CONCRETE (PAVEMENTS / ROADS) WITH TITANIUM DIOXIDE AS A PHOTO-CATALYST FOR REMOVING NOx (NITROGEN OXIDES) FROM THE AMBIENT ENVIRONMENT

By

MUHAMMAD SAQIB ALI

NUST201362287MSCEE65213F

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

In

Environmental Science

Institute of Environmental Sciences and Engineering (IESE)

School of Civil and Environmental Engineering (SCEE)

National University of Sciences and Technology (NUST)

Islamabad, Pakistan

2016

It is certified that the contents and forms of the thesis entitled

CONCRETE (PAVEMENTS / ROADS) WITH TITANIUM DIOXIDE AS A PHOTO-CATALYST FOR REMOVING NOx (NITROGEN OXIDES) FROM THE AMBIENT ENVIRONMENT

Submitted by

MUHAMMAD SAQIB ALI

Has been found satisfactory for the requirements of the degree of

Master of Science in Environmental Science

Supervisor: ____________________
Dr. Ishtiaq A. Qazi
Associate Professor
IESE, SCEE, NUST

Member: ___________________________
Dr. Zeeshan Ali Khan
Associate Professor
IESE, SCEE, NUST

External Member:____________________
Mr. Sajid Mahmood
Lab Assistant
Pak-EPA, CLEAN Lab, H-8/2 Islamabad.

DEDICATED TO…….

MY BELOVED PARENTS, SIBLINGS & RESPECTED TEACHERS,

WITHOUT THEIR SUPPORT ALL THIS WOULD NOT HAVE BEEN POSSIBLE

ACKNOWLEDGEMENTS

Praise be to **ALLAH** Almighty who is the ultimate source of knowledge. I am most grateful to Him, the most beneficent and the benevolent of all, whose protection is sorted by all and who bestowed me the mental abilities and wisdom from His unfathomed treasure to complete this research.

I would like to express my special gratitude to my thesis supervisor **Dr. Ishtiaq A. Qazi** (IESE) for his invaluable guidance and support throughout my stay at IESE. I am grateful to him for his continuous moral support, motivation, appreciation, enthusiasm and patience with which he has mentored me and helped me through all steps of my research and thesis writing.

I would like to thank **Dr. Zeshan** (IESE), for his continuous support throughout the research. His efforts gave a whole new dimension to the research work. I would also like to thank **Mr. Sajid Mehmood** (Pak-EPA) for his unfailing moral support as my external advisor. I am also grateful to the staff of the **Waste Water Lab**, IESE for their technical assistance. I am also indebted to the most welcoming and supporting staff of **Structures Lab,** NICE.

I would also like to offer my profoundest gratitude to my **Parents** and **Siblings** for always believing in me and giving me the confidence to stand on my own, and for always been there for me with their undying support.

Last but not the least, I am indebted to all my friends who offered unlimited accompaniment during the nervous breakdown periods to relax me for efficacious work. The special thanks is extended to all of them.

Muhammad Saqib Ali

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

COx	Oxides of carbon
EDS	Energy Dispersive Spectroscopy
IESE	Institute of Environmental Sciences and Engineering
MCS	Mortar concrete samples
MCS-C	Mortar concrete samples – Control
MCSP	Mortar concrete samples (Pure TiO_2)
MCSD	Mortar concrete samples (Doped TiO_2)
NOx	Oxides of Nitrogen
PCS	Mortar concrete samples
PCS-C	Mortar concrete samples – Control
PCSP	Mortar concrete samples (Pure TiO_2)
PCSD	Mortar concrete samples (Doped TiO_2)
SEM	Scanning Electron Microscopy
TiO_2	Titanium Dioxide
TNPs	Titania nanoparticles
UV	Ultra Violet
VOCs	Volatile organic compounds
XRD	X - Ray Diffraction
λ	Wavelength
USEPA	United States Environmental Protection Agency

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Climate change is one of the most pressing concerns of the planet Earth today. And the main cause of climate change in general is the air pollution and in particular the "greenhouse gases". NOx is a family of various oxides of nitrogen that exist in the atmosphere. The most important oxide of Nitrogen however, from climate's point of view is the nitrogen dioxide (NO_2) as it reacts in the atmosphere to form tropospheric Ozone and acid rain. Through Ozone and nitrous oxide (N_2O) formation NOx contribute towards global warming and thereby climate change. Photocatalytic compounds are known to have the properties of removing pollutants from air and water. In this research titanium dioxide was used as an additive to concrete samples for photocatalytic removal of NOx from the air. The work has already been carried out in the past, however, the innovation in this study was a comparison between the removal efficiencies of both Pure as well as Iron-Doped titanium dioxide nano-particles, when applied to concrete samples. Two types of concrete specimens namely mortar concrete samples and pervious concrete samples were constructed, and based on the findings of previous researches, by Hassan et al., and Maria Christina Burton, two best found methods of TiO_2 application for NOx removal were chosen. After the application and curing periods the samples were orderly subjected to porosity tests, compressive strength tests, and finally the environmental tests. The results show that the addition of TiO_2 to pervious concrete does reduces its porous nature to some extent, however even with the highest concentration of Titania (15%) all the pervious concrete samples were found to be within the target porosity range of 15% to 20%. Compressive strength tests of both the mortar and pervious concrete samples suggested that the strength of the concrete increased as the concentration of the TiO_2 was increased from 0% to 15% replacement by weight of cement. Finally, the environmental tests were performed and it was found that the photocatalytic NOx removal efficiency of the concrete increases with the increasing concentration of TiO_2. However, increasing concentration of TiO_2 may not always be beneficial for concrete, as in the pervious concrete it reduce its porosity. Similarly in case of the mortar concrete the compressive strength starts decreasing when more than 18% of the cement is replaced with TiO_2, (Husnain, 2015). Therefore an optimum concentration TiO_2 was chosen to be 15% replacement by weight of cement as even at this concentration significant quantities of NOx removal were achieved during the environmental tests.

Chapter 1

INTRODUCTION

The world faces a significant challenge in controlling air pollution resulting from transportation activities and the growing population density. High traffic volumes cause high concentrations of nitrogen oxides (NOx) and volatile organic compounds (VOCs) to be released into the air, which have been linked with serious health hazards to the public. These pollutants may also travel long distances to produce secondary pollutants such as acid rain or ozone. Although attempts have been made to lower vehicle emission standards, a method is needed to remove air pollutants once they are emitted to the atmosphere. This is particularly important in urban and metropolitan areas, where tall buildings prevent the dispersion of air pollutants originating at the street level from road traffic.

Heterogeneous photo-catalysis is an illustration of the developing environmental control choice for an effective remediation of chemicals and pollutants in air and water. This procedure includes a nano-solid semiconductor catalyst, normally titanium dioxide (TiO_2). In this research titanium dioxide was used as an additive to concrete samples for photocatalytic removal of NOx from the air. The work has already been carried out in the past, however, the innovation in this study was a comparison between the removal efficiencies of both Pure as well as Iron-Doped titanium dioxide nano-particles, when applied to pervious and mortar concrete samples.

Nitrogen oxides (NOx) are a very interesting and important family of air polluting chemical compounds. NO_x is not only an important air pollutant by itself, but also reacts in the atmosphere to form ozone (O_3) and acid rain. It is important to note that the ozone that we want to minimize is tropospheric ozone; that is, ozone in the ambient air that we breathe. Moreover, the oxides of nitrogen also react with water vapors in the atmosphere to form either nitric (HNO_3) or nitrous acid (HNO_2). Thus, NOx and its derivatives exist and react either as gases in the air, as acids in droplets of water, or as a salt. These gases, acid gases and salts together contribute to pollution effects that have been observed and attributed to acid rain (U.S EPA 1999).

1.1 Problem Statement

In order for the life to exist on the planet Earth air and water are the pre-requisites. The exceeding transportation frameworks and increasing vehicular load in urban areas create a lot of air contamination because of vehicular emissions, and they lessen the measure of groundwater recharge because of the broad utilization of impervious asphalts for road and pavement constructions. Moreover, the impermeable pavements add to the urban heat island impact. Such issues are not characteristic, and the bigger the urban areas develop, the greater is the damage to the quality of life on Earth and the situation will worsen. It is essential to keep our air and water clean and charged to acceptable natural groundwater levels so that the Earth can have a sustained and balanced ecosystem for our generations to come, without being devastated.

1.2 Objectives

The objectives of this research work were:

(i) To evaluate the effectiveness of TiO_2 treated concrete for NOx removal.
(ii) To compare the process efficiencies between pure and doped Titania nano-particles.
(iii) To compare the process efficiencies between pervious and impervious (mortar) concrete samples.
(iv) To evaluate the impact of Titania nano-particles on the porosity and strength of concrete.

1.2.1 Significance of Work

Coating of Titania nano-particles on pavements and roads is an effective way of controlling many hazardous air pollutants including NOx, COx and various other VOCs. This research work primarily focuses on the photo-catalytic removal of NOx, which is a very significant air pollutant and is a precursor to several environmental problems such as photochemical smog, tropospheric ozone formation, and acid rain.

Air and water are the basic life necessities for the people of Earth. Cities and urban centers with growing populations and ever increasing traffic and transport systems contribute a major amount of air pollution in the form of vehicular emissions.

This is not a natural phenomenon, the larger the cities grow the greater is their contribution towards the disruption of natural ecosystems and air quality. Therefore the removal of NOx and other air pollutants from the ambient air stream is of prime importance for not only improving the quality of life today, but also for the folks to follow.

LITERATIRE REVIEW

2.1 Background

Fujishima and Honda were the principal researchers to find photocatalytic synergistic properties of Titanium dioxide (TiO_2). TiO_2 additionally called "titania" is a semiconductor and happens in three diverse crystalline structures; anatase, rutile, and brookite. According to research TiO_2 in anatase form shows the most astounding photo-catalytic efficiency. It is because of these properties that when TiO_2 upon exposure to UV radiation knocks the electrons (e-) out subsequently creating oxidizing holes (h^+). These light generated electrons and holes then react with water vapors in the environment to produce hydroxyl radicals and superoxide ions as shown by the following chemical equations:

$$TiO_2 + hv \rightarrow h^+ + e^-$$

$$OH^- + h^+ \rightarrow OH^\cdot$$

$$O_2 + e^- \rightarrow O_2^-$$

These hydroxyl radicals and superoxide ions play a vital role in photocatalytic redox reactions. A similar reaction which oxidizes the NOx in the atmosphere can be shown as follows:

$$NO + OH^- \xrightarrow{TiO2} NO_2 + H^+$$

$$NO_2 + OH^- \xrightarrow{TiO2} NO_3 + H^+$$

The nitrates that result as a consequence of these photo-catalytic reactions are washed away by the following rain in case of Mortar concrete, and in case of pervious concrete they leach down to the soils where they may be taken up by nitrogen fixing bacteria thereby not only reducing air pollution but also improving soil fertility.

2.2 Introduction to Nitrogen Oxides

NOx is a group of highly reactive gases which are oxides of Nitrogen with varying amounts of nitrogen and oxygen. Most of the nitrogen oxides have no color or odor except for a common air pollutant the nitrogen dioxide (NO_2) which has reddish-brown color and its particulates can be seen as a brownish layer over numerous urban regions. NOx are generated upon fuel combustion at high temperatures, as in vehicular emissions. The typical sources of NOx are vehicular exhausts, electric appliances, and other industrial, commercial, and residential sources that burn fuels.

NOx is one of the main constituents responsible for the development of ground level ozone, which can trigger genuine respiratory issues. In the atmosphere it reacts to form nitrate particles, corrosive mist concentrates (acid rain), aerosols and NO_2, which likewise bring about respiratory issues. NOx adds to the formation of atmospheric particulates thereby causing visual impairments. In addition to these NOx contributes to the formation of secondary pollutants that in turn result in global warming.

2.2.1 NO_x Sources in the Atmosphere

Nitrous oxide (N_2O), NO, and NO_2 are the most prevalent nitrogen oxides in the atmosphere. Most of NOx in the air coming from burning processes are principally in the form of NO. With the exception of NO from soils, lightning and natural fires, NO is to a great extent anthropogenic (i.e., produced by human activities). Biogenic sources are by and large thought to represent under 10% of aggregate NO outflows.

2.2.2 NO_x Toxicity

NOx causes a variety of health and environmental impacts. In the atmosphere it excels the generation of photochemical smog and Tropospheric Ozone when upon interacting with VOCs (volatile organic compounds) in the daylight and heat. Kids and individuals with lung ailments, for example, asthma, and individuals who work or practice outdoors, are defenseless to different unfavorable impacts, for example, harm to lung tissue and decrease in lung capacity. Additionally this tropospheric ozone likewise creates destructive impacts for vegetation and crops, subsequently reducing product yields.

NO produces the same inability to assimilate oxygen into the blood as carbon monoxide (CO). Notwithstanding, since NO is just sparingly soluble in water, it represents no genuine risk except to newborn children and extremely sensitive people. NOx react with ammonia and water vapors to form nitric acid fumes which if breathed in can bring about extreme lung and respiratory system damage and may even lead to premature deaths. Small nitric acid particles can infiltrate deep into the lungs and intensify lung illnesses, for example, emphysema and bronchitis and aggravates heart illnesses.

Another unsafe effect of raised barometrical NOx concentrations is the acid rain. NOx experiences different responses in the climate which incorporate the development of nitic (HNO_3) and nitrous (HNO_2) acids. At the point when these acids come down with precipitation they harm the vegetation, infrastructure and damage the water quality in lakes and water streams (pH changes), along these lines causing harm to aquatic life. Elevated nitrogen content of the water bodies promotes eutrophication eventually causing higher COD and BOD, thus making the environment unfavorable for the aquatic life.

2.2.3 NOx Treatment Methods

There are various techniques for controlling NOx discharges. Gas scrubbing is a standout amongst the most widely recognized types of NOx treatment, with sodium hydroxide being the customary scouring medium. Scouring or scrubbing agents containing hydrogen peroxide are also viable at controlling NOx. A few different alternatives of such substance scrubbers are available as well, however these strategies can only be applied for NOx removal at smaller scales i.e industrial exhausts and chemical processes. The removal of NOx from the surrounding air requires a somewhat all the more generally pertinent and in addition monetarily plausible methodology. Photocatalytic NOx expulsion from the encompassing air stream is therefore observed to be a suitable choice, using the semiconductor TiO_2 (titanium dioxide) nano particles. TiO_2 is excited by the ultraviolet radiation present in the sunlight. Titanium dioxide as "anatase" has been the favored choice because of its strong oxidizing power under UV light, its chemically stable nature and the absence of toxicity (R.W. Methews, 1986).

These reactions are exceptionally appealing for treating contamination issues on the grounds that:

- They change pollutants into harmless items in majority of the cases.
- They have low selectivity, in this manner allowing the treatment of an extensive variety of contaminants (E. Pellizzetti et al., 1991).

2.3 Titanium Dioxide

Titanium dioxide occurs naturally and is used in a variety of daily use products such as toothpaste, sunscreen, paint, plastics, beauty care products, and different items. Since it is white, safe, and economical, TiO_2 powders have been known to be used as white pigments (Hashimoto, Irie, and Fujishima, 2005). It is also an ingredient to sun-block and sunscreens owing to its assimilative properties towards the UV rays (Katzman, 2006).

