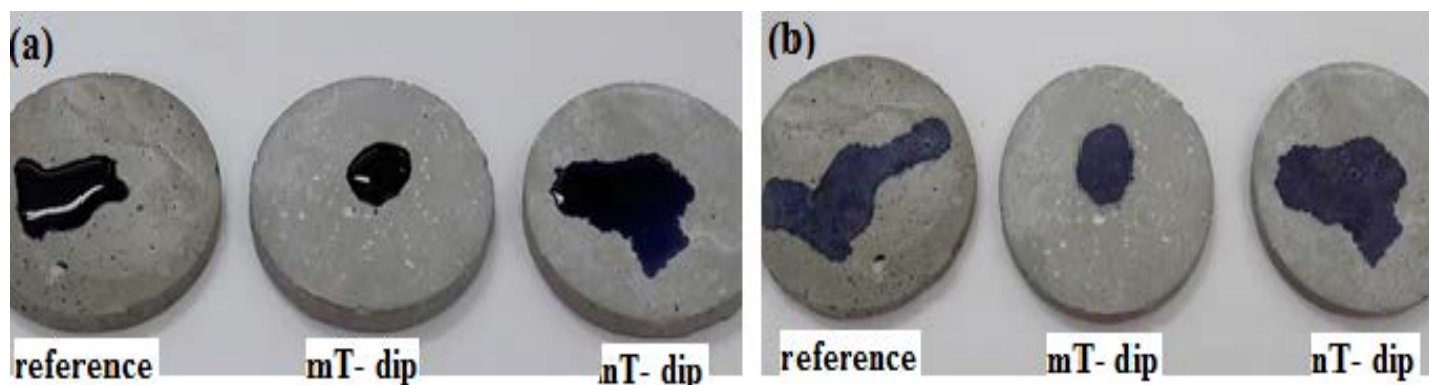


Figure 4.24- micro and nano dip coatings: (a) samples before exposure to halogen light; (b) samples after 10 h exposure to halogen light

The surface pigmentation area increased when the dye was exposed on the surface of the nT-modified PC specimens. This increase was more visible with the PC specimens that contained high amounts of nT. This behaviour can be interpreted as the surface hydrophilicity, which makes dirt and solid particles easily slip off.

It is expected that a portion of the methylene blue dye penetrated into the PC matrix in proportion to the porosity of the matrix, which reduces the dye's expansion area. The observed performance of the PC specimens was modified with nano-TiO₂, which have more voids, as evident previously in Fig. (4.6), contradicts this expectation and confirms the hydrophilicity of this matrix.

The discolouration of the dye was well noticed for the nT-modified PC specimens (3% and 6 % mixed nT percents) which indicates better degradation for organics and stains that can be obtained by using these percentages of replacements. These results contradict the conclusion of (Folli et al. 2012), where micro-TiO₂ performs better or at least as well as nano-TiO₂.

5 min mT- sprayed specimens performs better than nT- sprayed in dye discoloration, this could be explained due to the high agglomeration of mT particles on the specimen surface which increases its reactivity for colour degradation, while nT particles may be adsorbed through specimen pores which

reduce its activity. nT- dipped specimens shows more dye degradation than mT- dipped specimens, this result is expected due to high activity of the nT coating which may form a thin film over the specimen surface.

4.6.2 Contact angle measurement

This test is conducted for all types of samples (mixtures and coatings) in order to investigate the surface hydrophilicity for the applied TiO₂. Titanium dioxide has a superhydrophilic specification. Fig. (4.25) represents computer image obtained for the contact angle measurement, and Table 4.8 shows summary of the contact angle results for the tested specimens.

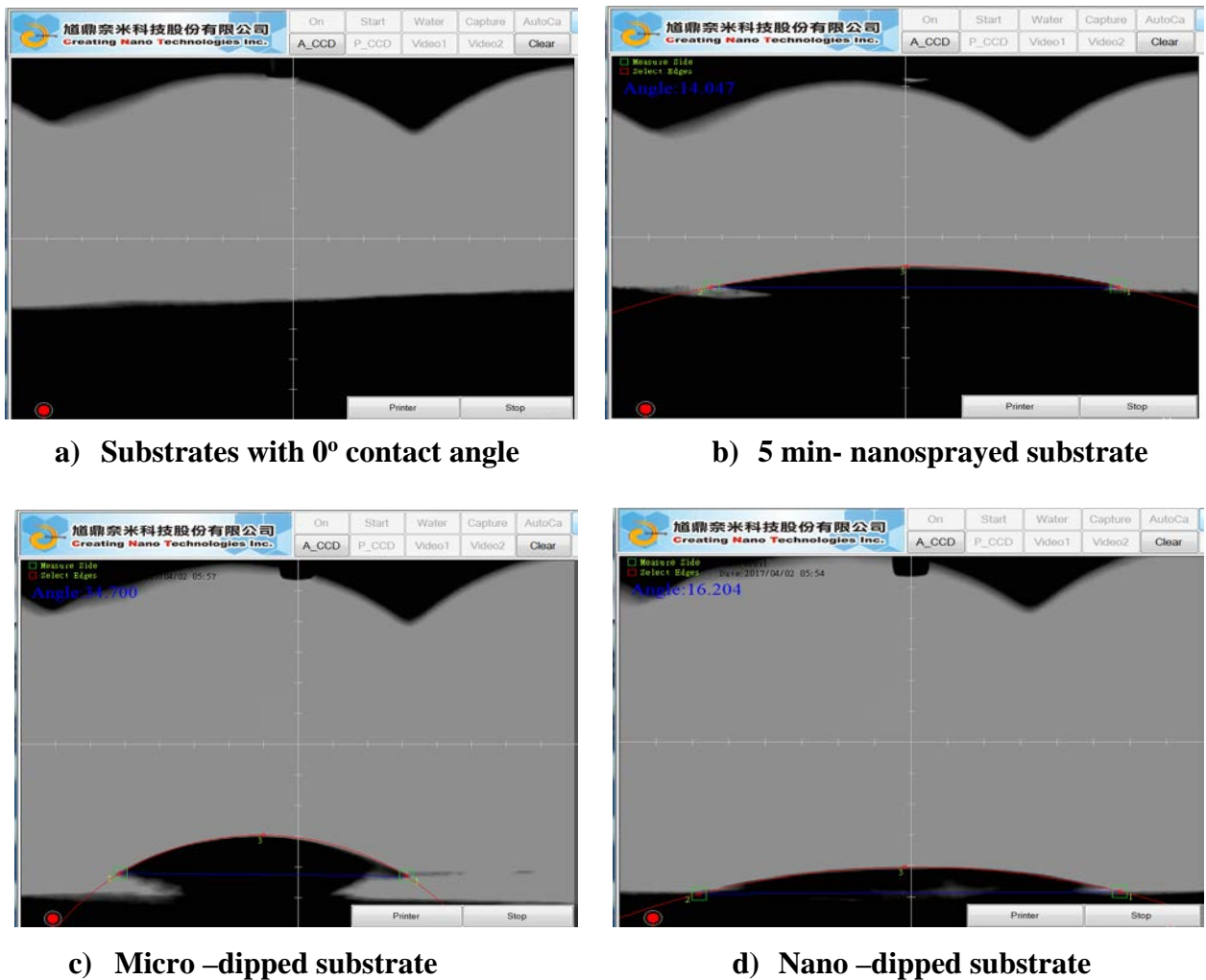


Figure 4.25- Contact angles images for various substrates

Micro, nano PC mixtures ,(1 min, 5 min)- mT, and 1min- nT sprayed specimens have a contact angle equals to 0° , while thin film that may be formed during 5 min- nanospray, micro and nano dipping increases the contact angle to 14.04° , 34.7° and 16.2° respectively. Increasing the hydrphilicity of the cementitious material may help in removing solid pollutants that adhere on surfaces by washing in addition to the photochemical reaction.