2.3.1 Titania Polymorphs

Titania exists in three polymorphs i-e anatase, brookite and rutile. It has been seen that photocatalytic degradation involves only anatse and rutile phase (Augugliaro et al., 1988). Almost all studies have used Anatase and Rutile phase of TiO_2 in photocatalytic degradation processes. Of the two, the Anatase phase is the preferred polymorph having highest photo-catalytic degradation activity (Beydoun *et al.,* 1999; Carp *et al*., 2004). Crystal structure of polymorphs of TiO_2, Rutile, Anatase, Brookite are shown in Fig.2.1

Titania exists in three polymorphs i-e anatase, brookite and rutile. It has been seen that photocatalytic degradation includes just anatse and rutile phases (Augugliaro et al., 1988). All studies have utilized Anatase and Rutile phases of TiO_2 in photocatalytic degradation procedures. Of the two, the Anatase stage is the favored polymorph having most elevated photocatalytic degradation action (Beydoun et al., 1999; Carp et al., 2004). Crystalline structure of polymorphs of TiO_2, Rutile, Anatase, Brookite are depicted in Fig.2.1

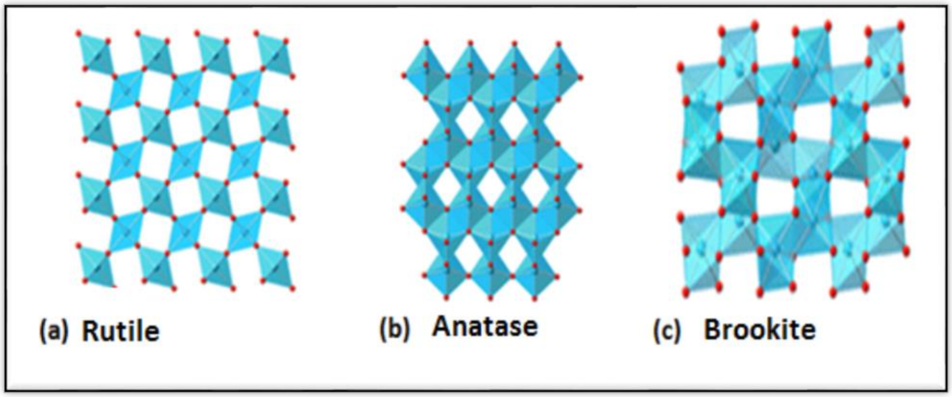

Figure 2.1: Crystal Structures of Polymorphs of TiO_2

Table 2.1: Required Wavelengths for activation of Polymorphs of TiO_2

Polymorph	**Band Gap Value**	**λ Photo-excitation (nm)**
Rutile	3.2 eV	Upto 385
Anatase	3.02 eV	Upto 385
Brookite	2.96 eV	Upto 375

4.3.2 Applications of Titania Nanoparticles

While, natural contamination remediation, self-cleaning and self-sanitization are the key utilizations of titania based photo-catalytic building materials (Chen et al., 2012), there is a possibility for utilizing chromium-tanned leather as a part of structural designing to get specialized, monetary and ecological advantages (Oliveria et al., 2012). Titania usage for sequestering NOx and volatile organic compounds has attracted prominent consideration of the civil engineering groups in light of the potential advantages in controlling environmental contamination (Cardenas et al., 2012). White cement with Titania not only possesses photo-catalytic properties for harmful air pollutant removal from the urban environment, but also keeps up the tasteful traits of cement overtime. White cement is also known to increase the compressive strength of concrete (Cassar et al., 2003).

Moreover, a few nanomaterials including Titania can be utilized as a part of cementitious materials to enhance their physicochemical properties in cement, mortar and concrete (Chen et al., 2012). Correspondingly, appropriate replacement of cement with nanophase Titania particles enhances the compressive strength of mortar and concrete (Nazari et al., 2010). The introduction of nano-titania powders in cement is known to reduce the porosity of these materials significantly, thereby, increasing their mechanical strength. Hence, the compression strength of concrete and mortar increases, essentially at the early stage (Meng et al., 2011).

4.3.3 Photocatalytic Effect of TiO_2

In sunlight TiO_2 exhibits photocatalytic properties and transforms into a "photo-active bleach" (Hashimoto et al., 2005). A photocatalytic material makes use of sunlight to catalyze chemical processes without being expended or exhausted all the while" (Chusid, 2006). Photo-catalysis of TiO_2 powders initiated fashioning mechanical innovation in the 1980s (Hashimoto et al., 2005). Diverse photocatalytic reactions have been examined for over half a century (Puzenat, 2009). European and Japanese scientists have been busy examining the photocatalytic mixes in order to find how they can be fashioned to decrease contamination for more than 4 years, starting 2006 (Katzman, 2006).

During the day time in the sunlight TiO_2 is stimulated by the UV rays (Wavelength < 390 nm) and thus the air pollutants are oxidized. Examples include nitrogen oxides (NO_x) and volatile organic compounds (VOCs). These pollutants are broken down into simpler inorganic complexes. This happens in a photocatalytic reaction in the presence of TiO_2 whereas, no chemical reactants are exploited. There is no consumption of TiO_2 in the process, therefore, it can hypothetically be utilized indeterminately. Photo-catalysis by TiO_2 can even take place in weak UV light (Hashimoto et al., 2005). The band-gap of TiO_2 in the anatase phase is quite wide and thereby, requires a UV light with wavelength under 387 nm (Fernandez-Rodriguez et al., 2009; Hong et al., 2005).

Pollutants such as dirt, biological organisms (mold, algea, bacteria and allergens), aerosols (VOCs, NOx, and Sox) and odor causing chemicals are decomposed by the photocatalysts activated by UV radiations (Chusid, 2006). Majority of the inorganic pollutants such as rust stains are resistant to catalysis (Chusid, 2006). The disintegration products in these reactions are normally oxygen, carbon dioxide, water, sulfate, nitrate, and other inorganic particles.

A variety of market products use these photocatalytic reactions and thus have self-sanitizing properties (Puzenat, 2009). Some of the examples include glasses, tiles, and concrete etc. Cement industry makes use of titanium dioxide as an additional ingredient to the cement for synthesizing ceramics for tiles etc., however the product is photo-catalytically active at the surface where photocatalytic particles are exposed to the environment (Puzenat, 2009). Such products have self-cleaning characteristics and sequester NOx in the surroundings. These usage techniques are primarily created in Japan specifically by Toto Company as well as in Europe with their product TX Active, by Italcementi.

A cement developed recently by an Italian company "Italcementi" included Titanium dioxide and was named "TX Active" ("cement with a capacity to absorb pollutants," 2006). Experimentation of this cement after applying to the road have been found to reduce up to 65% NOx and cabon monoxide. This removal percentage was found to be higher on days with brighter sunlight

Cement with photocatalytic properties is starting to find its use as a part of design and structural building ventures in various parts of the world. Advantages of photocatalytic cement are that it helps decay the chemicals that add to soiling and reduce atmospheric contamination, the concrete stays tidier and sends greater proportions of sunlight back by reflection due to its white color, thereby decreasing heat absorption (Chusid, 2006). The prepared cement based Jubilee Church of Rome which was constructed in the year 2003 incorporated white-cement blocks that at a height of 85 feet. In order to keep it clean in the contaminated locality in which it is located, a photocatalytic concrete "TX Active" was utilized (Chusid, 2006).

As it has recently been found that TiO_2 is an amazing photo-catalyst that can be used in pavement engineering for controlling vehicular emissions (Chen & Liu, 2010). The photo-catalytic effect of Titania on a concrete pavement supporting transport is illustrated by the Fig. 2.2. Emission from the vehicular exhausts get adsorbed to the pavement right near the source and the air remains cleaner. The TiO_2 photo-active coating on the surface of the concrete breaks down the pollutants and the final products, nitrates in case of NOx, desorb from the pavement with the following rainfall and the pavements becomes ready to adsorb more pollutants.

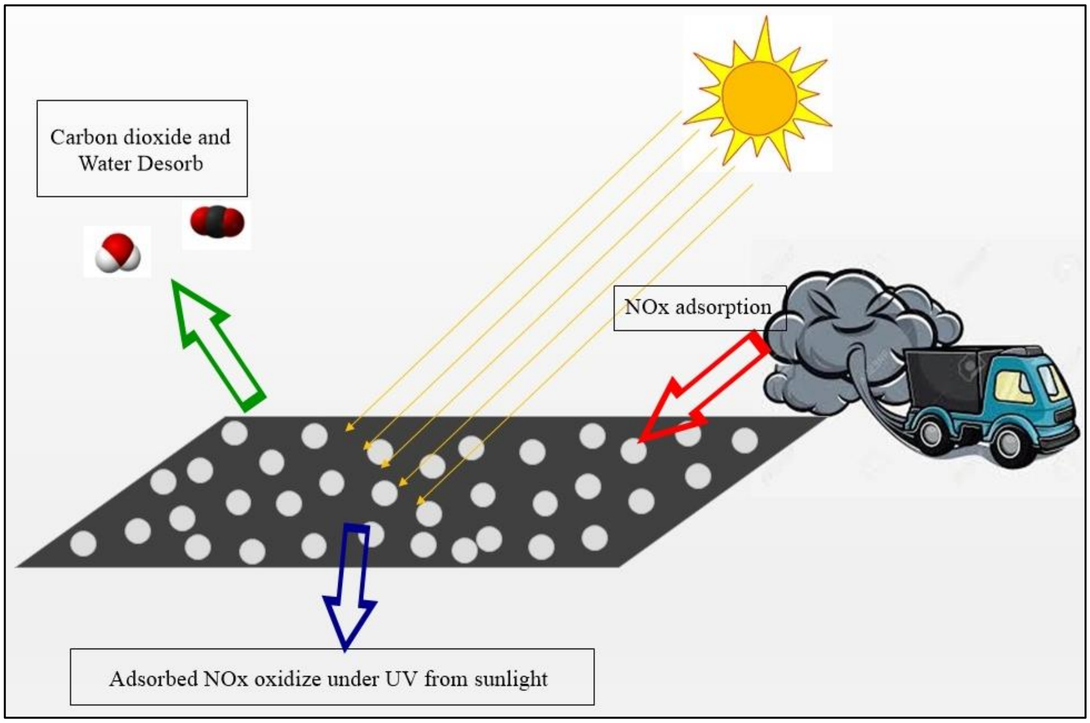

Figure 2.2: Photo-catalysis through titanium dioxide in sunlight

4.3.4 Photocatalytic Effect in Water

In addition to TiO_2 being utilized for evacuating toxins that are airborne, but also it has been utilized for treating contaminations in water. In 2006 TiO_2 was utilized in a photo-catalytic process for treating benzene, toluene, ethylbenzene, and xylene isomers contamination in groundwater, and was found to be a powerful ex-situ strategy in groundwater disinfection. Despite that the photocatalytic degree of natural toxins in water treatment works, this is however, hard to isolate and recover the little TiO_2 suspended particles (Bolt et al., 2011; Shi et al. 2009). Since this can be a noteworthy issue, Bolt et al. (2011) proposes a more reasonable option is to consolidate TiO_2 into cementitious development materials, which will immobilize the TiO_2 while still permitting photocatalytic process to happen.

4.3.5 Hydrophilic Effect of TiO2

At the point when photocatalytic oxidation decays recoloring aggravates that are consumed on a surface, the surface is cleaned and changed over into a very hydrophilic state (Hashimoto et al., 2005). The adsorbed blemishes and pollutants on the concrete surface can be drained off the hydrophilic surface of TiO_2 effectively by the water, devouring a self-sanitizing capacity. It is also possible to defog some surfaces like glasses and mirrors that normally develop mist or fog by applying TiO_2 on the surface due to its hydrophilic properties. Films of Titanium dioxide when coated to glass can oxidize tinges on the windows by the process of photocatalysis when exposed to sunlight. It can also remove various biological and nonliving unwanted mineral substances in the presence of moisture (photoinduced superhydrophilicity) (Puzenat, 2009).

4.3.6 Factors Affecting Photocatalytic Effect

Different environmental factors that influence the process of photocatalysis include the wavelength of light and its intensity, the relative humidity level, as well as the air temperature and the speed of wind. The finest outcomes of the photocatalytic process can be observed at elevated temperatures and on bright sunny days light intensities of light above 300nm (Katzman, 2006). A hot and sunny day with suppressed humidity level and low wind speed would be an ideal set of conditions to sequester air contaminants through photocatalysis.

Elements that have the ability to influence the photocatalysis of TiO_2 as an additive to cement might involve the concrete porosity, the relative humidity level, the size and type of aggregate being made use of, as well as the application procedure etc.

In 2009 Ramirez et al. watched improved maintenance of TiO_2 particles on the specimen exterior and observed an advanced toluene capture efficacy as the specimens with greater porosities were used. Increasing humidity hindered the removal efficiency of nitric oxide (Dylla et al., 2010). Coats with coarser aggregates had greater NOx expulsion effectiveness as compared to the coats with fine aggregate (sand) (Dylla, 2010). In a concrete application study conducted by (Hassan, Dylla, & Rupnow, 2010), it was found that abrading reenactment by stacked wheel tests uncovered a percentage of the TiO_2 particles applied to the exterior thereby increasing the NOx evacuation effectiveness, whereas, upon application of rotary-abrasion tests appeared to diminish the efficiency of NOx expulsion. (Hassan, Dylla, & Rupnow, 2010)

4.4 Titania as Cement Additive

The quality of photo-catalysis of titanium dioxide in concrete is being used for capturing smog (brown haze reduction), biocidal effect, super hydrophilic and self-cleaning properties. The role of TiO2 in diminishing Nitrogen Oxides (NOx) and Volatile Organic Compounds (VOC's) has been an eye-catching development for civil engineers in view of its potential advantages while diminishing contamination (Maggos et al., 2007).

One of the key ingredients for decorative and architectural concrete is the white cement which, nowadays, contains TiO_2 as an additive. It not only give the concrete greater mechanical strength but a higher aesthetic value as well. White cement with TiO_2 contributes to atmospheric cleaning over the time due to its photo-catalytic properties and removes various potentially dangerous pollutants from the ambient urban air stream. Moreover titanium nanoparticles are used to increase mechanical strength (compressive strength) of the concrete (Moiz et al., 2013).

The advancement in research essentially stimulates the pragmatic utilizations of Titania nanoparticles specifically in the field of innovative photo-catalytic construction and building materials. The popularity of Titania embedded building materials has been sky-rocketing because of the fact it has been conventionally used as a part of the white pigment. Prominent uses of Titania based photo-catalytic construction materials include natural contamination remediation, environmental pollution control, self-cleaning and self-purifying. The upside of utilizing daylight and water as main thrust has prompted a new area for environmental friendly products and building materials (Chen et al., 2009). Nano-particles have also been found useful for various applications in the medicine industry (Yang Xia et al., 2008).

4.4.1 Coating of Concrete and Asphalt Pavements

Chen working with his co-worker Liu in 2010 found that nano-TiO_2 has the ability to cleanse vehicular emissions in a real traffic environment (Chen & Liu, 2010). They were successful in removing NOx from the vehicles with the help of TiO_2 incorporated to concrete roads. Filtering the transportation transmitted NOx demonstrated great sterilizing impacts, with a removal rate higher than 20%. They also found a direct relationship between the NOx removal percentage and increasing humidity level of the air. In relatively drier environments (little moisture), the moist film formation on the TiO_2 had little effect.

In spite of the fact that TiO_2 behavior on concrete has been demonstrated to expel contaminations of the transportation discharges (Chen & Liu, 2010), studies are still carried out on developing the TiO_2 treatment into a safe mean of pollution sequestration against vehicular discharges as well as the characteristic disintegration of concrete. Recently, three distinct procedure of TiO_2 application to concrete have been reported in a study carried out in Louisiana (Hassan et al., 2010). In the first method an application of cement-water coating with ultrafine sand and TiO_2 was applied to the surface of concrete blocks, in the second an ultra-thin layer of water based TiO_2 was applied to the surface (PURETI), and in the third powdered nano sized TiO_2 was sprinkled over the fresh concrete surface prior to curing. After the experiments for environmental tests were run the first type of coating which was a cement-water mix with ultra-fine sand and a 5% concentration of TiO_2 nano-particles was fond to have achieved the highest percentage of NOx removal, exhibiting an efficiency of 26.9%. The environmental tests were carried out for 5 hours in an experimental setup capable of simulating different environmental conditions. The conditions set for these test however included a 50% humidity, room temperature, florescent and UV light sources, a pollutant gas flow-rate of 9 L/min, and starting NOx concentration levels of 410 ppb.

Concrete with TiO_2 coatings was introduced to atmospheric conditions for varying periods in 5 distinctive streets in Hong Kong, (Chen-Mei Yu, 2003). The photocatalysis of the TiO_2 covered blocks diminished in overwhelming passerby activity ranges, as contaminants amassed at the concrete exterior (Chen-Mei Yu, 2003). Streets with low passerby movements produced very insignificant difference in NOx removal activity of these blocks. Responsive surface region was rendered ineffective due to amassing of dust, oily discharges and also disposed of bubble gum (Chen-Mei Yu, 2003)

In 2009 Ramirez with his co-workers tried 8 distinctive cement based material specimen sorts with two different TiO_2 coating methods: dip-coating and sol-gel (Ramirez, 2009). A try was made to sequester toluene and evaluate the effectiveness of the process and resistance against weathering, portrayed under various streams of ir as well as water in order to simulate different weather conditions. Of all the samples, four were the regular marketable constituents including cement/mortar constituents essentially utilized in floor/wall covering. Remaining four specimens included substrate constituents, including one commercially available white cement and 3 cement slabs produced via various treatment procedures.

4.5 Other TiO2 Applications

Different building resources for nitrogen oxides' sequestration occur for open-air and enclosed environments. In 2007 an inorganic paint available commercially containing 3 % TiO_2 accomplished a NOx evacuation of about 0.21 µg / m^2 s (Chen & Yuan, 2007). Another lustrous dye containing 5 % TiO_2 accomplished a NOx evacuation of about 0.06 µg / m^2 s. TiO_2 is also utilized to purify the air pollution, avert natural products and grocery items etc. from rotting thereby expanding their shelf life (Frazer, 2001).

More usages of TiO_2 are wastewater remediation and purification, disinfection of rice-hull, treatment of water and riding it of hydrophobic culture systems, soil treatment, sequestration of VOCs from air as well as effective water vaporization from hydrophilic faces (Hashimoto, Irie, & Fujishima, 2005)

4.6 TiO_2 Cost

United States has diminutive marketable obtainability of photocatalytic construction resources (Katzman, 2006). Starting in 2006, TiO_2 atmospheric contamination control items were primarily obtained from two companies Essroc and Green Millenium. An organization in U.S. outlined a procedure in 2004 which utilizes an electrical spraying equipment to coat a water dissolved TiO_2 to an assortment of surfaces. Such items sprayed with TiO_2 are employed to retain the cleanliness of the surfaces, for example, infrastructure, airplane, ships, rugs, and windows.

4.7 TiO_2 Maintenance

Sequestration of nitrogen oxides through TiO_2 is self-sustained once it in incorporated in the concrete. The adsorbed calcium nitrate at concrete exterior is drained and flushed off by precipitation (Chen et al., 2007). This happens during a photocatalysis reaction driven by TiO_2, which itself remains unconsumed in the process, and therefore can hypothetically be utilized indeterminately.

Research is going on to find the most feasible method of TiO_2 treatment for concrete surfaces to counter the effects of increasing traffic and natural weathering. In Louisiana State University, in December 2010, the first air cleaning concrete pavement of US was laid (Berthelot, 2010). Before field usage, research center assessment led at the State University Louisiana, demonstrated 25.0% proficiency of NOx expulsion with the concrete samples sprayed with water soluble TiO_2. Similarly 39 to 52% productivity of NOx sequestration was achieved utilizing the sprayed covering on concrete (Hassan, Dylla, & Rupnow, 2010)

4.8 Pure Titania (TiO_2) Vs Iron-doped ($Fe\text{-}TiO_2$)

Titania (TiO_2) nano-particles have already been successfully used in some researches involving NOx removal from air streams. Moreover, there has been a huge literature already present about the fact that the efficiency of semi-conductor nanoparticles increases manifolds when they are doped. We are also familiar with the fact that similar doping techniques have already been used to increase the efficiency of various solar cell systems. Therefore, the primary focus of this research is to make a comparison between the NOx removal efficiencies of both the pure and doped Titania nano-particles.

4.9 Mortar Concrete

Mortar concrete is peculiarly used in various applications for road and pavement construction as they offer numerous benefits including high rigidity and consequently a good load distribution on the base and an excellent fatigue behavior. Mortar concrete has a sublime resistance to wear and rutting and edges that do not erode. It has a bright color and is resistant to damages caused by oil spillages, organic wastes and chemicals etc. The concrete is resistant to slips and offers safety in winter, moreover it is ecologically friendly. Mortar concrete pavements have a longer life span too and entail little maintenance, especially if they have been designed appropriately and finished professionally.

4.10 Pervious Concrete

Pervious concrete is a type of concrete with high porosity, which permits complete water infiltration through its structure. It make use of coarse aggregates, Portland cement, and water. The high void ratio in pervious concrete is kept up by utilizing aggregates that are for the most part are all one sized to abstain from filling the voids with fines. The aggregates with similar diameter aggregates make the structure for pervious concrete (Yang and Jiang, 2002), and the aggregates are bound together with cement-water paste, as appeared in Figure 2.2. The voids kept up all through the structure because of the same sized aggregates being held together with the slim cement paste permit air or water to enter through the pervious cement. Since the cement layer that ties the structure together is pretty slim, this lowers the mechanical strength of the concrete. Therefore, pervious concrete would not be suitable for interstate highway use, as it would need to suit for a high volume of substantial vehicle movement every day. It could however be used on the highway shoulders, which don't convey the repetitive loads of vehicle activity every day. Likewise, in light of the fact that pervious concrete has various voids presented to the surface, it is inclined to be clogged up with garbage, which could prevent water from invading through the structure. This can be countered with appropriate upkeep methods.

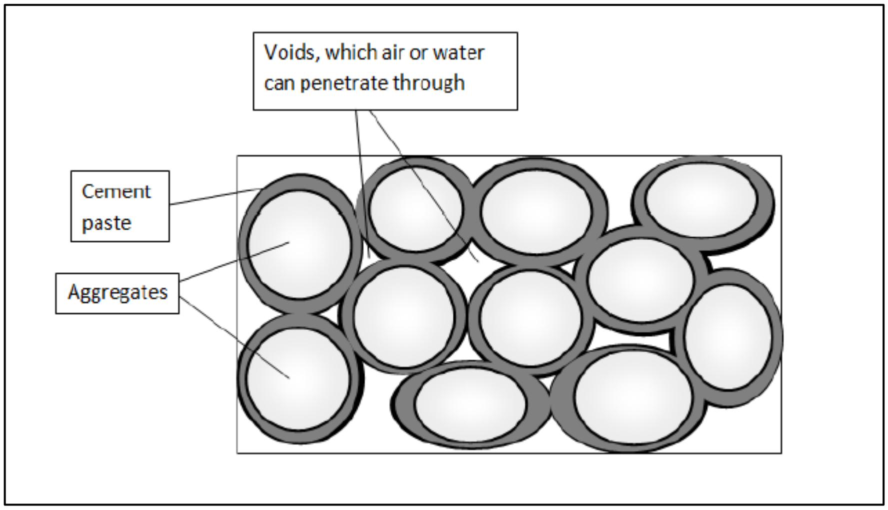

Figure 2.3: A schematic diagram of pervious concrete structure

4.10.1 Pervious Concrete Applications

Pathways, parking area, ways in parks, tennis courts, yards, shoulders, slant adjustment, base of swimming pool, floors of green house, zoo territories, channels, clamor hindrances, carports, can be equipped with pervious concrete for volume reduction of the applied concrete (Obla, 2007). Likewise it can be utilized to permit green development, for example, using it onto the floor of ocean to develop and grow ocean seaweed and reefs for fish and thus it restores the vanishing environment of marine life because of contamination and misuse (Li, 2011). The permeable base is favorable to the seaweed’s clinging, which in turn provides the feeding grounds that the fish and shellfish need.

4.10.2 Advantages of Pervious Concrete

The quality of the environment in cities can be improved by the application pervious concrete pavement. Groundwater resources can also be aided with the use pervious concrete for construction of pavements that can filter the rain water into the ground (Yang & Jiang, 2002). The air and water permeability of pervious concrete always keeps the underneath soil wet and clean. Thus the plantation in the surroundings of parking lots that are equipped with pervious concrete also get more water and air to the roots. In a Salt Lake City parking lot a large silver maple tree died just because of lack water and air availability into its roots from the non-primitive concrete around its surrounding (Rocke & Bowers, 2009). Permeable concrete also addresses the comfort of driver and other pedestrian by absorbing the noise from the interaction of tyre and road and it also reduces the slippery and hydroplaning effect during high rains. Snow can also drain through the pervious concrete in the winter, when it starts to melt, thus leaving very low amount of snow on the surface of pavements as compared to the pavements of non-pervious concrete. Urban heat island effect can be controlled by the use of pervious concrete unlike traditional non-pervious concrete pavements do. Because of the insulating capability and special void structure of pervious concrete, during the daytime heating cycle the base temperatures of the pervious concrete remain similar to cooler surfaces like lighter concrete and soil (Haselbach, 2009).

Pervious concrete is so much environmental friendly, moreover it also has an aesthetically pleasing effect on human life. In Beijing Olympics of 2008 in China, multi-colored pervious concrete of about 2.7 million square feet was used in dock frontage for the sailing venue and rowing (Rocke & Bowers, 2009). Top layer is colored and has smaller aggregates whereas the bottom “lift” layer has bigger aggregates.

4.10.3 Pervious Concrete Cost & Maintenance

Materials used for the composition of pervious concrete are similar to the regular concrete, which include aggregate, cement, and water therefore, the cost for materials is almost the same for both kinds of concrete. A change in the quantities would be there as lesser cement is required for pervious concrete, similarly there will not be any fines (sand), and the amount of aggregates required will be greater than the normal concrete. Pervious concrete was first developed and used in 1852 (Ghafoori & Dutta 1995; Obla, 2007), however, the concept is still comparatively new in most countries. Due to higher initial costs associated with pervious concrete construction and lack of awareness on part of manufacturers, many are still reluctant to make use of pervious concrete in public as well as local projects. Nonetheless, when we talk about pervious concrete in the long run, the benefits will pay off the initial cost. Making use of pervious concrete lessens the expenses in installing of extensive drainage and storm water management schemes.

Proper maintenance of pervious concrete requires washing to clear the pores once a year. Mechanical suction or pressure washing with water to flush out debris from the voids are some of the cleaning options that may be incorporated.

MATERIALS AND METHODS

The research involves the evaluation of the effectiveness of varying concentrations of Titania nano-particles in removing atmospheric pollutants like NOx from the air. Many treatment methods have already been successfully tested in various international researches, therefore the main objective of this research is to compare the effectiveness of the photocatalytic process under same concentrations of titania nano-particles coated on both the mortar and pervious concrete samples.

3.1 Test Materials

Materials used in this research were of scientific standard. Titania (GPR, BDH Chemicals Ltd. Poole England), Ferric nitrate nona-hydrate [Fe $(NO_3)_3.9H_2O$]. Cement, sand and gravel (3/8 inch) were purchased from the local market. NOx cylinder was borrowed from EPA CLEAN Labs Islamabad, and distilled water was used throughout the experiments, obtained from IESE water lab.

3.2 Test Instruments

Instruments used during the research included a Scanning Electron Microscope (JEOL JSM-6460), X-ray diffraction (XRD, JEOL JDX-II), Energy-dispersive spectroscopy (EDS, JEOL JSM-6460), Acrylic environmental chamber, gas flow controllers, White florescent lamp (8W), UV lamp (8W), Pure air generator, and NOx analyzer.

3.3 Test Procedures

3.3.1 Synthesis of Titania Nanoparticles

Liquid Impregnation method (Khan *et al.*, 2013; Younas *et al.*, 2014) was used for the synthesis of pure and 1% Fe – doped Titania nanoparticles as described below Fig.3.1.

(i) Mixing

Slurry of TiO_2 nanoparticles was prepared in water by mixing 100 g of TiO_2 in a 500 ml beaker at a time and continuous stirring for 24 hours. In case for Fe doped

Titania nano-particles Ferric nitrate nona-hydrate [Fe $(NO_3)_3 . 9H_2O$] was also added in the mixing step to get a 1% Fe doping rate. Rest of the steps were same for both kinds of nano-particles.

(ii) Settling

This solution was allowed to settle, for 24 hours so that proper settling of the solids could take place.

(iii) Drying

After decanting the supernatant, the solid material was placed in oven for 12 hours at 105^0C so that water could evaporate.

(iv) Calcination

After drying, the material was crushed properly using a pestle and mortar and placed in china dishes. The china dishes were placed in a muffle furnace for 6 hours at 550^0C to obtain the pure and Fe-doped TiO_2 nanoparticles respectively (Sahoo *et al*., 2005).

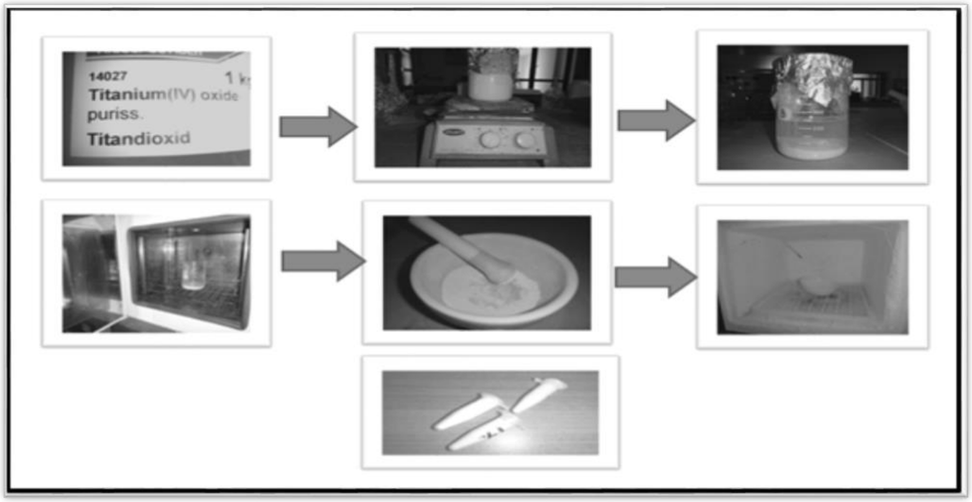

Figure 5.1: Steps Involved for the synthesis of Titania Nanoparticles

3.4 Characterization of Nanoparticles

3.4.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscope (SEM) is a powerful technique which uses a focused beam of electrons to obtain largely magnified picture. The high-resolution, three-dimensional images produced by SEM provide information like;

- Topography
- Morphology
- Chemistry
- Crystallography

The topography and morphology of the Titania, was carried out using scanning electron microscope (JEOL JSM-6460) at 10,000x magnifications. Scanning Electron Microscopy was used for the direct estimation of particle size and examination of sample powders. It is the type of electron microscope that uses focused beam of electrons to scan a sample for image production. It has the resolution of less than 1 nm. X-rays informed us about the elemental and chemical composition of the sample as shown in Fig. 3.2 (Goldstein *et al*., 1981).

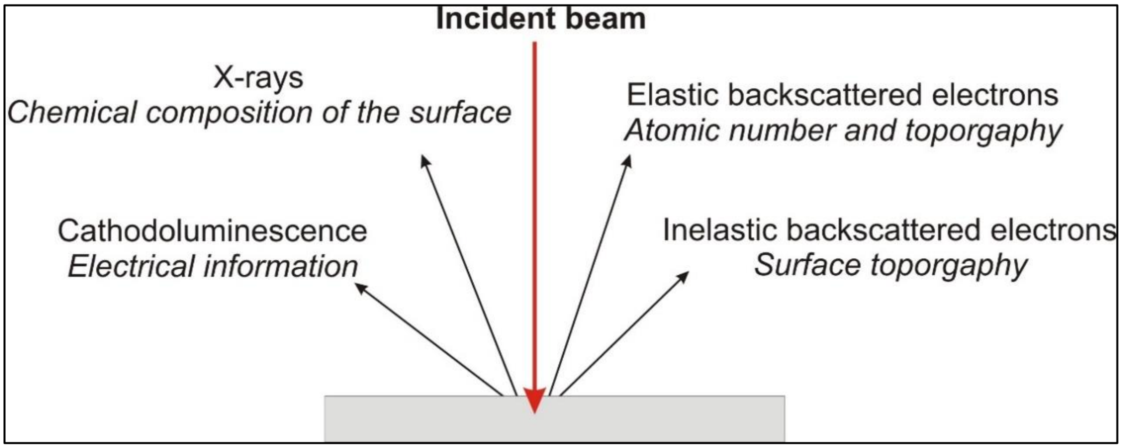

Figure 5.2: SEM working Principle

3.4.2 Energy Dispersive Spectroscopy (EDS)

Energy-dispersive spectroscopy (EDS, JEOL JSM 6490A) was used to identify the elements present in the nanoparticles. The principle of EDS is shown in Fig. 3.3 which involves the electron beam which falls on the sample atom. Due to the excitation in the inner shell of atom, every element produces x-rays. This moves the outer shall electrons to move towards inner shall to cover the gap. This difference in outer and inner shell is released in the form of x-rays. These x-rays form the specific peaks for each element which is detected by EDS as each element has a different atomic structure with different peaks on x-ray atomic spectrum. Thus from the controlled beam of electron it can also tell us about elemental composition of a selected area. The percentage composition of specific element can be determined by the number of counts on the graph (Goldstein *et al.*, 2003).