Table 4.8- Contact angle results for the PC mixtures and coated mortar specimens

Sample Type	Contact Angle	Description
Reference cement paste	0	superhydrophilic
Micro mixture (3%)	0	superhydrophilic
Micro mixture (6%)	0	superhydrophilic
Nano mixture (3%)	0	superhydrophilic
Nano mixture (6%)	0	superhydrophilic
Reference mortar sample	0	superhydrophilic
1 min- mT spray	0	superhydrophilic
5 min- mT spray	0	superhydrophilic
1 min- nT spray	0	superhydrophilic
5 min- nT spray	14.04°	superhydrophilic
Micro dip	34.7°	superhydrophilic
Nano dip	16.20°	superhydrophilic

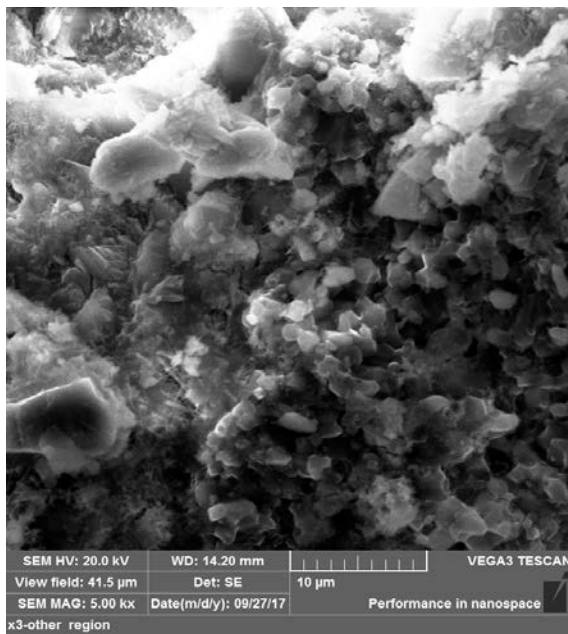
4.7 Microstructure for the applied TiO_2

To explain the different behavior for the applied micro and nano TiO_2 , the microstructure for the PC modified mixtures and coated mortars have been studied. Different particles shapes and clusters between the micro and nano specimens have been noticed as stated by (Folli et al. 2012). Well dispersion and big particles size

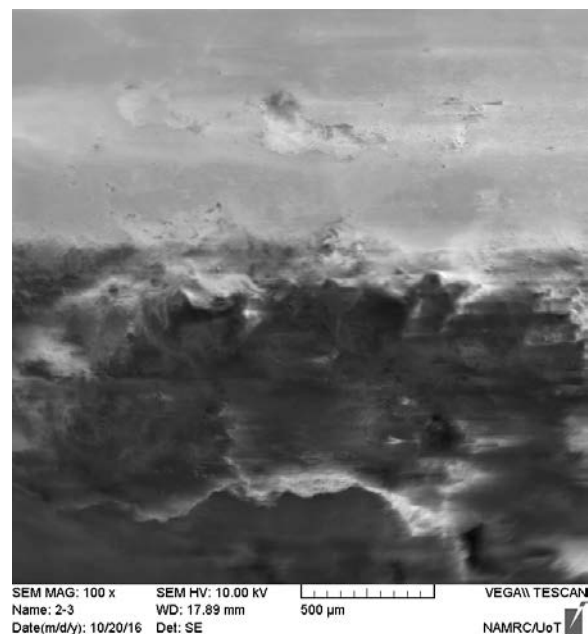
with granular shapes for the 6% mT make gases removal efficiency higher than 3% mT especially in the saturated conditions (as shown previously in Table 4.2) where the removal was even higher than nT due to the available surface area for the reaction.

PC modified specimens with nT show a flocculated not well dispersed agglomerates which give the structure a fabric shape rather than granular shape, this leads to increase its voids ratio (as shown previously in Fig. 4.6), so gas can be adsorbed easily through the specimen, in the same time this structure could be affected in the presence of humidity which reduces its efficiency due to saturation with water molecules. Fig. 4.27 represents PC modified mixtures compared with Fig. 4.26a which represents reference specimens.

Furthermore, spreading dye over a large area for the nT PC modified mixtures is enhanced due to the flat surface (superhydrophilic) obtained by this fabric structure which increases with increasing the added nT percent in a specific concentration.

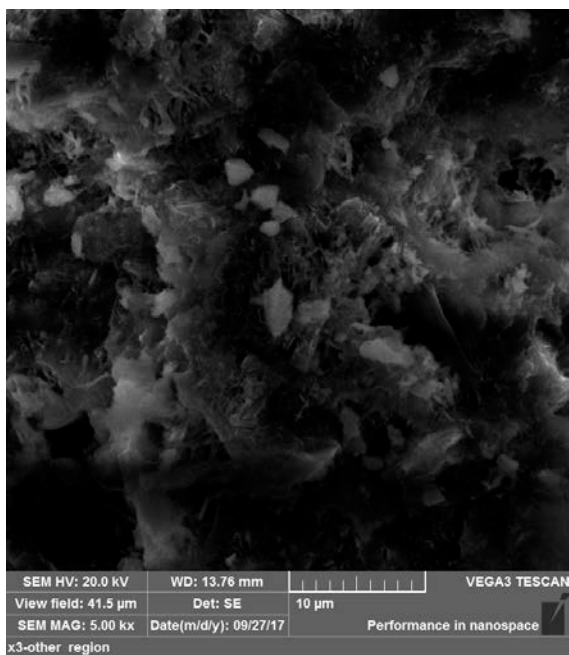


a) Reference cement paste

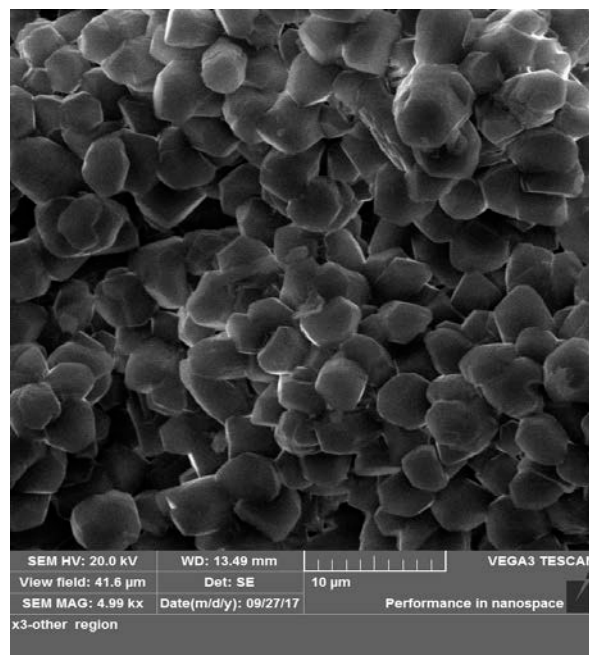


b) Reference mortar specimen

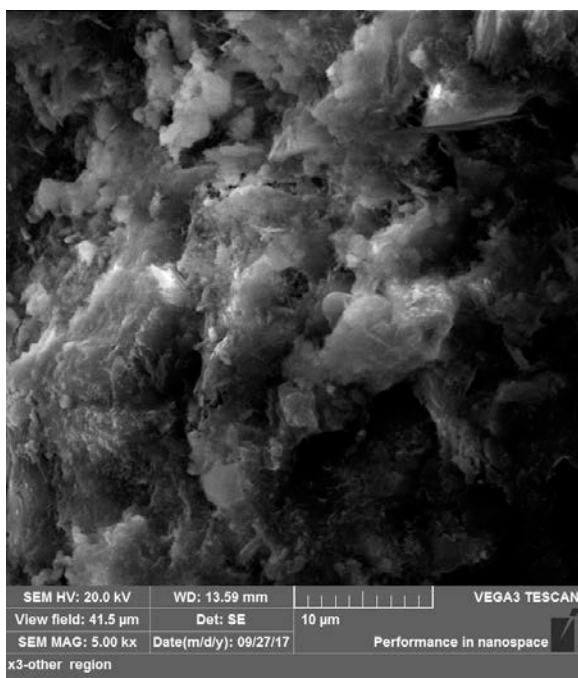
Figure 4.26- SEM images for reference cement paste and mortar specimen



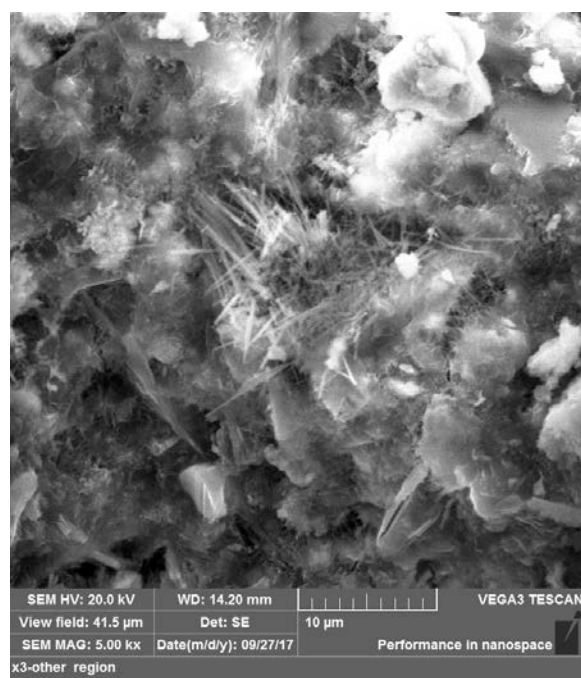
a) 3% mT



b) 6% mT



c) 3% nT



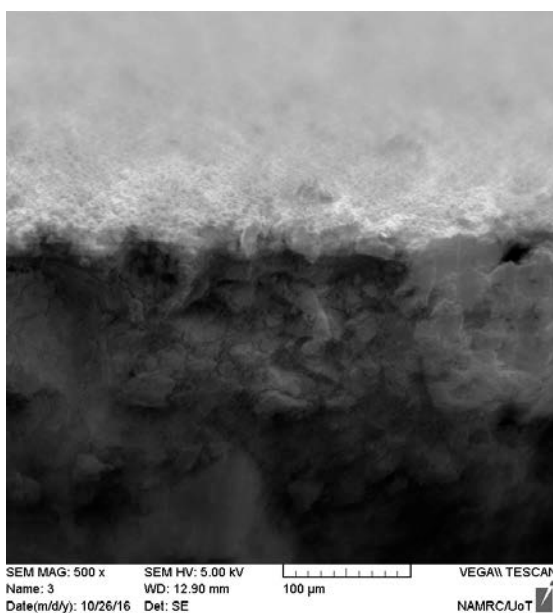
d) 6% nT

Figure 4.27- SEM images for the PC modified mixtures

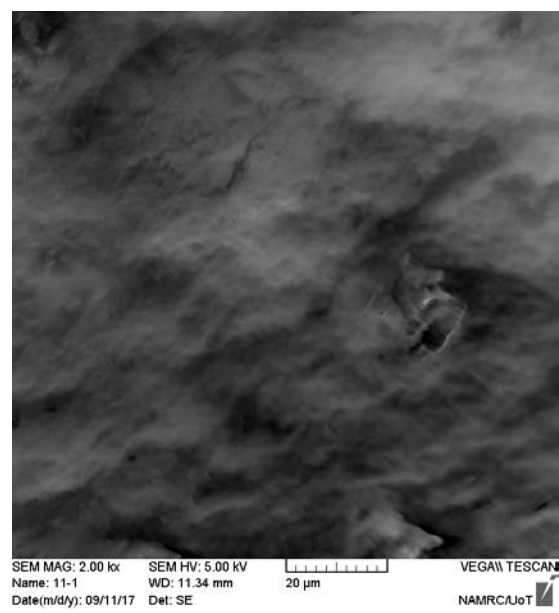
Regarding coated specimens, 5 min- mT sprayed specimen shows a homogenous coated layer, spraying for 5 minutes results in covering specimen with multilayers which may reduce gas removal efficiency due to shielding the bottom layers from illumination as stated by (Faraldos et al. 2016), spraying specimens for 1 min will be enough for gas accessibility with continuous washing and maintenance. mT –dip specimen shows good binding with cement matrix and more available surface area for gas adsorption than mT-sprayed samples.

5 min- nT sprayed specimens show almost thin film homogenous layer which is well bounded with mortar matrix. The structure for the nT- dip shows flocculated agglomerations with fabric appearance which is mixed and well bounded with the mortar mixture. This similar structure between nT- sprayed and dipped specimen is confirmed in the NO and toluene removal efficiencies results which were equal, as shown in Tables 4.4 and 4.5. Figs. 4.26(b) and 4.28 represent reference and coated specimens surface morphology, respectively.

The layer which was formed when spraying micro and nano coatings makes the spreadable dye over the specimen surface more than dipped micro and nano specimens regardless dye discoloration which depends on the amount of the dye absorbed by the specimen and the available reactive surface area.



a) 5 min- mT spray



b) 5 min- nT spray

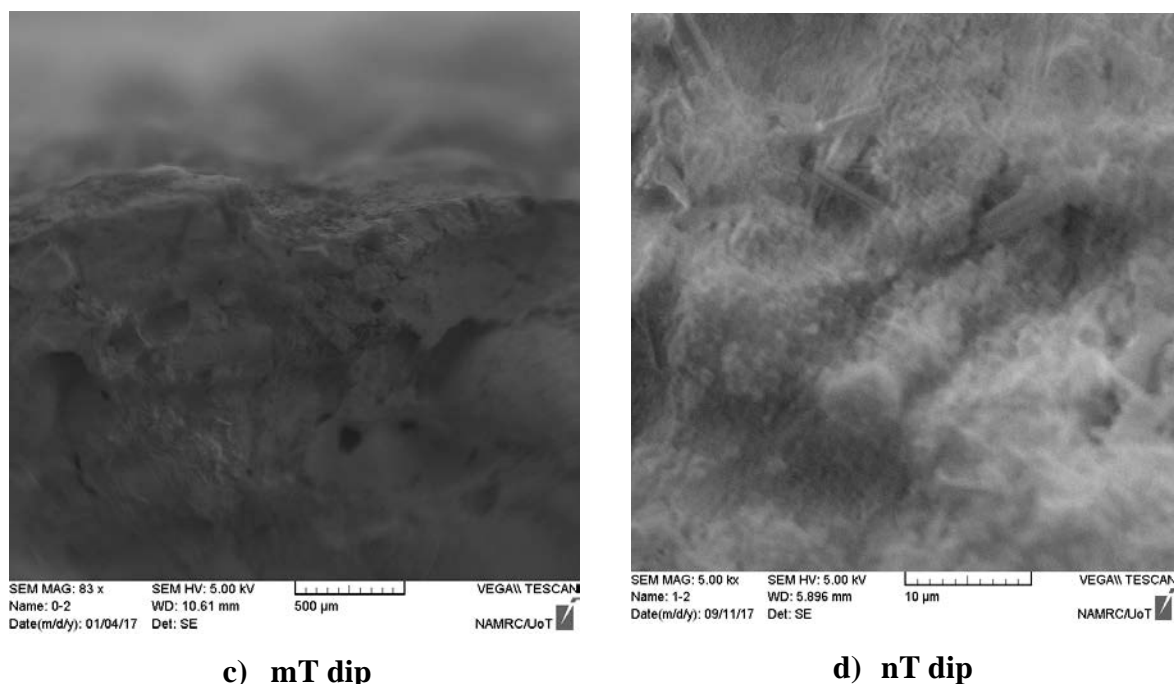


Figure 4.28- SEM images for the mortar spray and dip coatings

4.8 Environmental reality for air pollutants in Baghdad city

Data has been collected from ministry of environment which gives an indication about nitric oxide (NO), nitrogen dioxide (NO₂), ozone (O₃) and non-methane hydrocarbons (NMHC) in Baghdad. The main dependent stations for air pollutants monitoring are Al-Wazeerya and Al-Andalus during the years 2011 to 2014.