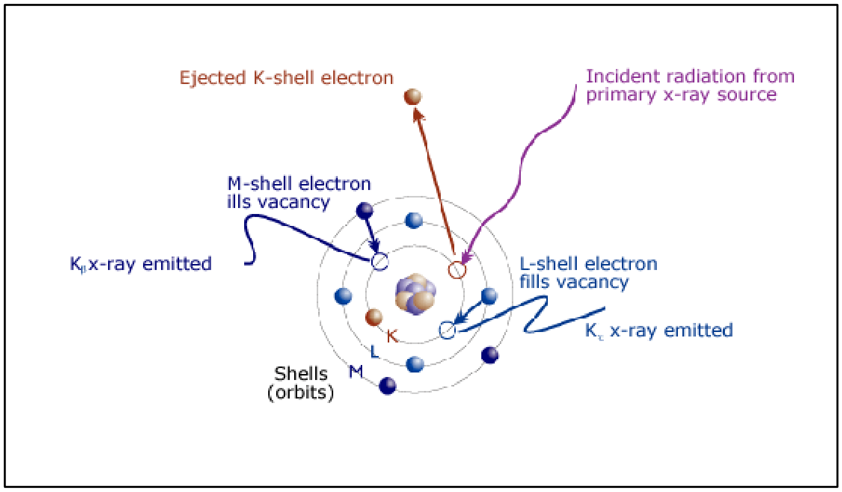

Figure 5.3: EDS working Principle

3.4.3 X-Ray Diffraction (XRD)

X-ray Diffraction (XRD, JEOL JDX-II) was used to find out the crystalline phase and size of nanoparticles. Average crystalline size of nanoparticles was determined by using the Scherer formula (Younas *et al.*, 2014). Principle mechanism of XRD is shown in Fig. 3.4 in which the x-rays fall on the specimen atoms and diffracted into many directions.

$$L = K\lambda / \beta \cos\theta$$

Where,

L = Average particle size,

K = 0.891; λ = 0.1542,

β = full width of a diffraction line at one half of maximum intensity (FWHM) radian,

θ = the diffraction angle of crystal phase.

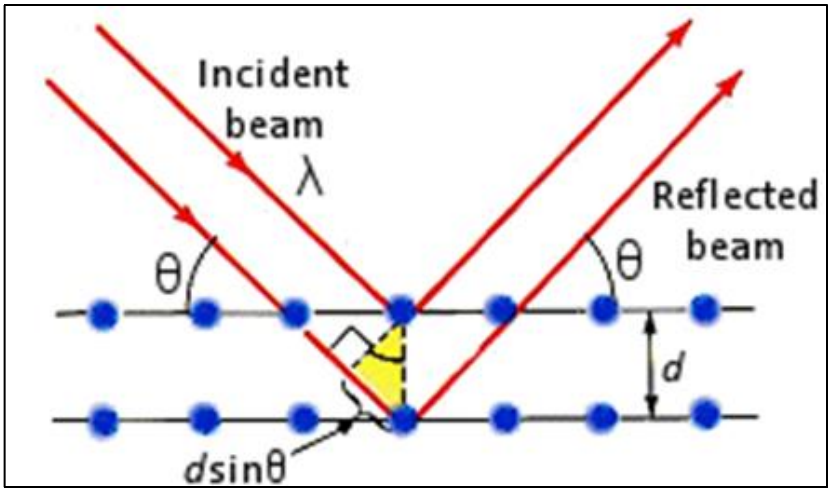

Figure 5.4: XRD working Principle

3.5 Casting of Concrete Samples

Two types of concrete specimens were casted in this research. One type was comprised of the regular Mortar Concrete Samples that are impervious and are meant to achieve higher strength values. The other type of specimens casted were Pervious Concrete Samples, as pervious concrete is a very good option for drive-ways and parking lots because of their advantages in storm water management as well as noise reduction.

3.5.1 Mortar Concrete Samples

For the mortar specimens used in this research, a water to cement ratio (W/C) of 0.5 was selected. Ordinary Portland cement was used with sand to cement ratio (S/C) of 4. Based on these ratios the components cement sand and water were weighed and mixtures for every sample were made separately. The mixtures were casted into 100 x 100 x 100 mm molds and were left to set for 24 hours. Following the 24 hours casting time the samples were demolded, labelled and were submerged in a water tank for curing period of 28 days to achieve the desired strength.

The average volume of all mortar concrete samples was calculated to be 1049 cm^3 and cement mortar density was 2162 kg/m^3. Dry mass of mortar specimen calculated was 270.25 g containing 135.12 g of cement and same amount of sand. Total number of mortar concrete samples casted was 20. Two out of these 20 samples were control samples with no Titania in the top surface (0% cement replacement with Titania). The remaining 18 samples were further sub-divided into two classes, one with pure Titania nano-particles and the other with iron doped Titania nano-particles. There were 3 samples each with 5%, 10%, and 15% cement replacement with pure Titania. In the exact same way 3 samples each with 5%, 10%, and 15% cement replacement by iron doped Titania nano-particles were also prepared.

3.5.2 Mortar Concrete Treatment with TiO_2

For Mortar concrete samples surface mixtures with 5%, 10% and 15% cement replacement with TiO_2 were prepared separately and then applied to each sample as a 10 mm (1 cm) thick layer on the top. This application method was adopted as it has been found to be one of the best methods of TiO_2 application to Mortar Concrete for atmospheric NOx removal, based on a research work carried out by Hassan et al. in 2011. For this purpose surface mixtures composed of ordinary Portland cement, nano-sized titanium dioxide (separate mixtures for pure and Fe-doped Titania), and aggregate (sand with a maximum particle size of 1.18 mm) were prepared. Water to cement ratio for the surface mixtures was also kept at 0.5 and it was applied to the mortar concrete samples as a 10 mm thick surface layer. Detailed compositions based on calculations of these samples are given in the table:

Table 5.1: Detailed composition of mortar concrete samples

Concrete sample	**Naming Convention**	**Pure/Fe-Doped TiO_2 (kg)**	**Cement in top 1 cm Layer (kg)**	**Total Cement (kg)**	**Aggregate (kg)**	**Water (kg)**
Samples with Pure TiO2						
Control-1	MCS-C	0	0.06	0.6	2.4	1.2
5% TiO2	MCSP 1	0.003	0.057	0.597	2.4	1.194
10% TiO2	MCSP 2	0.006	0.051	0.594	2.4	1.1885
15% TiO2	MCSP 3	0.009	0.042	0.591	2.4	1.1825
Samples with Fe-doped TiO2						
5% Fe-TiO2	MCSD 1	0.003	0.057	0.597	2.4	1.194
10% Fe-TiO2	MCSD 2	0.006	0.051	0.594	2.4	1.1885
15% Fe-TiO2	MCSD 3	0.009	0.042	0.591	2.4	1.1825

3.5.3 Pervious Concrete Samples

In addition to mortar concrete samples, 20 pervious concrete samples were also casted to compare the results of NOx removal efficiency as well as to determine the feasibility of cement replacement by Titania nanoparticles as it may have an effect on the compressive strength of the concrete. For these samples a W/C ratio of 0.35 was adopted and, as the case is with pervious concrete, an aggregate (gravel) to cement (A/C) ratio of 4. Aggregate used for pervious concrete was 3/8 inch gravel instead of sand to improve the porous nature of concrete and to achieve porosity between of 15% to 22%.

3.5.4 Pervious Concrete Ball Test

In order to check the consistency of pervious concrete the “ball test” was performed. The test is to ensure that the concrete is porous and still contains adequate cement to hold its structure together. Too thin of a concrete paste will be too much pervious and therefore, very less mechanical strength, resulting in easy crumbling of the concrete. On the other hand too thick of a paste will form a concrete with greater strength but a very little or negligible porosity thus failing to produce the desired results again. The ball test ensure the balance between the two contrasting states. Therefore, it requires the addition of water in very small increments at a time to prevent trashing the whole mix.

The test involves forming a handful of concrete into a ball like structure that should neither crumble (not enough water) nor should it lose its void structure (too much water). It should be able to hold a ball shaped structure as shown in the Fig3.5:

Figure 5.5: Pervious concrete ball test

3.5.5 Pervious Concrete Treatment with TiO_2

In contrast to a TiO_2 application method used for Mortar concrete the cement replacement by Titania in Pervious concrete was rather simple. This is because in this the total mass of cement used for each block was replaced as a whole by 5%, 10%, and 15% concentrations of both pure and doped titanium dioxide nano-particles respectively. The idea behind this method was to evaluate the impact of TiO_2 addition to pervious concrete towards its strength and porosity dynamics. Detailed compositions based on calculations of these samples are given in the table 3.2:

Table 5.2: Detailed composition of pervious concrete samples

Concrete sample	Naming Convention	Pure/Fe-DopedTiO2 (kg)	Cement (kg)	Aggregate (kg)	Water (kg)
Samples with Pure TiO2					
Control-1	PCS-C	0	0.6	2.4	0.21
5% TiO2	PCSP 1	0.03	0.57	2.4	0.1995
10% TiO2	PCSP 2	0.06	0.54	2.4	0.189
15% TiO2	PCSP 3	0.09	0.51	2.4	0.1785
Samples with Fe-doped TiO2					
5% Fe-TiO2	PCSD 1	0.03	0.57	2.4	0.1995
10% Fe-TiO2	PCSD 2	0.06	0.54	2.4	0.189
15% Fe-TiO2	PCSD 3	0.09	0.51	2.4	0.1785

3.6 Laboratory Tests

Two different kind of tests were performed on the concrete samples namely; Porosity tests, Compressive strength tests to evaluate the physical attributes of the samples. The Porosity test, however was performed only for pervious concrete to ensure the porosity was within the desired range.

3.6.1 3.5.1 Pervious Concrete Porosity Test

Porosity tests were performed for pervious concrete samples only. This was done to check whether the target porosity range (15%-20%) in all samples were achieved or not. Each PCS was subjected to the test according to the method proposed by Montes et al. (2005). According to this method two different weights for each sample were determined. Dry weight (W_D) of the sample in air was determined after placing the samples in oven at 70° C for 3 hours. Then the samples were submerged in water for 30 minutes and their submerged weight (W_S) was determined using a spring balance. After the dry and submerged weights were determined the porosities of the samples were calculated using the following equation:

$$P\ (\%) = [1 - ((W_D - Ws) / \varrho_w) / V_t] \times 100$$

Figure 5.6: Pervious concrete porosity testing apparatus

3.6.2 Compressive Strength Test

All the Mortar and Pervious concrete samples were tested for their respective compressive strengths in order to determine whether they had achieved the required target strength for road or pavement construction purposes, as per international requirements or not. ASTM C39/C39M standard test method was used to perform compression strength of the samples.

Figure 5.7: Compressive strength testing

3.7 Environmental Tests

In order for a quantitative analysis of the efficiency of both pure and doped titania nano-particles on concrete surfaces, for atmospheric NOx removal, a laboratory scale experimental setup was devised. The setup had the ability to simulate varying environmental conditions. All the experiments were run in a controlled environment.

3.7.1 Experimental Setup for Environmental Tests

As evident from the Fig.3.7, the experimental setup was modified from the "Japanese Industrial Standard" (JIS TR Z 0018 "Photocatalytic materials – NOx air purification test procedure"). The experimental setup had the capacity to simulate varying environmental conditions such as air flow rate, light intensity and the relative humidity. All the concrete samples, both pervious and mortar concrete samples, were subjected to experimentation one by one.

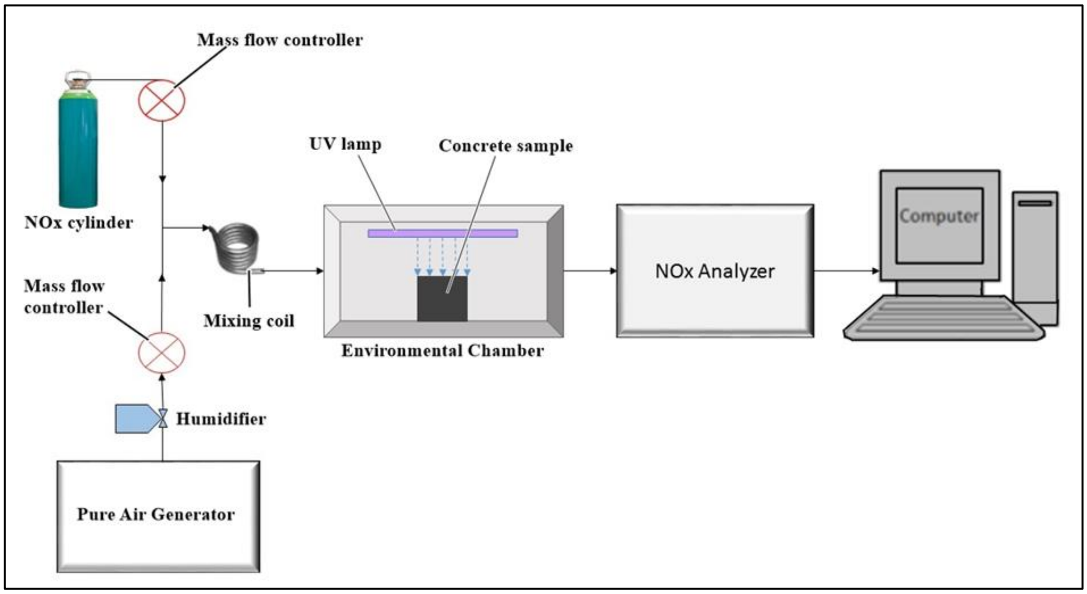

Figure 5.8: Experimental scheme for environmental tests

Tests for each sample were run for 5 hours with an initial concentration of NOx set at 410 ppb and a gas flow rate of 9 L/min whereas, the air flow rate through all the experiments was kept at 17 L/min. The NOx laden air was continuously circulated through the environmental chamber and the NOx concentration was monitored at the outlet with the help of a NOx Analyser. After achieving a steady state NOx concentration of 410 ppb the light was turned on and the decline in the NOx concentration over time was monitored with the Thermo NOx analyzer. The same experiment was repeated for all the mortar and pervious concrete samples, at 25° C and a relative humidity of 50%, with exposure to two different light conditions i.e both white florescent and UV light tests were performed separately and the results were compared. The figure 3.8 shows the experimental setup for Environmental Tests.

Figure 5.9: Laboratory experimental setup

RESULTS AND DISCUSSION

4.1 Characterization of Nanoparticles

4.1.1 Scanning Electron Microscopy (SEM) – Analysis

(i) SEM Analysis of Pure and Doped Titania Nano-particles

SEM analysis was carried out in order to be certain that the nano-particles synthesized were within the size range of 100 nm. As it can be observed from Fig. 4.1 and 4.2 the average particle size observed at a 10,000x magnification level was 71 nm and 73 nm for pure and doped Titania nano-particles respectively. The images clearly show a highly complex, very porous, rough and heterogeneous structure with a high surface area for pollutant adsorption.