The Iraqi ministry of environment legislated NO₂ international limit equals to 0.05 ppm as an average daily exposure, 0.24 ppm NMHC as three hours daily exposure and 0.06 ppm as an average hourly exposure for ozone.

The average annual concentration shows exceeded values from the international limit in the concentrations of (NMHC) at both stations and some exceeding in NO₂ concentrations were found at Al-Andalus station. Al-Andalus zone is considered one of the most crowded areas in Baghdad, traffic jams in addition to the electric generators and hospitals incinerator emissions increase the

concentration of air pollutants in this area. Most of the exceeded values are found in summer season (Jun.-Aug.) and some exceeded values are found in January. Generally, increasing in concentrations happened in stagnant air conditions where pollutants are not transmitted due to slow air movement.

During the years 2011- 2012, 22% of the readings at Al- Wazeerya station exceeded NO₂ acceptable limit which is 0.05 ppm, while 31% of the readings exceeded the acceptable limit at Al- Andalus station (Ministry of Environment 2012).

Concerning NMHC; high concentrations have been monitored during the years 2011- 2012 due to increasing the used cars and fuel combustion beside other sources of gas generation. At Al-Wazeerya station 84% of the readings exceeded the international limit which is 0.24 ppm; Al- Andalus station shows 98% of the values exceeded the limit.

Ozone readings exceeded the international limits (0.06 ppm) where about 6% of the readings at Al-Wazeerya station and 4% at Al-Andalus station exceeded the limit.

Fig. (4. 29) represents NO, NO₂ and O₃ concentration levels during the years 2012, 2013 and 2014, at Al-Wazeerya station. According to data some exceeding readings appeared in July-2012. Generally; an improvement in the concentration levels was noticed although the great variance which appears between NO and NO₂ concentrations.

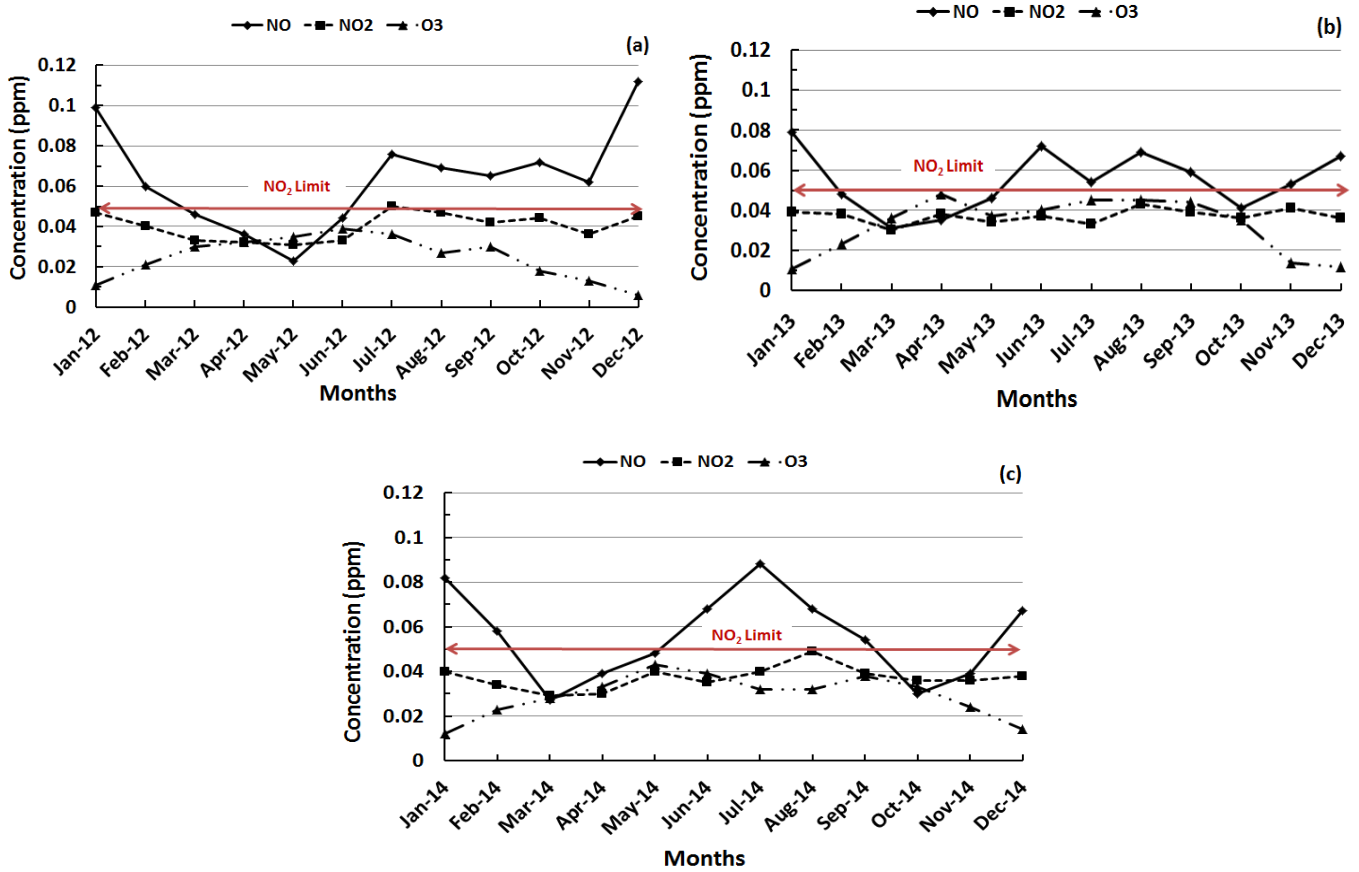


Figure 4.29- Al-Wazeerya pollutants monitoring station through the years: a) 2012; b) 2013; c) 2014 with NO₂ average daily exposure limit equals to 0.05 ppm

Fig. (4.30) shows NO, NO₂ and O₃ concentration levels at Al- Andalus station for the years 2012, 2013 and 2014. An increasing in the concentration levels appeared at July-2012 and August- 2013, in 2014 the concentrations seems to be within exposure limits. The great variance between NO and NO₂ was also noticed.

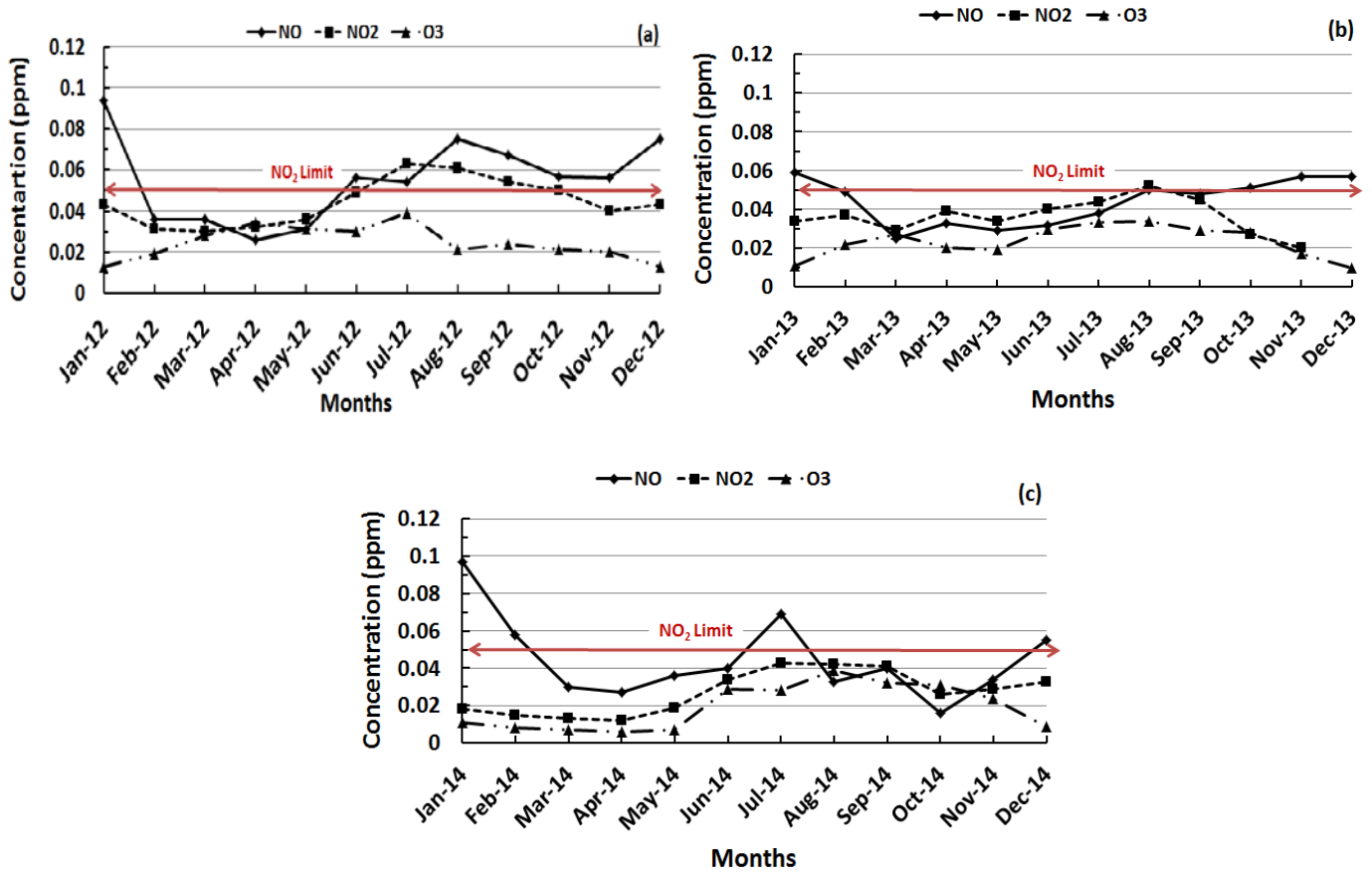


Figure 4.30- Al-Andalus pollutants monitoring station through the years: a) 2012; b) 2013; c) 2014 with NO₂ average daily exposure limit equals to 0.05 ppm

The approximate average annual concentration appeared in Fig. (4.31) for NO, NO₂ and O₃ seem to be within the acceptable limits for both stations, while the average annual concentration for NMHC presented in Fig. (4.32) shows high amounts of exceedings for both stations.

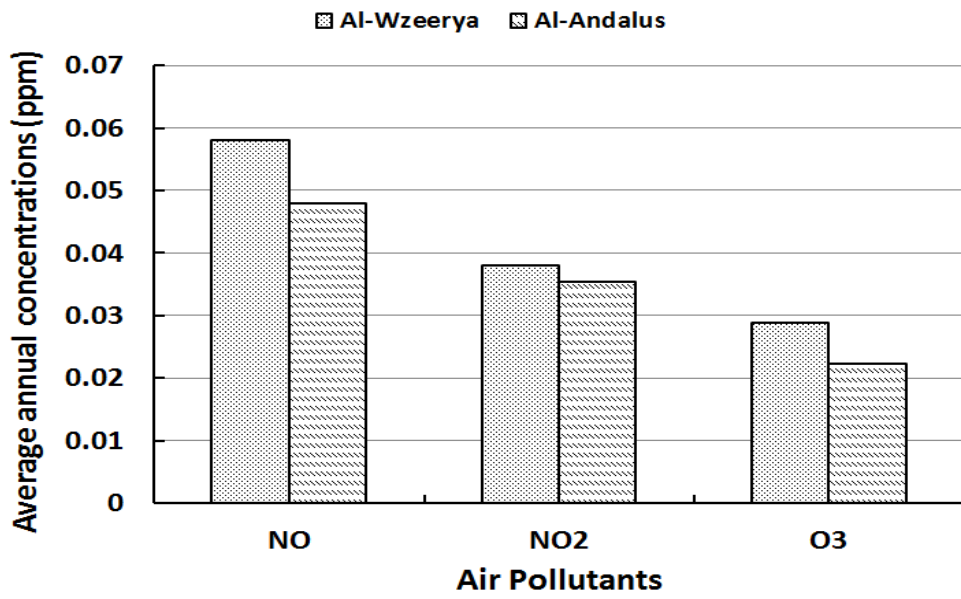


Figure 4.31- Average annual concentration for NO, NO₂ and O₃ in Baghdad city

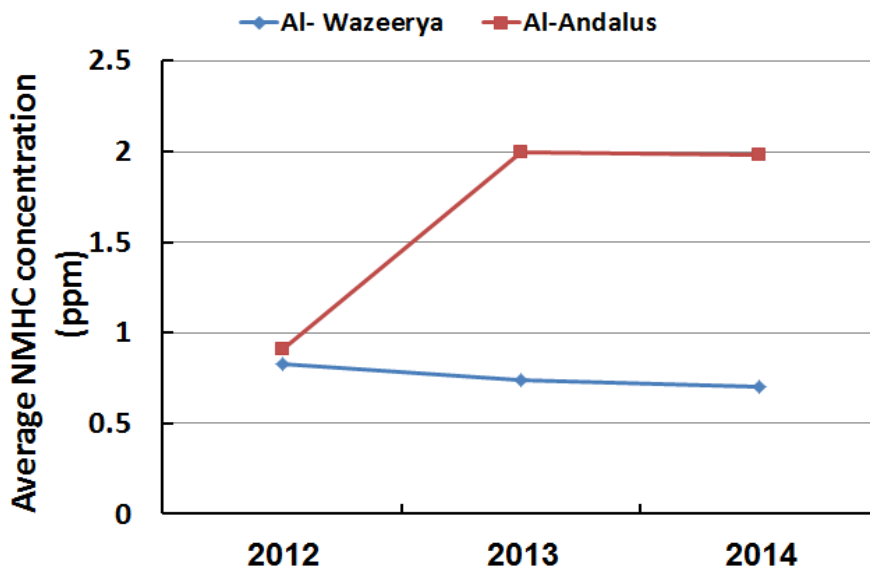


Figure 4.32- Average annual concentration for NMHC in Baghdad city

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

Chapter Five

Conclusions and Recommendations

5.1 General

This chapter introduces the most important conclusions obtained from analyzing and discussion of the results. Recommendations for the benefits of the use of this technology and recommendations for further studies are also presented.