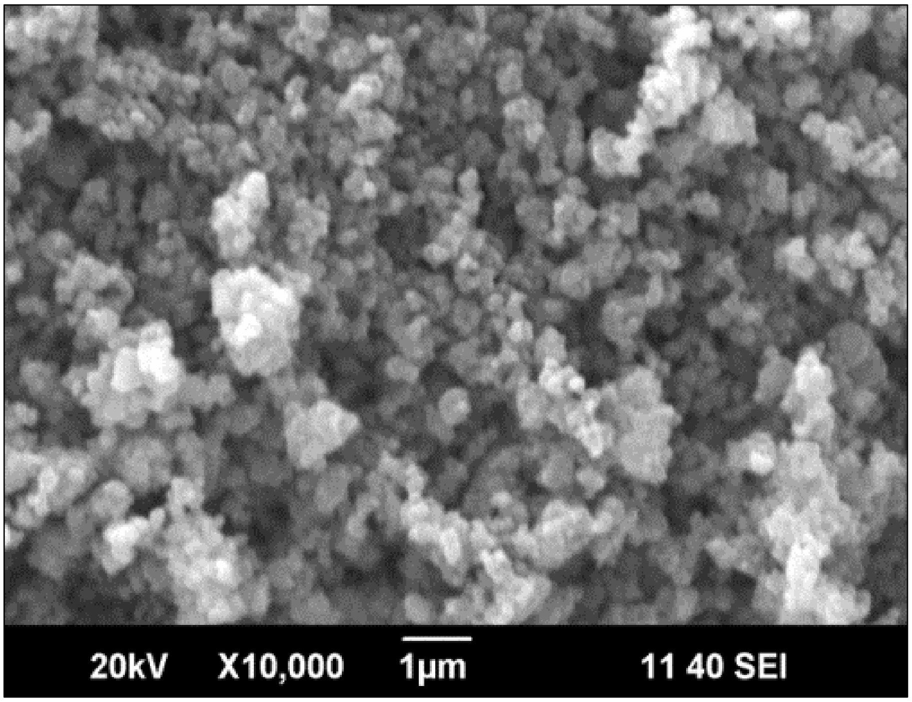

Figure 4.1: Pure Titania nano-particles

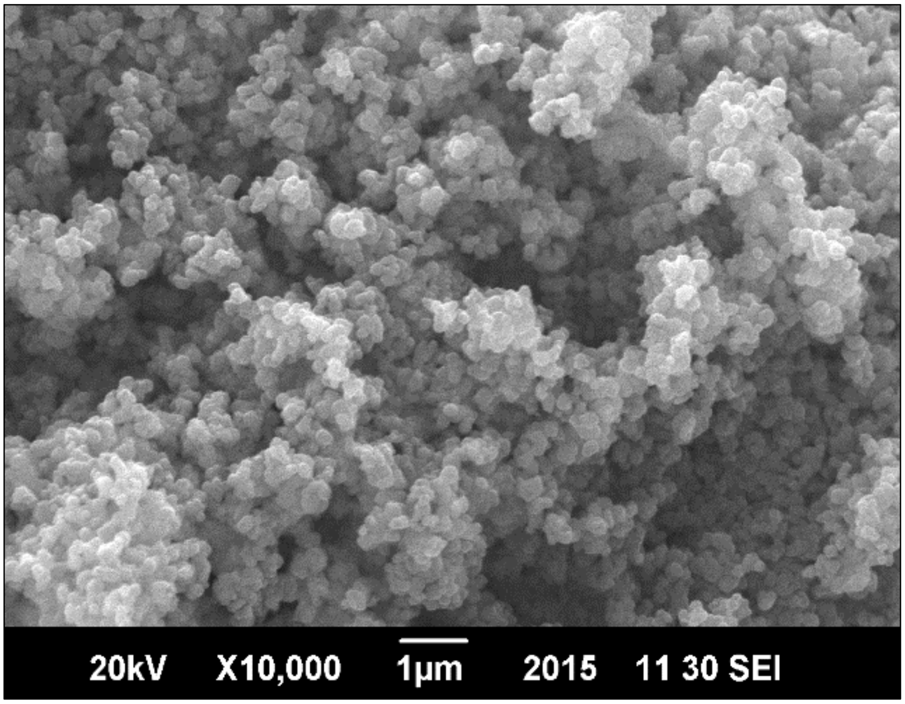

Figure 4.2: Fe-doped Titania nano-particles

(ii) SEM Analysis of Concrete Samples

The Scanning Electron Microscopy images show surface morphology of Titania nanoparticles in the top surfaces of the both mortar concrete samples and the pervious concrete samples. The images indicate a relatively uniform distribution of Titania nano-particles which is very important for maximum exposure of the surface particles to the UV rays in the sunlight. However, in case of mortar concrete sample (figures 4.3, 4.4, and 4.5), the surfaces seems much smoother than the surfaces of pervious concrete samples (figures 4.6, 4.7, and 4.8). This suggests that pervious concrete might just have a slightly greater pollutant removal efficiency due to increased surface area.

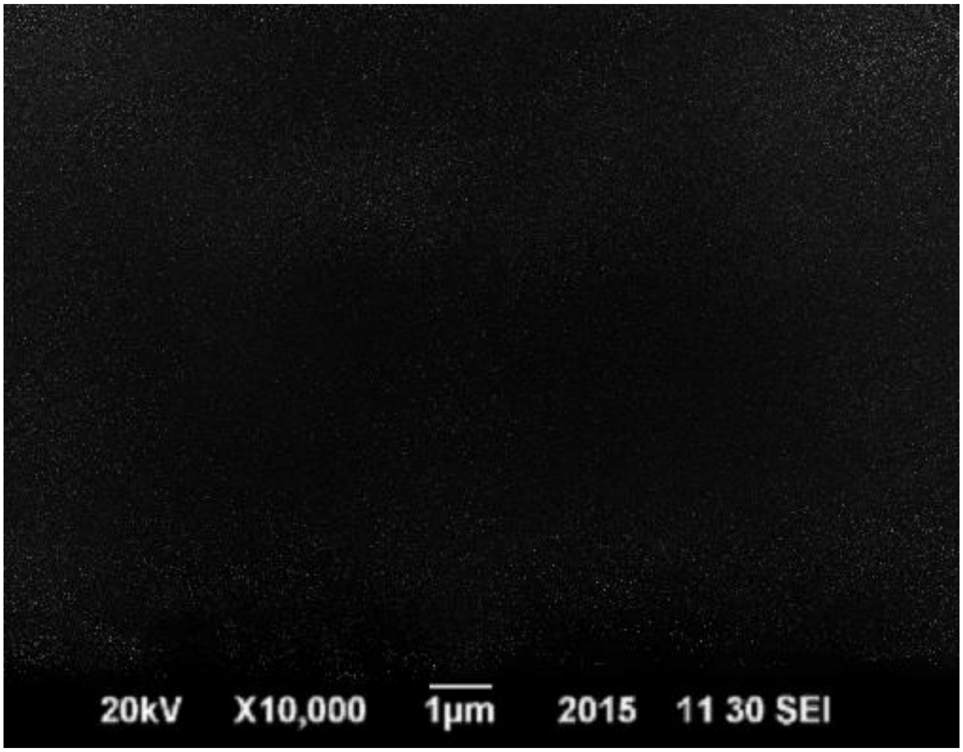

Figure 4.3: SEM image of Mortar concrete sample (5% TiO_2)

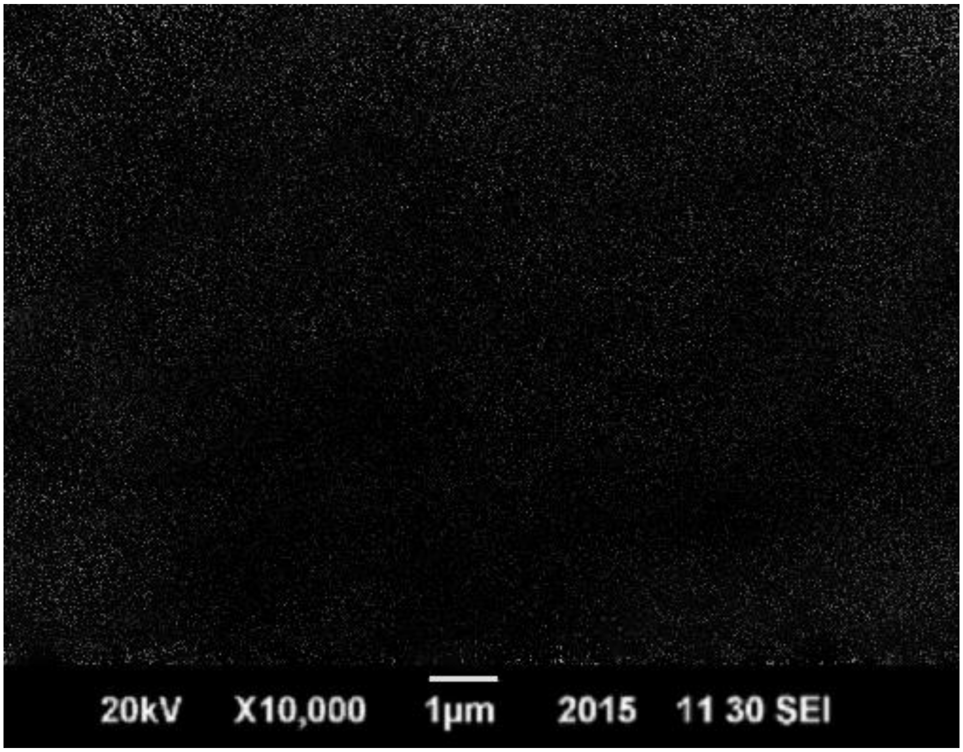

Figure 4.4: SEM image of Mortar concrete sample (10% TiO2)

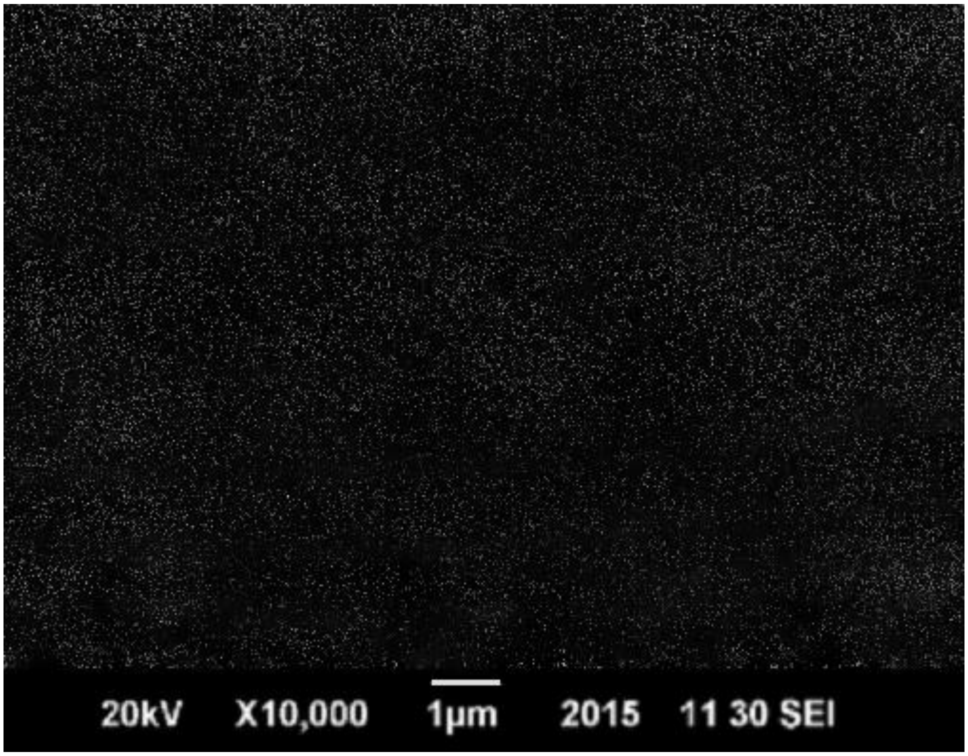

Figure 4.5: SEM image of Mortar concrete sample (15% TiO2)

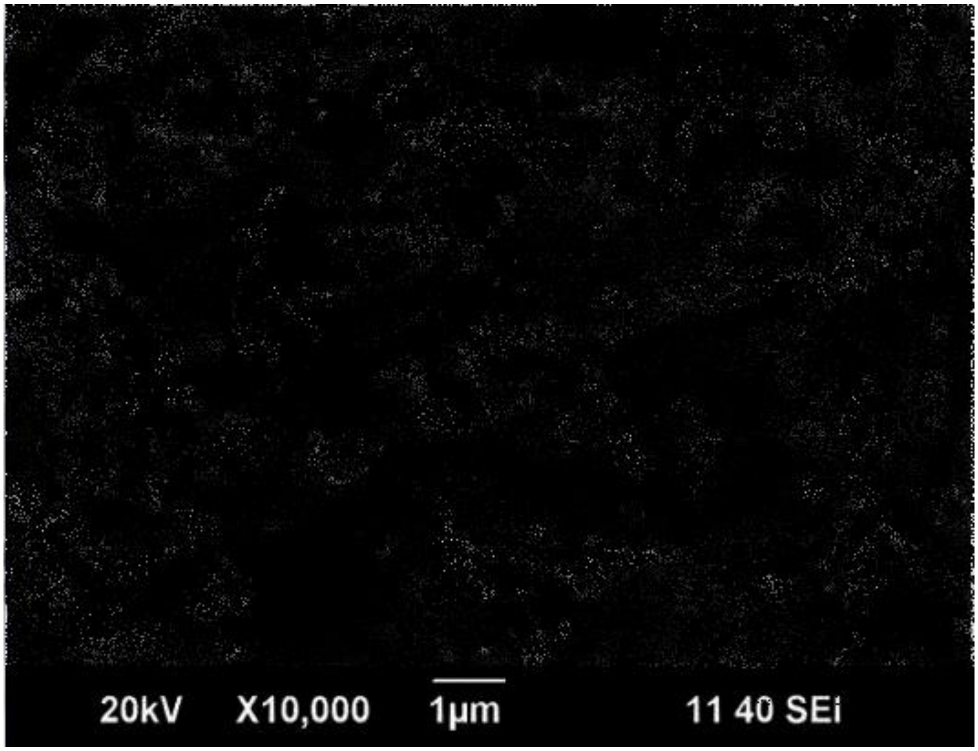

Figure 4.6: SEM image of Pervious concrete sample (5% TiO2)

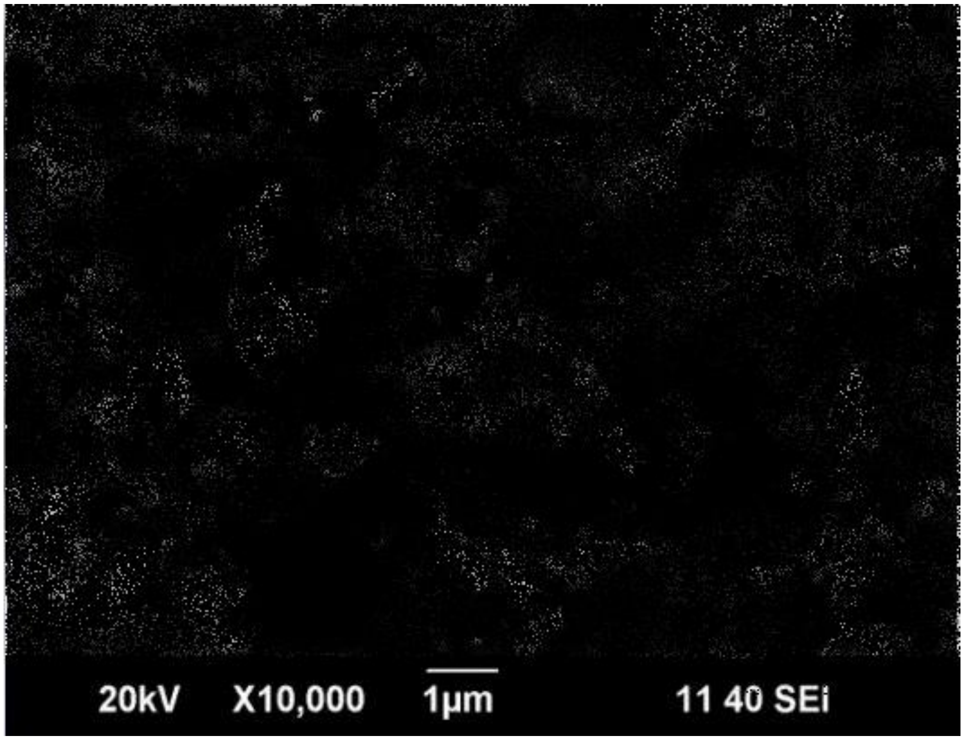

Figure 4.7: SEM image of Pervious concrete sample (10% TiO2)

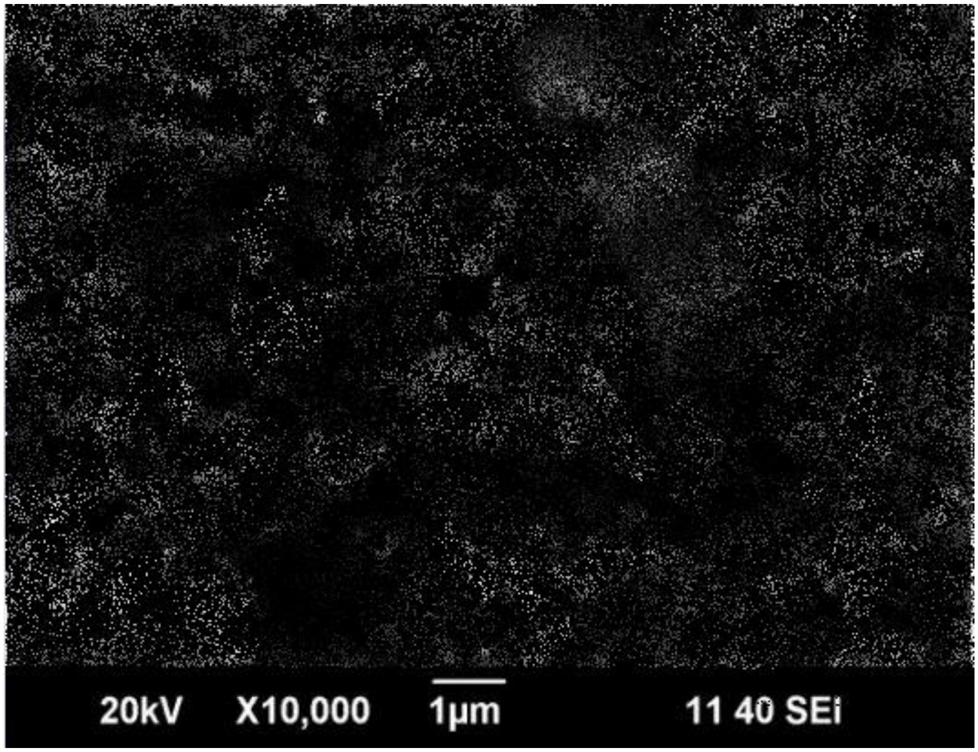

Figure 4.8: SEM image of pervious concrete sample (15% TiO2)

4.1.2 Energy Dispersive Spectroscopy (EDS) Analysis

EDS test is carried out in order to determine the elemental composition as well as to do the quantitative analysis of the sample. In this research the EDS tests of powdered forms of both the pure and 1% Fe – doped Titania nano-particles was carried out to confirm whether the fabricated particles had the desired composition or not .