5.2 Conclusions

According to the applied study and the obtained results for the micro and nano TiO₂ PC modified mixtures and coatings; the following conclusions could be drawn:

5.2.1 Early age properties

1. Using micro and nano TiO₂ reduced the final setting time for the used 3% and 6% PC replacements with differences in the time required for the setting between various percentages. Nano TiO₂ replacements increased the hydration process which led to reduce setting time as compared to the micro TiO₂ replacements.
2. A general reduction in compressive strength shown for the 3%, 6% micro TiO₂ and 3% nano replacements at age of 28 days. A little increment has been shown in compressive strength for the 6% nano TiO₂ due to the formed microstructure for the nano material.

5.2.2 PC TiO₂ modified mixtures removal efficiency

1. The use of nT improves the photocatalytic efficiency of PC mixtures subjected to different weather conditions. The levels of improvement

for all PC mixtures with 3% or 6% nT replacements are relatively similar, which indicates that even small concentrations of nT replacement are almost as beneficial as larger concentrations of replacement.

2. Weather conditions strongly affect the PC mixtures modified with TiO₂. In dry conditions, better photocatalytic efficiencies are obtained by PC mixtures modified with nano-titanium dioxide, due to less competition with water molecules and NO as a pollutant gas.
3. In saturated conditions, better efficiencies are obtained by PC mixtures modified with micro-titanium of large particles size and concentration can resist the amounts of excessive water bounded with cement matrix and enhance NO removal efficiency.
4. Toluene was better removed in the moderate weather condition, which is the normal state, because of the sharing of water molecules in the reaction, whereas in the saturation state, no removal appeared because the titanium dioxide particles bound with water molecules and prevented the reaction with toluene.
5. The use of TiO₂ for toluene removal works well at high gas concentrations with increasing residence time for the removal; no removal was observed at low gas concentrations.

5.2.3 Removal efficiency of the Coated specimens with TiO₂ aqueous solution

1. Economic simple methods of spray and dip coatings were adopted on cementitious materials by preparing an aqueous solution contain micro or nano titanium dioxide.
2. Coatings with micro titanium dioxide were less efficient in the removal of NO gas especially when spray method was used, the removal needs

more time to be exhibited.

3. Coatings with micro titanium dioxide were less efficient in the removal of toluene gas especially to the low gas concentration, while the removal enhanced when the inert gas concentration and the time of spraying was increased due to increasing the photocatalytic micro aqueous solution adsorbed by specimen surface.

4. Using dip coating method with micro titanium dioxide solution enhanced the NO gas removal efficiency than spray coating method. Toluene gas removal efficiency was also increased for the high gas concentration.

5. Both dip and spray coatings have the same activity in the removal of NO gas when nano aqueous solution was used.

6. Increasing spraying time to 5 min for the used nano aqueous solution did not affect the removal of both NO and toluene gases. Furthermore, spraying specimen for 5 min may prevent or reduce gas removal efficiency due to shielding the bottom layer from illumination; so spraying for 1 min will be enough for applying a cover layer with continuous washing and maintenance for the coating layer.

7. Both dip and spray coatings were less susceptible to high toluene concentrations, better results were obtained at low gas concentration.

8. Washing nano sprayed specimens showed reduction in the removal efficiency while dipped samples did not reduced the removal efficiency for the specimens.

9. The use of this technology is so important to be applied in the city of Baghdad because of increasing air pollution levels especially near road constructions and other crowded zones. The spray method can be used economically even for the previously constructed buildings.

5.2.4 Self- cleaning performance

1. Self- cleaning performance for the PC modified mixtures was well observed in the 3% and 6% nano- titanium mixtures with high dye degradation and spreading observed in the 6% nT. This indicates the obtained superhydrophilic surface for the specimen when nano- titanium used which helps in the removal and slipping of dirt and easy surface washing.
2. Dye degradation was observed with less surface spreading when micro spray solution used for specimen coating, while nano spray coating showed less dye degradation as compared with micro titanium coating. This could be explained due to the adsorption of nano titanium particles through specimen pores which reduces its activity.
3. Using dip method with nano titanium increased dye degradation and spreading, this is expected due to high activity of nano titanium coating which forms a thin layer over the specimen surface.

5.3 Recommendations

To get the full benefits from this type of photocatalyst as an environmently friendly material; the following applied suggestions and recommendations for future studies are presented:

1. More researches are needed to reach the optimal dose compatible with PC modified specimens while sustaining the material characteristics in the removal of air pollutants due to its formed

microstructure, taking into consideration mechanical properties for the substrates.

2. More percentages between 1% and 6% for the micro and nano titanium dioxide can be investigated to reduce air pollutants.
3. Using titanium dioxide replacements with various cement mixtures by using natural material like recyclable glass, metal cans, rice husk and others.
4. Using nT sprayed with different periods of time for the previously constructed concrete buildings, the around pollutants concentrations can be studied as an applied study for the pollution in Baghdad.
5. Applied study can also be proposed by spraying crowded areas like tunnels with TiO_2 aqueous solution to reduce photochemical pollutants, UV lamps could be used inside these tunnels to help in the reaction with TiO_2 particles.
6. More than one type and concentration of coating solutions, alone or mixed with types of polymers, can be investigated for the mitigation of air pollutants.
7. The photocatalytic efficiency for other types of titanium dioxide (e.g. rutile) with various percent can be studied.
8. Dipping with micro and nano solution can be applied effectively for the precast concrete projects and studying the cost involved by using this method.
9. Studying the effect of the combined gases in the removal by ejecting two types of gases or more together (e.g. NO and toluene), the percent of material saturation can be investigated.

5.4 Recommendations for further work

1. More researches are needed to investigate the removal of other pollutant gases like: CO₂, SO₂, H₂S, CH₄ and other pollutants which can be transferred from one state to another complex type.
2. Researches are needed to the use of TiO₂ with white cement used in architectural purposes and to maintain the self-cleaning performance for the buildings.
3. Studying the aging and saturation limit for the used mixtures and coatings.
4. More researches are needed to study the effect of the surrounding weather parameters like temperature, flow rate, light intensity, pollutant concentration, also the effect of the interaction of the pollutants with each other.
5. Using more types of substrates that can be used in roads paving, roofs and floors finishing.

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Appendix

A-Sample of Nitrogen Oxides Readings

A-1)Portland Cement Mixtures

Normal Condition-3% mT

Time (min)	NO (ppm)	NO₂ (ppm)	NOx (ppm)
0	1	0	1
25	1	0	1
26	0.7	0	0.7
28	0.5	0.1	0.6
44	0.5	0.2	0.7
52	0.5	0.3	0.8
60	0.5	0.4	0.9
67	0.5	0.5	1
69	0.7	0.5	1.2
77	0.7	0.6	1.3
83	1	0.6	1.6
88	1	0.7	1.7
90	1	0.8	1.8
93	1	0.7	1.7
96	1	0.6	1.6
97	1	0.5	1.5
99	1	0.5	1.5
100	1	0.4	1.4
101	0.5	0.4	0.9
102	0	0.4	0.4

Normal Condition-6% mT

Time (min)	NO (ppm)	NO₂ (ppm)	NOx (ppm)
0	1	0	1
25	1	0	1
30	0.7	0.1	0.8
53	0.5	0.1	0.6
68	0.5	0.2	0.7
74	0.5	0.8	1.3
90	1	1.1	2.1
112	1	1.1	2.1