EDS analysis for the composition of pure nanoparticles shows the relative mass compositions in the table. As the results show that the only elements the sample contains are titanium (Ti) and oxygen (O) whereas no alien element or impurity is found in the test, this can also be seen in the Fig. 4.9. The quantitative analysis of this sample shows 55% Ti and 45% O with respect to molar concentrations.

On the other hand Fig. 4.10 shows the elemental composition of 1% Fe – doped Titania nano-particles. It can be seen that the sample contained Ti, O, and Fe in 34.9, 63.94, and 1.16% molar ratios respectively. While no external agent or unwanted impurity was detected.

Table 4.1: EDS results of Titania nanoparticles before and after chromium removal

Titania Nanoparticles	**Relative Elemental Mass Ratios**		
Pure TiO_2	**Ti%**	**O%**	**Fe%**
	55%	45%	0%
1% Fe – TiO_2	34.09%	63.94%	1.16%

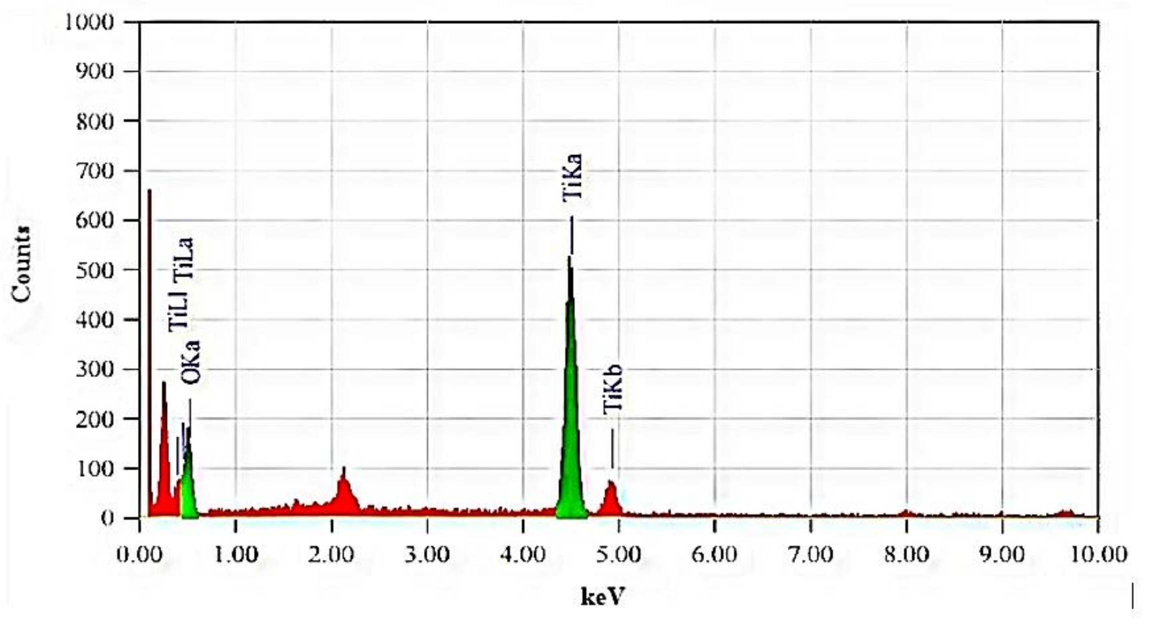

Figure 4.9: EDS spectrum of pure Titania nano-particles

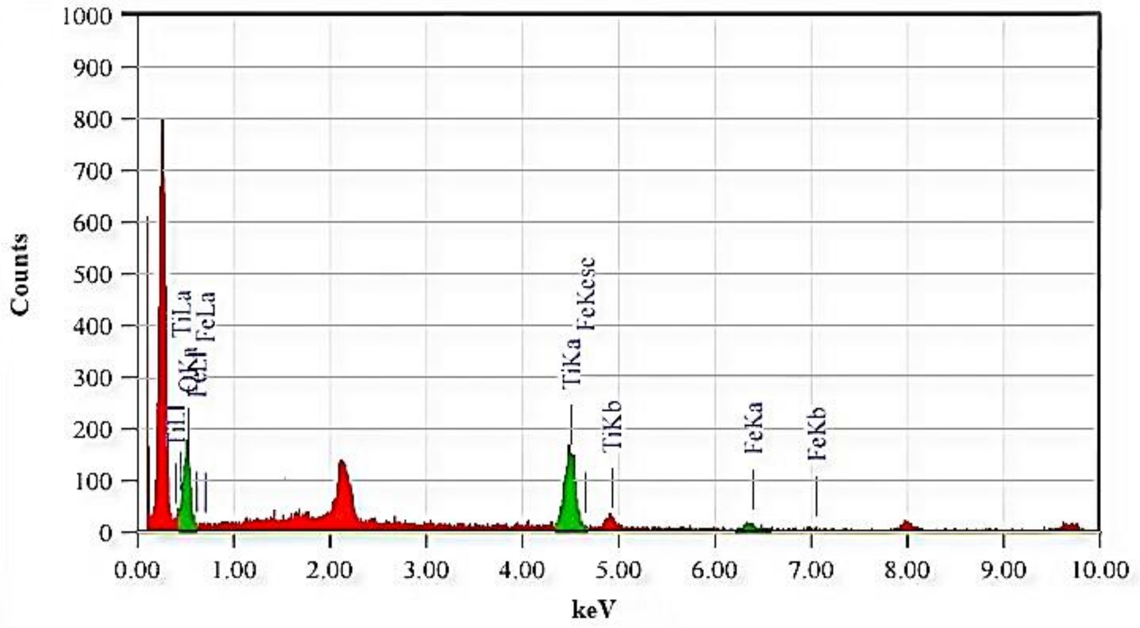

Figure 4.10: EDS spectrum of 1% Fe-doped Titania nano-particles

4.1.3 X-Ray Diffraction (XRD) Analysis

XRD results are illustrated in the Fig. 4.11 and 4.12. Structural analysis of pure and iron doped Titania nanoparticles was performed by X-ray diffraction (XRD) in the range of 2-theta ranging 20^o-80^o at room temperature.

The crystalline size of particles confirmed to be in the nano range that is less than 100 nm. Peaks of XRD results in Fig 4.11 reveal that pure Titania nanoparticles have the desired anatase crystalline structure. Crystalline phase of pure Titania was found to be 89%. Fig 4.12 shows the anatase phase of the iron doped Titania nano-particles with a crystalline phase of 94%.

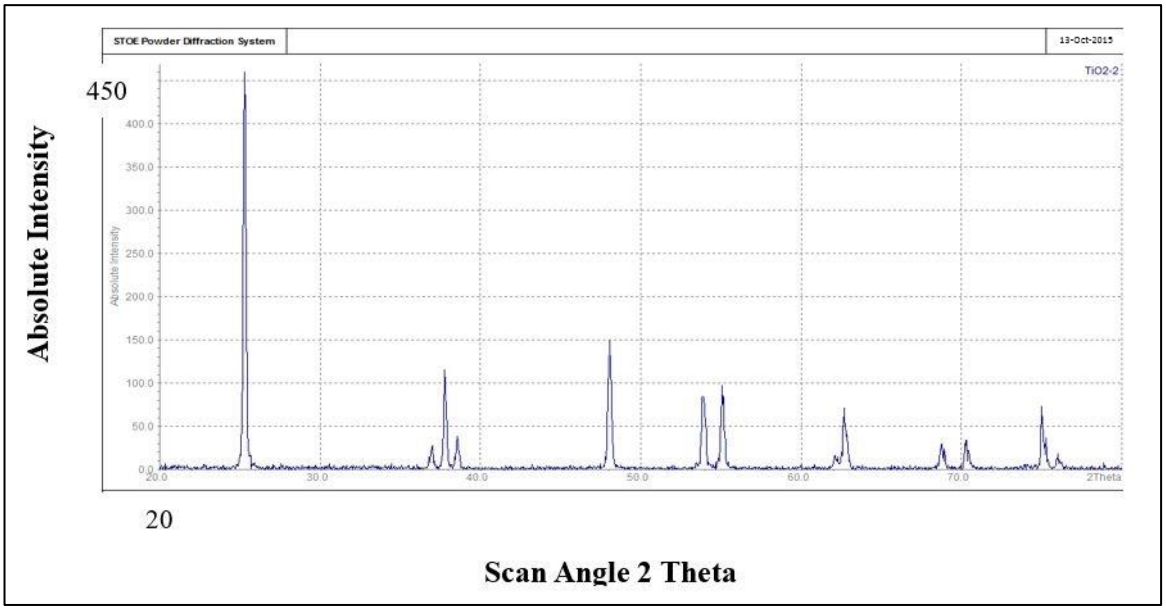

Figure 4.11: XRD image of Pure Titania nano-particles

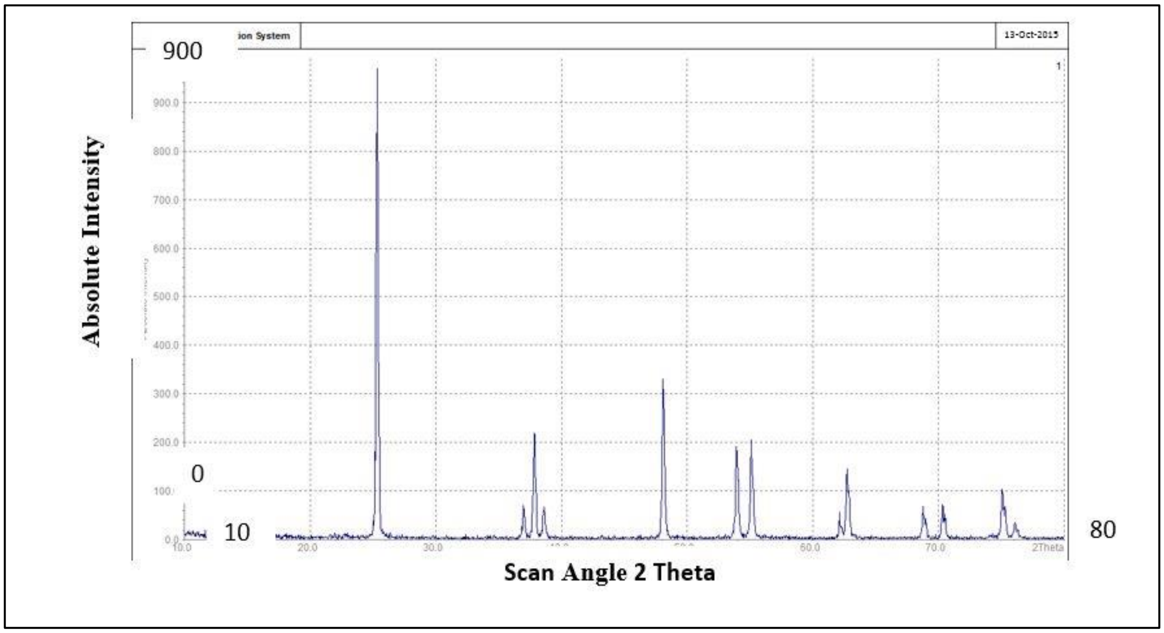

Figure 4.12: XRD image of 1% Fe-doped Titania nano-particles

XRD image of pure titania nanoparticles shows two high peaks at 25.3° and 48° and it also shows peaks at regular intervals at angles 37.8°, 53.8°, 68.7° and 78.6° along with higher peaks mentioned above, revealing its anatase crystalline phase (Reyes *et al*., 2008). The main reason behind this high crystalline nature is calcination of nanoparticles at 550°C for 6 hours.

4.2 Porosity Tests

Porosity tests were performed for the pervious concrete samples only. This is because of the fact that Pervious concrete is used for storm water management purposes and Mortar concrete is largely impervious. The target porosity range to be achieved in this research was between 15 to 20%. As already discussed the porosities of the samples were calculated according to a method proposed by Montes et al., using the following equation:

$$P\,(\%) = [1 - ((W_D - W_S) / \varrho_w) / V_t] \times 100$$

Where,

P = Porosity

W_D = Dry weight of the sample

W_S = Submerged weight of the sample

ϱw = Density of Water

and V_t = Volume of the sample

Table 4.1: Pervious concrete porosity test results

Sample	**W_D (g)**	**W_S (g)**	**V_t (cm3)**	**Density of Water (g/dm3)**	**Porosity (%)**
PCS-C	1996	1159	1049	1	20.20972
PCSP-1	1983	1149	1049	1	20.49571
PCSP-2	1982	1130	1049	1	18.77979
PCSP-3	1985	1109	1049	1	16.4919
PCSD-1	1992	1156	1049	1	20.30505
PCSD-2	1996	1142	1049	1	18.58913
PCSD-3	1989	1129	1049	1	18.01716

The results of porosity tests suggested that with the increasing concentrations of both pure and doped titanium dioxide nano-particles the porosity of the pervious concrete samples decreased. However, at all the replacement concentrations (5%, 10% & 15%) the porosity achieved for each sample was well within the target range of (15% - 20%). This trend of porosity changes is shown in the Fig 4.13.