Normal Condition-3% nT

Time (min)	NO (ppm)	NO ₂ (ppm)	NO _x (ppm)
0	1	0	1
25	1	0	1
26	1	0.1	1.1
26.5	0.5	0.2	0.7
27	0	0.2	0.2
30	0	0.3	0.3
39	0	0.4	0.4
55	0	0.5	0.5
79	0	0.6	0.6
90	0	0.7	0.7
101	0.3	0.6	0.9
125	0.5	0.6	1.1
128	0.7	0.6	1.3
130	1	0.6	1.6
135	0	0.7	0.7
137	0	0.6	0.6
142	0	0.6	0.6

Normal Condition-6%nT

Time (min)	NO (ppm)	NO ₂ (ppm)	NO _x (ppm)
0	1	0	1
25	1	0	1
25.5	0.5	0.1	0.6
29.5	0.5	0.2	0.7
30.5	0.3	0.2	0.5
32.5	0	0.2	0.2
37.5	0	0.3	0.3
46.5	0	0.4	0.4
61.5	0	0.5	0.5
78.5	0	0.6	0.6
90	0	0.7	0.7
120	0.3	0.6	0.9
121	0.5	0.6	1.1
122	0.7	0.5	1.2
124	1	0.5	1.5
126	0	0.5	0.5

Saturated Condition-6%**mT**

Time (min)	NO (ppm)	NO₂ (ppm)	NO_x (ppm)
0	1	0	1
25	1	0	1
26	1	0.1	1.1
27	0.7	0.1	0.8
28	0.5	0.1	0.6
31	0.5	0.2	0.7
36	0.3	0.2	0.5
38	0	0.3	0.3
45	0	0.4	0.4
54	0	0.5	0.5
63	0	0.6	0.6
75	0	0.7	0.7
90	0	1.3	1.3
150	0	1.3	1.3

Saturated Condition-3% **nT**

Time (min)	NO (ppm)	NO₂ (ppm)	NO_x (ppm)
0	1	0	1
25	1	0	1
26	1	0.1	1.1
28	1	0.2	1.2
30	0.7	0.2	0.9
34	0.5	0.3	0.8
47	0.5	0.4	0.9
52	0.3	0.4	0.7
64	0	0.5	0.5
84	0	0.6	0.6
90	0	0.6	0.6
150	0	0.6	0.6

Saturated Condition-3% mT

Time (min)	NO (ppm)	NO₂ (ppm)	NO_x (ppm)
0	1	0	1
25	1	0	1
26	0.7	0.1	0.8
34	0.5	0.1	0.6
35	0.5	0.2	0.7
44	0.5	0.3	0.8
47	0.5	0.4	0.9
48	0.5	0.5	1
49	0.5	0.6	1.1
50	0.5	0.7	1.2
51	0.5	0.8	1.3
52	0.3	0.8	1.1
56	0	0.8	0.8
61	0	0.8	0.8
90	0	0.8	0.8
150	0	0.8	0.8

Saturated Condition-6%nT

Time (min)	NO (ppm)	NO₂ (ppm)	NO_x (ppm)
0	1	0	1
25	1	0	1
28	1	0.1	1.1
31	0.7	0.1	0.8
36	0.7	0.2	0.9
39	0.5	0.2	0.7
49	0.5	0.3	0.8
64	0.3	0.4	0.7
69	0	0.4	0.4
81	0	0.5	0.5
90	0	0.5	0.5
150	0	0.5	0.5

Dry Condition-3% mT

Time (min)	NO (ppm)	NO₂ (ppm)	NO_x (ppm)
0	1	0	1
25	1	0	1
26	0.5	0	0.5
28	0.3	0	0.3
38	0.5	0	0.5
48	0.7	0	0.7
50	1	0	1
60	1	0	1
90	1	0	1
100	1	0	1
103	0.7	0	0.7
104	0.5	0	0.5
105	0.3	0	0.3
106	0	0	0

Dry Condition-6% mT

Time (min)	NO (ppm)	NO₂ (ppm)	NO_x (ppm)
0	1	0	1
25	1	0	1
26	0.5	0	0.5
27	0	0.1	0.1
28	0	0.2	0.2
41	0	0.3	0.3
60	0	0.4	0.4
76	0.3	0.5	0.8
79	0.5	0.5	1
87	0.7	0.5	1.2
89	1	0.5	1.5
90	1	0.5	1.5
100	1	0.5	1.5
101	0.7	0.5	1.2
102	0.5	0.4	0.9
103	0.3	0.4	0.7
105	0	0.3	0.3

Dry Condition-3% nT

Time (min)	NO (ppm)	NO ₂ (ppm)	NO _x (ppm)
0	1	0	1
25	1	0	1
25.5	0	0.1	0.1
26	0	0.2	0.2
43	0	0.3	0.3
45	0	0.4	0.4
73	0	0.4	0.4
90	0	0.4	0.4
91	0	0.3	0.3
92	0.3	0.3	0.6
94	0.5	0.3	0.8
100	0.7	0.3	1
105	1	0.3	1.3
110	1	0.3	1.3
111	0.7	0.3	1
112	0.5	0.3	0.8
113	0.3	0.3	0.6
115	0	0.3	0.3

Dry Condition-6% nT

Time (min)	NO (ppm)	NO ₂ (ppm)	NO _x (ppm)
0	1	0	1
25	1	0	1
25.5	0	0.2	0.2
26	0	0.3	0.3
32	0	0.4	0.4
60	0	0.5	0.5
90	0	0.5	0.5
91	0	0.4	0.4
92	0.3	0.3	0.6
93	0.5	0.3	0.8
138	0.7	0.3	1
143	1	0.3	1.3
148	0	0.2	0.2

A-2) Spray Coating Method

1 min-mT spray

Time (min)	NO (ppm)	NO ₂ (ppm)	NO _x (ppm)
0	1	0	1
25	1	0	1
27	0.5	0.1	0.6
29	0.5	0.2	0.7
34	0.5	0.3	0.8
42	0.5	0.4	0.9
45	0.3	0.5	0.8
63	0	0.6	0.6
68	0	0.7	0.7
77	0	0.8	0.8
90	0	0.9	0.9
91	0.3	0.8	1.1
92	0.5	0.8	1.3
100	0.5	0.7	1.2
102	0.7	0.7	1.4
112	1	0.6	1.6

5 min-mT spray

Time (min)	NO (ppm)	NO ₂ (ppm)	NO _x (ppm)
0	1	0	1
25	1	0.2	1.2
26	0.5	0.3	0.8
29	0.5	0.4	0.9
32	0.5	0.5	1
34	0.3	0.5	0.8
44	0	0.6	0.6
49	0	0.7	0.7
59	0	0.8	0.8
90	0.5	0.8	1.3
91	0.5	0.7	1.2
93	1	0.7	1.7

1 min-nT spray

Time (min)	NO (ppm)	NO₂ (ppm)	NO_x (ppm)
0	1	0	1
25	1	0	1
25.5	0.5	0.1	0.6
26	0	0.2	0.2
26.5	0	0.3	0.3
37	0	0.4	0.4
49	0	0.5	0.5
90	0	0.1	0.1
92	0.5	0.1	0.6
96	0.7	0	0.7
101	1	0	1

5min-nT spray

Time (min)	NO (ppm)	NO₂ (ppm)	NO_x (ppm)
0	1	0	1
25	1	0	1
25.5	0.5	0.1	0.6
26	0	0.2	0.2
31	0	0.3	0.3
38	0	0.4	0.4
43	0	0.5	0.5
54	0	0.6	0.6
72	0	0.7	0.7
90	0	0.7	0.7
91	0	0.6	0.6
92	0.5	0.6	1.1
97	0.5	0.5	1
108	0.7	0.4	1.1
128	1	0.3	1.3

A-3) Dip Coating Method

mT- Dip

Time (min)	NO (ppm)	NO ₂ (ppm)	NO _x (ppm)
0	1	0	1
25	1	0	1
25.5	1	0.1	1.1
26	0.5	0.2	0.7
26.5	0	0.3	0.3
27	0	0.4	0.4
28	0	0.5	0.5
29	0	0.6	0.6
30	0	0.7	0.7
33	0	0.8	0.8
36	0	0.9	0.9
38	0	1	1
40	0	1	1
44	0	1	1
48	0	1	1
51	0	1	1
54	0	1	1
57	0	1	1
60	0	1	1
63	0	1	1
69	0	1	1
74	0	1	1
79	0	1	1
87	0	1	1
90	0	1	1
91	0	0.9	0.9
92	0	0.8	0.8
93	0	0.7	0.7
99	0	0.6	0.6
109	0	0.5	0.5
110	0	0.4	0.4

nT-Dip

Time (min)	NO (ppm)	NO₂ (ppm)	NO_x (ppm)
0	1	0	1
25	1	0	1
25.5	0.5	0.2	0.7
26	0	0.3	0.3
26.5	0	0.4	0.4
28	0	0.5	0.5
29	0	0.6	0.6
35	0	0.7	0.7
47	0	0.8	0.8
65	0	0.9	0.9
90	0	0.8	0.8
91	0	0.5	0.5
92	0	0.4	0.4
94	0.3	0.4	0.7
95	0.5	0.4	0.9
105	0.7	0.3	1
115	1	0.3	1.3

B- Sample of Toluene Readings

B-1)Portland Cement Mixtures

Normal Condition-6%*m*T

Residence Time	Toluene Concentration (ppm)
0	5
25	5
61	4
121	4
151	4

Normal Condition-3% *n*T

Residence Time	Toluene Concentration (ppm)
0	5
25	5
36	4
96	4
126	4

Normal Condition-6%*n*T

Residence Time	Toluene Concentration (ppm)
0	5
25	5
33	4
93	4
123	4

Dry Condition-6%*n*T

Residence Time	Toluene Concentration (ppm)
0	5
25	5
52	4
112	4
119	5

B-2) Spray Coating Method

1 min& 5min-microspray-3 ppm

Residence Time	Toluene Concentration (ppm)
0	3
25	3
85	3
136	0

1 min- nanospray-3 ppm

Residence Time	Toluene Concentration (ppm)
0	3
25	3
70	2
130	2
136	3

5 min -nanospray-3ppm

Residence Time	Toluene Concentration (ppm)
0	3
25	3
62	2
122	2
130	3

1 min- microspray-5 ppm

Residence Time	Toluene Concentration (ppm)
0	5
25	5
85	5
136	0

5 min- microspray-5 ppm

Residence Time	Toluene Concentration (ppm)
0	5
25	5
83	4
143	4
148	5

1 min- nanospray-5 ppm

Residence Time	Toluene Concentration (ppm)
0	5
25	5
51	4
111	4
121	5

5 min- nanospray- 5ppm

Residence Time	Toluene Concentration (ppm)
0	5
25	5
41	4
101	4
111	5

B-3) Dip Coating Method

Microdip-3ppm

Residence Time	Toluene Concentration (ppm)
0	3
25	3
85	3
136	0

Nanodip-3ppm

Residence Time	Toluene Concentration (ppm)
0	3
25	3
62	2
122	2
139	3

Microdip-5 ppm

Residence Time	Toluene Concentration (ppm)
0	5
25	5
54	4
114	4
116	5

Nanodip-5 ppm

Residence Time	Toluene Concentration (ppm)
0	5
25	5
45	4
105	4
111	5

الخلاصة

يعد استخدام المواد القابلة للتحفيز او للتفاعل بوجود الضوء مع مواد البناء واحدة من الطرق الحديثة الاستخدام في العقود الاخيرة باعتبارها مواد صديقة للبيئة لحل مشكلة تلوث الهواء الناجم من مصادر التلوث المختلفة كاحتراق الوقود. فبوجود اشعة الشمس ممكن ان تتحول هذه الملوثات الى مواد اكثر تعقيدا مكونة الضباب الدخاني او الضبخان و الاوزون الضار.

تمكنت هذه الدراسة من مقارنة فعالية التحفيز الضوئي لعجينة الاسمنت باضافة نسب معينة من ثاني اوكسيد التيتانيوم بقياس نانوي مع نفس هذه النسب المضافة باستخدام القياس المايكروبي حيث كان كلاهما من نوع اناتس 100%. ولمحاكاة ظروف الجو الطبيعية خلال فصول السنة المختلفة عرضت نماذج الاسمنت الى ظروف رطوبة مختلفة شملت الحالة الطبيعية بنسبة رطوبة 50% والحالة المشبعة بنسبة رطوبة 100% والحالة الجافة بنسبة رطوبة 0%. قورنت فعالية التفاعل الضوئي (القابلية لازالة الغاز الملوث) باستخدام ثاني اوكسيد التيتانيوم مع نماذج مرجعية بدون اضافة. كما تم تحضير خلطة خرسانية اخرى و طلاء قسم من النماذج بمحلول التيتانيوم النانوي والقسم الاخر بمحلول التيتانيوم المايكروبي، استخدمت طريقتي الرش والتغطيس في عملية الطلاء. قياس ازالة الملوثات كان باستخدام مفاعل ضوئي مختبري صمم طبقا للمواصفة العالمية رقم 1-22197 لسنة 2007، كانت الغازات الملوثة المستخدمة هي غاز احادي اوكسيد النتروجين وغاز التولوين. بالاضافة الى ذلك تمت دراسة قابلية التنظيف الذاتي لجميع النماذج المحضرة باستخدام صبغة الميثيلين الزرقاء على سطح النموذج ولوحظ التغيير الحاصل بلون الصبغة مع الزمن بتعريض النماذج الى ضوء الهالوجين.

لمعرفة مستويات تلوث الهواء في مدينة بغداد تم جمع بيانات تراكيز الغازات من محطتي رصد هما محطة الوزيرية ومحطة الاندلس للفترة الزمنية 2012-2014.

أظهرت النتائج بان عجينة الاسمنت المخلوطة مع التيتانيوم النانوي كانت اكثر كفاءة في الجو الجاف. على العكس من ذلك فان النماذج المخلوطة مع التيتانيوم المايكروبي كانت افضل في الجو الرطب. وفيما يخص النماذج المطلية اظهرت النتائج ان الطلاء بالمحلول المايكروبي كان اقل كفاءة في ازالة احادي اوكسيد النتروجين والتولوين خصوصا عند استخدام طريقة الرش في الطلاء، تبين ان النماذج تحتاج الى وقت اطول لحصول عملية الازالة. الطلاء بالتغطيس والرش كلاهما كانا بنفس الكفاءة في ازالة غاز اوكسيد النتروجين عند استخدام المحلول النانوي. كما

تحسنت صفة التنظيف الذاتي للمواد الاسمنتية عند استخدام ثاني اوكسيد التيتانيوم وبمختلف الصيغ.



جمهورية العراق
وزارة التعليم العالي والبحث العلمي
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قسم هندسة البناء والإنشاءات

تطوير قابلية التحفيز الضوئي للخرسانة باستخدام ثاني اوكسيد التيتانيوم لتقليل تلوث الهواء وتحسين ادائها في التنظيف الذاتي

اطروحة مقدمة الى قسم البناء والإنشاءات في الجامعة التكنولوجية كجزء من متطلبات نيل شهادة
دكتوراه في فلسفة الهندسة الصحية والبيئية

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