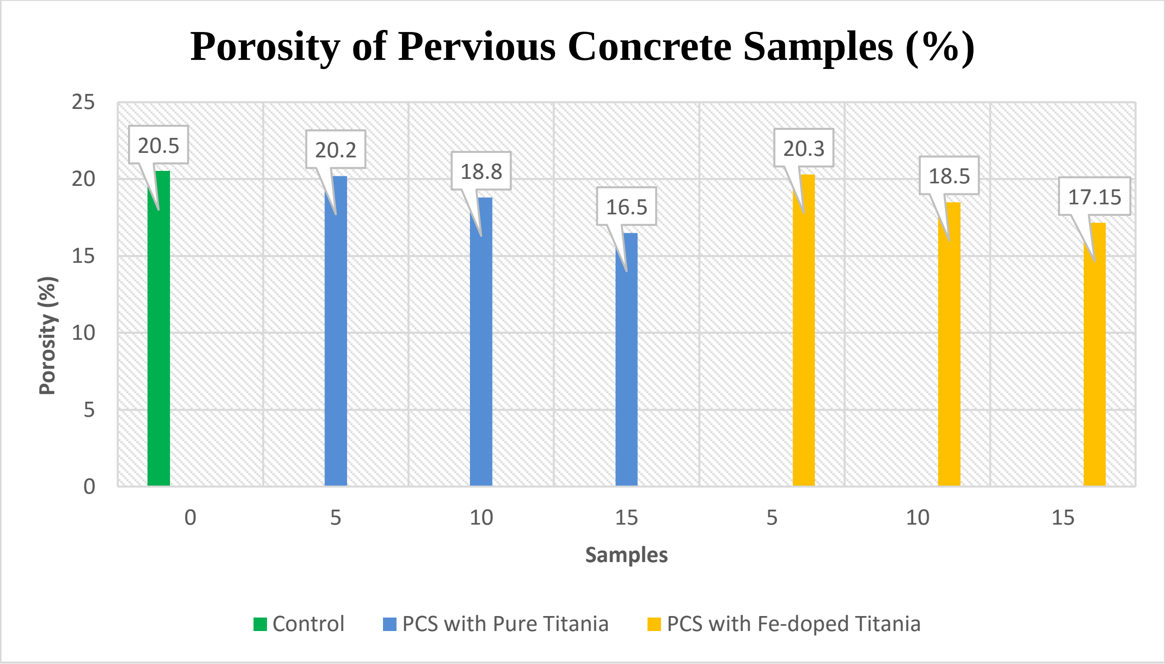

Figure 4.13: Porosity dynamics of pervious concrete at 5, 10 and 15% TiO_2 concentrations

The figure shows the Porosities of three different types of pervious concrete samples. The Green bar shows the average porosity for all the control samples (0% Titania). The Blue bars depict the average porosities of the samples with Pure Titania (TiO_2) at 5%, 10%, and 15% concentrations respectively, and the Yellow bars show the average changes of porosity when the samples had Iron-doped Titania (Fe-TiO_2) concentrations of 5%, 10% and 15% respectively. Another interesting observation that can be made from the graph above is that with the increasing concentrations of both the Pure and Doped TiO_2, the porosities of the pervious concrete samples decreased.

4.3 Compressive Strength Tests

The results of compressive strength testing were quite amazing, as in contrast to the decreasing porosity with increasing Titania concentrations, the compressive strengths of the samples increased with increasing concentrations of nano-particles. This observed trend is also supported by the recent findings by Ahmad Husnain (2015). Ahmad was working in National University of Sciences and Technology, Islamabad, on the immobilization of chromium removed from water on concrete specimens when he observed that the compressive strength of his concrete samples increased with the increasing concentrations titanium dioxide. He found that the strengths increased up to a replacement concentration of 15% and increasing the Titania concentration any further had a negative impact on the strength of concrete blocks. Compressive strength test results for both the Mortar and Pervious concrete samples can be seen from the table 4.2.

Table 4.2: Compressive strengths of concrete samples

Sample	**Compressive Strength (MPa)**
Mortar Concrete Samples	
MCS-C	48.5
MCSP-1	49.3
MCSP-2	51.7
MCSP-3	56.1
MCSD-1	49
MCSD-2	52
MCSD-3	55.3
Pervious Concrete Samples	
PCS-C	8.6
PCSP-1	12
PCSP-2	13.6
PCSP-3	14
PCSD-1	13.5
PCSD-2	14.2
PCSD-3	14.5

Results of these tests for mortar and pervious concrete blocks are plotted in the form of graphs shown in figures 4.14 and 4.15 respectively.

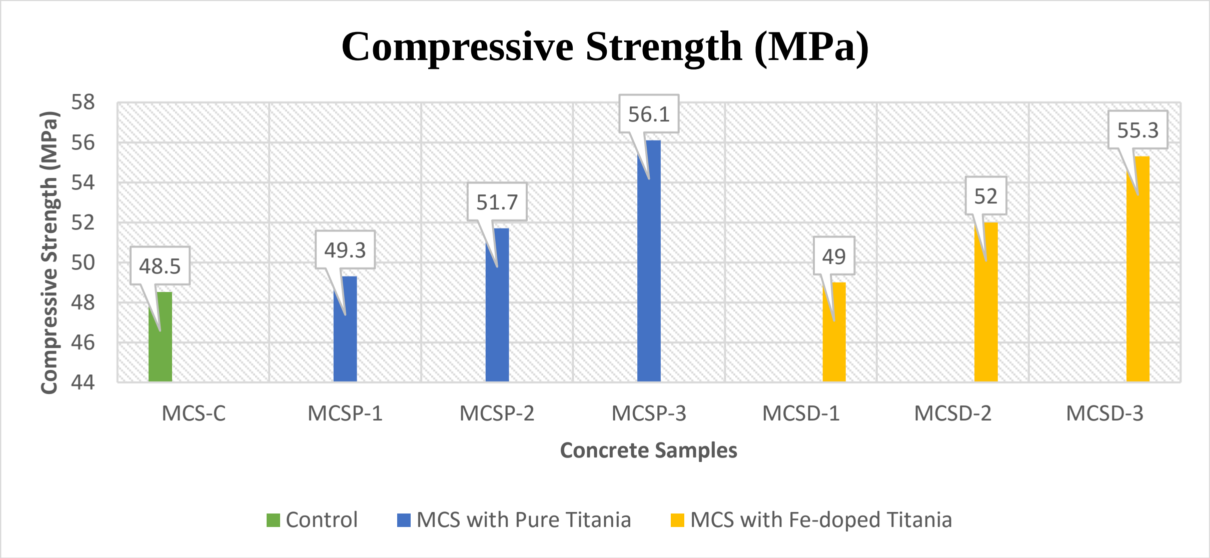

Figure 4.14: Compressive strengths of MCS at 5, 10 and 15% TiO2 Concentrations

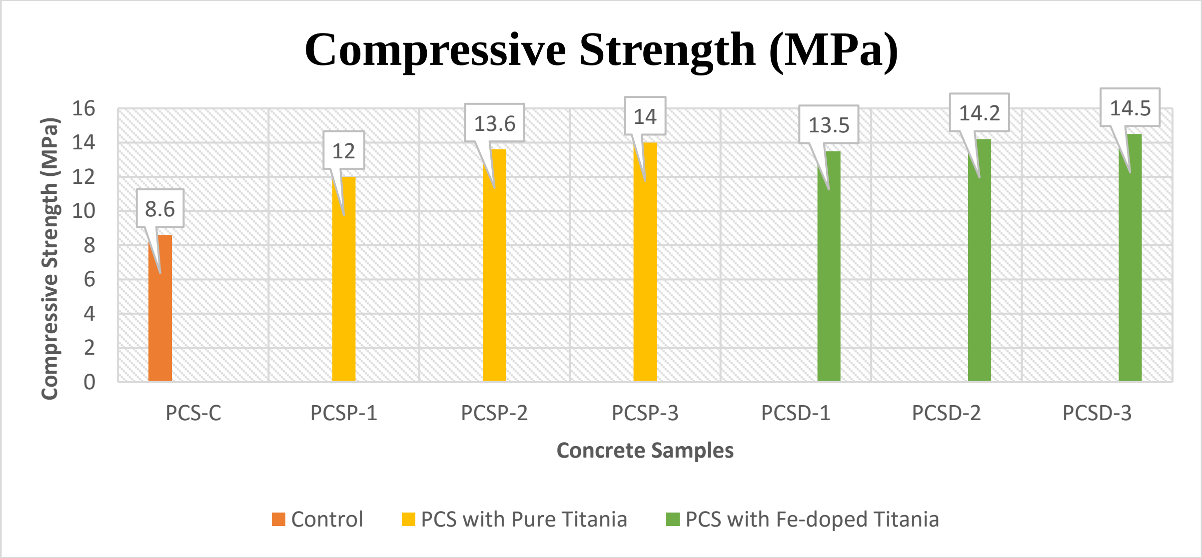

Figure 4.15: Compressive strengths of PCS at 5, 10 and 15% TiO2 Concentrations

This also makes sense by comparing the results obtained by compressive strength tests with the results of the porosity tests. It can be related that the decreasing voids and porosity within the concrete samples due to titanium dioxide, increases the strength of concrete in turn. The finding is specifically critical for pervious concrete which has considerably low compressive strength compared to regular mortar concrete. This makes titanium dioxide a good option to be used as an additive particularly in pervious concrete applications.

4.4 Environmental Test Results

4.4.1 NOx Removal in Visible (White) Light:

The results of NOx removal in environmental chamber when the samples were subjected to an 8 Watt florescent white light are shown in the following table.

Table 4.3: NOx removal rates for all samples in "Visible" (white) light

Concrete Sample	**Naming Convention**	**Pure TiO_2 (%)**	**Fe-doped TiO_2 (%)**	**Relative Humidity (%)**	**NOx Removal %**	**Time (hours)**
Mortar Concrete Samples						
Control-1	MCS-C	0	0	50	0.634146	5
5% TiO2	MCS 1	5	0	50	17.34146	5
10% TiO2	MCS 2	10	0	50	37.07317	5
15% TiO2	MCS 3	15	0	50	65.82927	5
5% Fe-TiO2	MCSD 1	0	5	50	32.43902	5
10% Fe-TiO2	MCSD 2	0	10	50	58.78049	5
15% Fe-TiO2	MCSD 3	0	15	50	83.82927	5
Pervious Concrete Samples						
Control-2	PCS-C	0	0	50	0.97561	5
5% TiO2	PCS 1	5	0	50	20.97561	5
10% TiO2	PCS 2	10	0	50	46.09756	5
15% TiO2	PCS 3	15	0	50	70.02439	5
5% Fe-TiO2	PCSD 1	0	5	50	36.39024	5
10% Fe-TiO2	PCSD 2	0	10	50	68.60976	5
15% Fe-TiO2	PCSD 3	0	15	50	80.97561	5

These results when plotted on a graph (Fig 4.16 & 4.17) show that the NOx removal efficiency increased with increasing TiO_2 concentrations in the concrete samples. However, increasing the concentration of TiO_2 beyond 15% of the mass of cement has a deleterous effect on the compressive strength of concrete (Husnain, 2015). Doping of TiO_2 nano-particles prior to coating, in this scenario, was therefore, adopted as an attempt to further increase the NOx removal efficiency of the process with a great success. Figures 4.16 and 4.17 compare the removal efficiencies of the concrete blocks treated with pure and doped TiO_2 in white (visible) light.

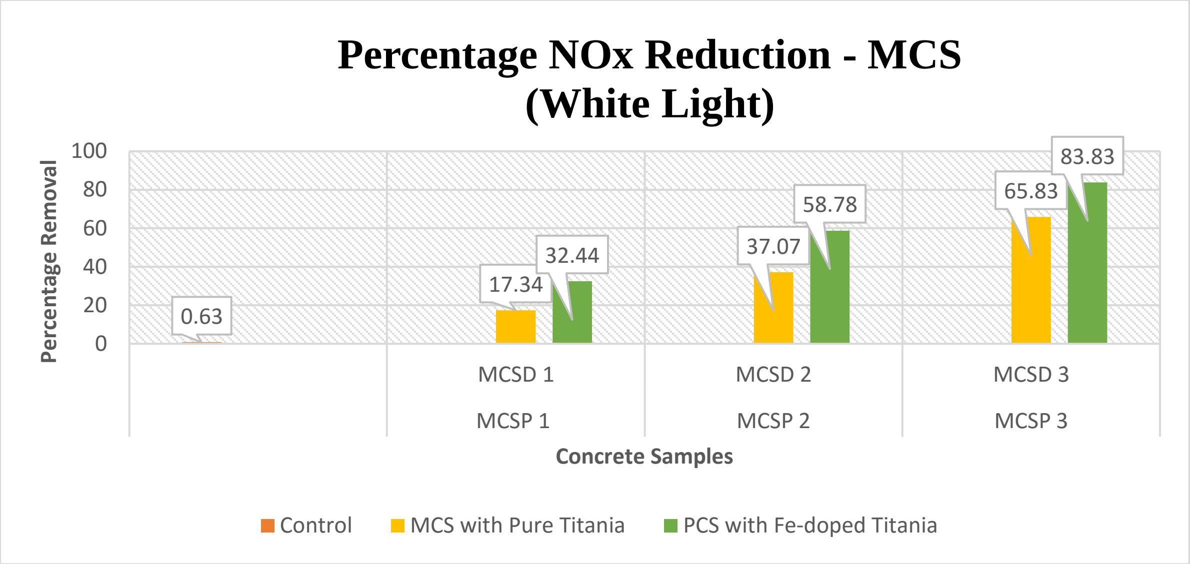

Figure 4.16: NOx removal percentages in MCS at 5, 10 and 15% Titania concentrations

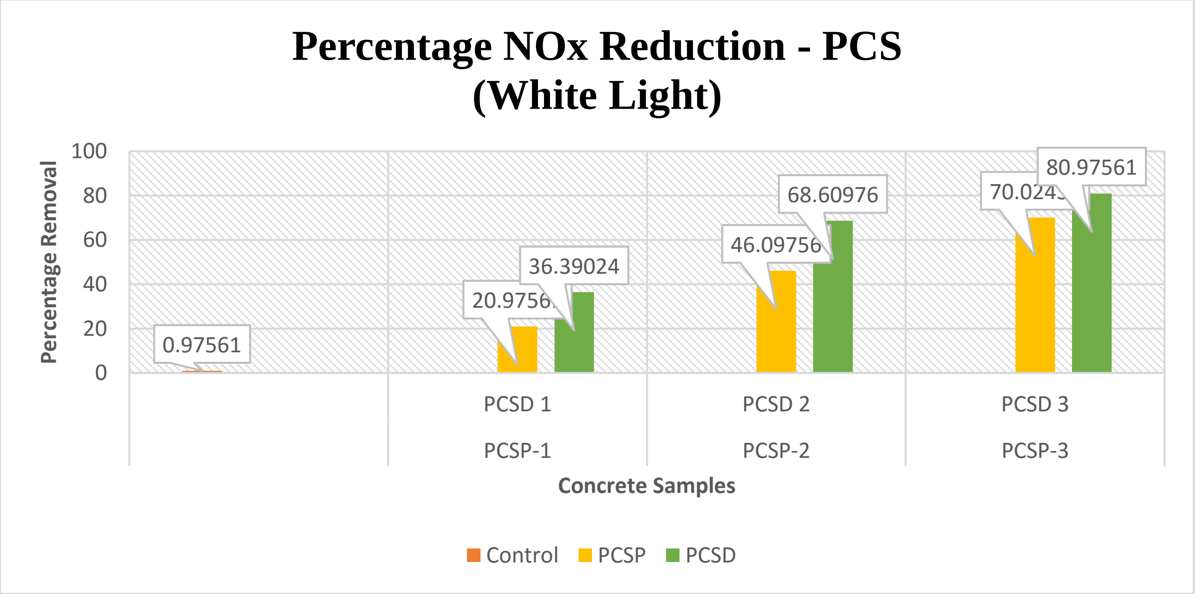

Figure 4.17: NOx removal percentages in PCS at 5, 10 and 15% Titania concentrations

4.4.2 NOx Removal in UV Light:

The results of NOx removal in environmental chamber when the samples were subjected to an 8 Watt ultra violet light are shown in the following table.

Table 4.4: NOx removal rates for all samples in "Ultraviolet" (UV) light

Concrete Sample	**Naming Convention**	**Pure TiO_2 (%)**	**Fe-doped TiO_2 (%)**	**Relative Humidity (%)**	**NOx Removal %**	**Time (hours)**
Mortar Concrete Samples						
Control-1	MCS-C	0	0	50	1.02439	5
5% TiO2	MCS 1	5	0	50	24.29268	5
10% TiO2	MCS 2	10	0	50	50.78049	5
15% TiO2	MCS 3	15	0	50	79.90244	5
5% Fe-TiO2	MCSD 1	0	5	50	42.63415	5
10% Fe-TiO2	MCSD 2	0	10	50	82.63415	5
15% Fe-TiO2	MCSD 3	0	15	50	96.07317	5
Pervious Concrete Samples						
Control-2	PCS-C	0	0	50	1.804878	5
5% TiO2	PCS 1	5	0	50	26.34146	5
10% TiO2	PCS 2	10	0	50	52.09756	5
15% TiO2	PCS 3	15	0	50	73.78049	5
5% Fe-TiO2	PCSD 1	0	5	50	49.5122	5
10% Fe-TiO2	PCSD 2	0	10	50	88.68293	5
15% Fe-TiO2	PCSD 3	0	15	50	98.60976	5

The NOx removal trends exhibited in the above two tables under two different light conditions clearly show that in an outdoor environment the NOx removal efficiency directly depends on the intensity to sunlight. Various other factors also infuence the removal efficiency such as humidity, air circulation rate, temperature as well as the concentration of TiO_2 used. However, as evident from the results above the removal efficiecy is greatly increased by the application of similar concentrations of doped TiO_2. These results when plotted on graphs (Fig 4.18 & 4.19) provided an excellent comparson of NOx removal efficiencies between pure and doped titania nano-particles in both white (visible) and UV lights as shown above.

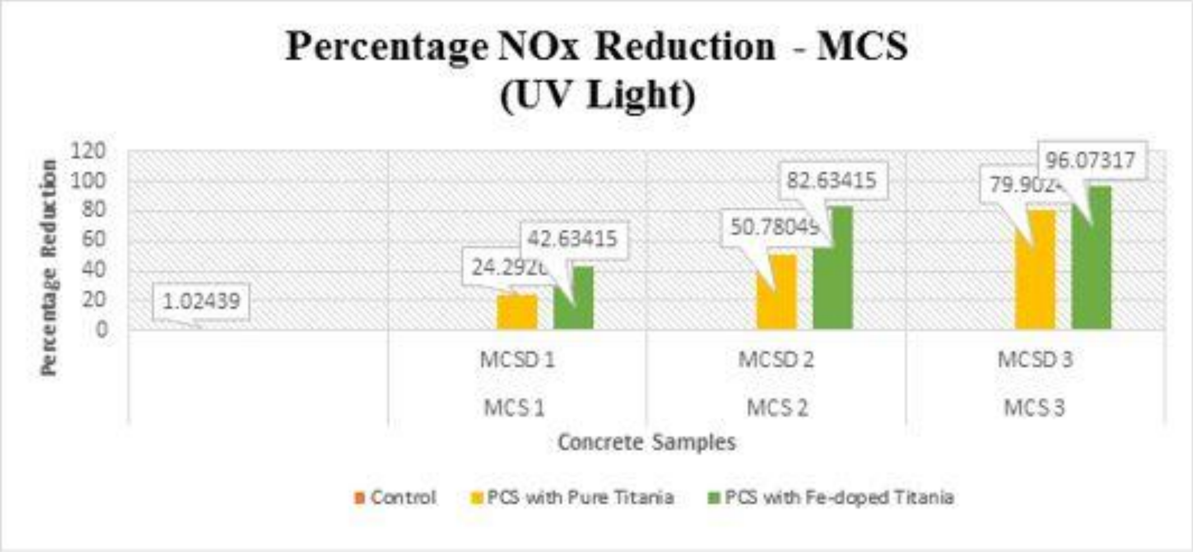

Figure 4.18: NOx removal percentages in MCS at 5, 10 and 15% Titania concentrations

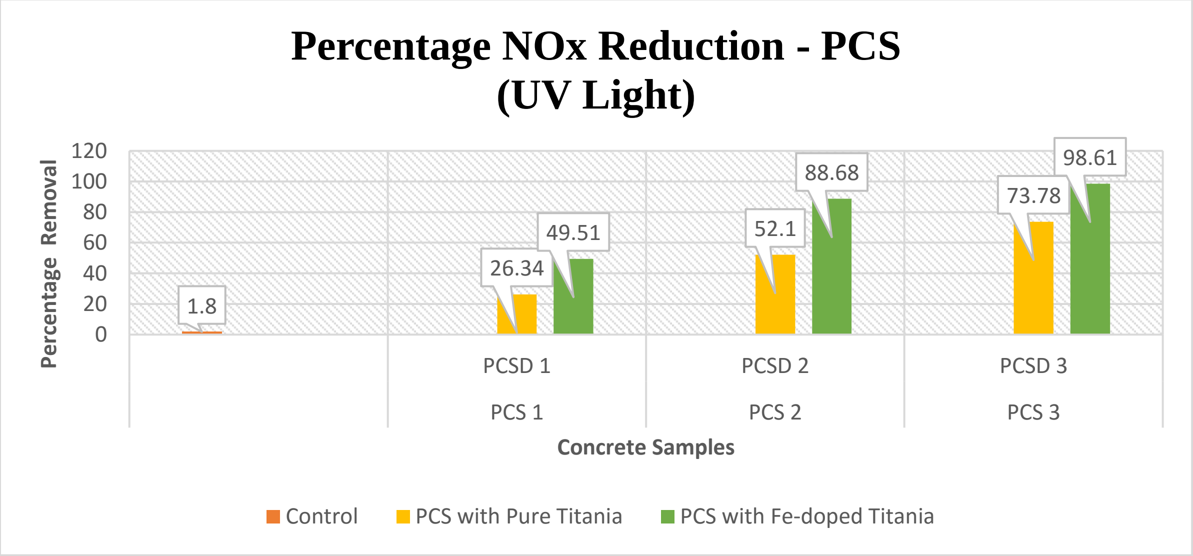

Figure 4.19: NOx removal percentages in MCS at 5, 10 and 15% Titania concentrations

Chapter 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Roads and pavements being a major part of the large urban centres have large surface areas directly in contact with the environment. It is due to this reason that treating them with photocatalytic TiO_2 nano-particles would allow removal of harmful air pollutants at street level, thereby providing a cleaner and greener environment for the general public. Although this research focuses only on the NOx removal from the environment, there are a variety of air pollutants such as toluene, trimethylebenzene and other VOCs, that can be adsorbed and decomposed using TiO_2 as a concrete additive not only to pavements and roads, but also to the rooftops of buildings and infrastrcture as well. The addition of TiO_2 to roads and pavements specifically has a greater significance as most of the transport related pollutants get adsorbed at the source, thereby controlling emissions of air pollutants to the environment significantly.

The research also concludes that TiO_2 when applied to pervious concrete makes it more efficient in pollutant removal than when applied in same concentration to mortar concrete, this is due to the fact that pervious concrete has a lot more surface area and it exposes way more TiO_2 particles to direct UV rays from the sun than the mortar and other conventional concretes. Similarly, pervious concrete gives additional benefits like storm-water management as it allows the water to infiltrate through it and percolate downwards to rechage groundwater aquifers. The porous nature of pervious concrete also protects TiO_2 particles from eroding or weathering of the surface due to abrasion and surface loading. Therefore, pervious concretes with TiO_2 provide a very sustainable transportation facility in urban centres besides improving the air quality.

However, for a country like Pakistan having a wide range of topography it is not always suitable to use pervious concrete for roads and pavements as in case of mountainous regions and some plateaus. As due to impacts for weathering and freeze and thaw cycles that follow every year in such regions may crack the pervious concrete. Therefore in regions like the himalayas and some parts of the potohar plateau and all other regions with these characteristics, it is more approprite to use mortar concrete instead of pervious concrete. From the environmental test results it can be seen that even though pervious concrete has an extra edge due to its stormwater management qualities, mortar concrete with TiO_2 also provides a very environmental friendly and sustainable transport system.

Moreover, the research also concludes that the atmospheric pollutant removal efficiencies, of both the mortar and pervious concrete, can dramatically be enhanced by replacing pure TiO_2 nano-particles with doped TiO_2 particles, which in this case were doped using an Iron salt, Ferric nitrate nona-hydrate [$Fe(NO_3)_3 . 9H_2O$].

Another benefit of TiO_2 addition to the concrete samples was the increse in their compressive strength. The maximum concentration was kept at 15% TiO_2 based on a previous research by Ahmed Husnain at IESE-NUST, in 2015. He found that the compressive strength of mortar concrete increases by increasing the concentration of the cement replaced by TiO_2 upto 15%, however when he increased the concentration to 20% the compressive strength decresed. Hence, addition of TiO_2 by cement replacement upto a certain concentration between 15 and 20% would increse the compressive strength of the both pervious and mortar concrete pavents/roads thereby providing additional economical benefits.

5.2 Recommendations

Since the TiO_2 application on concrete for photocatalytic removal of air pollutants is still a consierably new dimension of research, more research ought to be prescribed to assess the impacts of the TiO_2 addition to the concrete's microtexture and the effects of oil, trash, and deicing salts on the adequacy of the photocatalytic procedure. Research should also be directed to quantify the impacts of side effects coming about because of sanitization and the longterm adequacy of the photocatalytic procedure. The treated concretes still should be tried for resistance in varying weather and environmental conditions such as the fall, winter, and spring seasons.

REFERENCES

Agency, U. E. (1999). *Nitrogen Oxides (NOx), Why and How They are Controlled.* North Carolina.

Anwar, N. (2014). *Reduction of bacterial contamination on indoor surfaces using Titania nanostructures.* Islamabad: NUST.

ASTM C39 / C39M-15, (2015), Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens, ASTM International, West Conshohocken, PA.

Beeldens, A. (n.d.). *An environmental friendly solution for air purification and self-cleaning effect: the application of TIO2 as photocatalyst in concrete.* Brussels, Begium: Belgian Road Research Centre. Retrieved from a.beeldens@brrc.be

Berthelot, A. (2010). Concrete Steps: LSU Professor to Lay Pollution-Cleaning Pavement on Campus and Aster Street Dec. 13 – First time in United States that air purifying concrete and asphalt pavement have been laid. *Louisiana State University*. Retrieved January 2, 2011, from http://www.lsu.edu/ur/ocur/lsunews/MediaCenter/News/2010/12/item22709.html

Bolt, J. R., Zhuge, Y., & Bullen, F. (2011). Photocatalytic construction materials: An overview of recent developments and their application to permeable concrete. *Incorporating Sustainable Practice in Mechanics of Structures and Materials,* pp. 821-825.

Burton, m. C. (2011). *Pervious concrete with titanium dioxide as a photocatalyst compound for a greener urban road environment.* Washington state university.

Center, C. A. (n.d.). *Nitrogen Oxides (NOx), Why and How They are Controlled.*

Center, N. c. (2012). *Sustainable concrete pavements.* IOWA state unversity.

Chai-Mei Yu, J. (2003). *Deactivation and Regeneration of Environmentally Exposed Titanium Dioxidde (TiO2) Based Products*. Testing Report Departmental Order Ref. No. E183413, Environmental Protection Department (EPD), HKSAR.

Chen, D. H., Li, K., & Yuan, R. (2007). Photocatalytic Coating on Road Pavements/Structures for NOx Abatement. (Annual Project Report, Texas Air Research Center, Lamar University, 2007). *Houston Advanced Research Center and Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency*. Research Triangle Park, NC.

Chen, M., & Liu, Y. (2010). NOx removal from vehicle emissions by functionality surface of asphalt road. *Journal of Hazardous Materials*, Vol. 174, pp. 375-379.

Chusid, M. (2006). *Photocatalysts keep concrete clean and depollute the air we breathe*. Precast Solutions. http://www.solutions.precast.org/precast-concrete-depollution-and-photocatalysis-case-study. Accessed Jan. 2, 2011.

D.F. Ollis, E. Pellizzetti, Environ. Sci. Technol. 25 (9) (1991) 1523–1529.

Dylla, H., Hassan, M. M., Mohammad, L. N., Rupnow, T., & Wright, E. (2010). Evaluation of the Environmental Effectiveness of Titanium Dioxide Photocatalyst Coating for Concrete Pavement. *Transportation Research Board 89th Annual Meeting* (Publication No. 10-0963). Washington, D.C.

Fernandez-Rodriguez, H., Alonso, E., & Jose Cocero, M. (2009). *Synthesis of Doped Nanoparticles in Supercritical CO2*. International Society for Advancement of Supercritical Fluids. *9th International Symposium on Supercritical Fluids*. http://www.isasf.net/fileadmin/files/Docs/Arcachon/posters/p113-CO65%20alnso%209thMeeting_full_Alonso_Valladolid.pdf. Accessed March 7, 2011.

Frazer, L. (2001). Titanium Dioxide: Environmental White Knight? *Environmental Health Perspectives*, 109(4) A174-A177.

Ghafoori, N., & Dutta, S. (1995). Building and Nonpavement Applications of No-Fines Concrete. *Journal of Materials in Civil Engineering*, 7(4), 286-289.

Haselbach, L. (2009). Pervious Concrete and Mitigation of the Urban Heat Island Effect. Presented at 88th Annual Meeting of the Transportation Research Board, Washington, D.C.

Hashimoto, K., Irie, H., & Fujishima, A. (2005). TiO2 Photocatalysis: A Historical Overview and Future Prospects. *Japanese Journal of Applied Physics*, Vol. 44, No. 12, pp. 8269-8285.

Hassan, M. M., Dylla, H., Mohammad, L. N., & Rupnow, T. (2010). Effect of Application Methods on the Effectiveness of Titanium Dioxide as a Photocatalyst Compound to Concrete Pavement. Presented at 89th Annual Meeting of the Transportation Research Board, Washington, D.C.

Hassan, M., Mohammad, L. N., Dylla, H., Cooper, A. M., & Asadi, S. (2011). A Breakthrough Concept in the Preparation of Highly-Sustainable Photocatalytic Warm Asphalt Mixtures. Presented at 2011 NSF Engineering Research and Innovation Conference, Atlanta, Georgia.

Husnain, A. Immobilization in Mortar of Chromium Removed from Water using Titania Nanoparticles, Islamabad, NUST (2015).

Hong, X., Wang, Z., Cai, W., Lu, F., Zhang, J., Yang, Y., Ma, N., & Liu, Y. (2005). Visible-Light-Activated Nanoparticle Photocatalyst of Iodine-Doped Titanium Dioxide. *Chem. Mater*., Vol. 17, No. 6, pp. 1548-1552.

J.S. Dalton, P. J. (2001). *Photocatalytic oxidation of NOx gases using TiO2: a surface spectroscopic approach.* Bristol, UK: ELSEVIER. Retrieved from www.elsevier.com/locate/envpol

Katzman, L. (2006). Building Toward a Cleaner Environment: A New Role for an Existing Product, TiO2. *Sasaki Associates Inc*. Retrieved January 2, 2011, from http://ideas.sasaki.com/files/attachments/user370/cleaner%20environment.pdf

Li, Z. (2011). Development and Application of Eco-Friendly Concrete. *Advanced Materials Research*. Vols. 250-253, pp. 3827-3836

M.M. Ballari, M. H. (2010). *NOx photocatalytic degradation employing concrete pavement containing.* ELSEVIER.

Montes, F., & Haselbach, L. (2006). Measuring Hydraulic Conductivity in Pervious Concrete. *Environmental Engineering Science,* Vol. 23, No. 6, pp. 960-969.

Montes, F., Valavala, S., & Haselbach, L. (2005). A New Test Method for Porosity Measurements of Portland Cement Pervious Concrete. *Journal of ASTM International*, Vol. 2, No. 1.

Obla, K. (2007). Pervious Concrete for Sustainable Development. *Recent Advances in Concrete Technology.* Washington DC.

Puzenat, E. (2009). Photocatalytic self-cleaning materials: Principles and impact on atmosphere. *The European Physical Journal Conferences*, Vol. 1, pp. 69-74.

Ramirez, A. M., Demeestere, K., De Belie, N., Mantyla, T., & Levanen, E. (2009), Titanium dioxide coated cementitious materials for air purifying purposes: Preparation, characterization and toluene removal potential. *Building and Environment*, Vol. 45, pp. 832-838.

R.W. Matthews, in: E. Pelizzetti, M. Schiavello, *Photochemical Conversion and Storage of Solar Energy, Kluwer Academic Publishers, Dordrecht, 1991, pp. 427–449.*

Rocke, S., & Bowers, J. (2009). Use of pervious concrete is emerging in cold climates. *CE News*. Retrieved March 6, 2011 from http://www.cenews.com/print-magazinearticle-a_sustainable_pavement_alterna-6284.html

Shi, J., Chen, S., Wang, S., Wu, P., & Xu, G. (2009). Favorable recycling photocatalyst TiO2/CFA: Effects of loading method on the structural property photocatalytic activity. Molecular Catalysts, Vol. 303, pp. 141-7.

U.S EPA, Technical bulletin, “Nitrogen Oxides (NOx), Why and How They Are Controlled”, 1999.

Yang, J., & Jiang, G. (2003). Experimental study on properties or pervious concrete pavement materials. *Cement and Concrete Research*, Vol. 33, pp. 381-386.