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Photocatalytic Degradation of Harmful Pollutants emitted from the Vehicles by Titanium Dioxide (Tio2) incused Concrete Mix Pavements

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Abstract

This paper examines the major harmful pollutants emitted from the vehicles, their impact on human health and the environment and also introduces to a new concept of making pollution free environment along with the advancements in Engineering science. The data contents of this paper are: Current assessment of air pollution from the vehicles , Day-by-day increasing amount of harmful gas emissions, Description of Titanium dioxide (Tio2) and its behavior as a catalyst, Chemical science when Tio2 mixed with concrete and possible changes in its properties due to addition of Tio2, Comparison of sample concrete cubes with (a) Tio2 and (b) Tio2 along with co-doping of non-metals (B and N), Analyzing of degradation efficiency by standard tests under the action of UV-rays so as to convert harmful contaminants to harmless precipitate. Such eco-friendly way of degrading the emissions needs to be practiced. By this concept the environment also becomes fresh and pollution free and it also safeguards the public from many adverse health effects.

Keywords: - *Titanium Dioxide (Tio2), Photocatalytic Degradation, Precipitate, emissions, co-doping.*

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INTRODUCTION

Concern about the automobile as a source of air pollution has been expressed periodically, but national concern was first evidenced in the 1960s when California established the first new car emission standards. These were followed by U.S. federal standards in 1968. The 1970 Clean Air Act further imposed stringent HC, CO, and NOx reductions for 1975 and 1976. One of the goals of the Act was to set and achieve NAAQS in every state by 1975 in order to address the public health and welfare risks posed by certain widespread air pollutants. These reductions were subsequently delayed and changed by the 1974 Energy and Environmental Coordination Act and the 1977 Clean Air Act Amendments.[1] The scientific basis of this effort is the pioneering atmospheric chemistry research of A.J.Haägen-Smit, who showed that photochemical reactions among hydrocarbons (HC) and nitrogen oxides (NO x) produce the many secondary pollutants that reduce visibility and cause eye and nose irritation in the Los Angeles area. Previously notable works has been done for degrading these harmful emissions emitting from the vehicle by applying a coating of Tio2 on flexible bituminous pavements. [2] Now, most of the developed countries are been switching to rigid concrete pavements due to increased traffic intensity and vehicular load. So, such concept of photocatalysis for degrading harmful pollutants is been upgraded in this paper by using Tio2 catalyst directly in the concrete mix pavements. Considering the increasing amount of harmful pollutants emitting from the vehicles most of the automotive companies have come up with 3-phase catalytic convertor in-built in the vehicles as a remedy for this environmental imbalances.[3] Such research is made in this paper by introducing a catalyst in the cement concrete roads where the vehicles are constantly in contact (24 hrs) with it and also to achieve certain advancements in Transportation Engineering having much positive impacts on the Environmental Pollution.

METHODOLOGY AND MATERIALS

Removal of such air pollution which occurs from the automotive vehicles is of worldwide importance as such it goes beyond the national borders of each and every nation. In recent times, the essentiality to maintain a good eco-friendly nature has come up with the destruction of various pollutions in the atmosphere due to environmental contamination which occurs in any form of untreated hazards disposal or discharge of material into water, land, or air that causes

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or may cause acute (short-term) or chronic (long-term) detriment to the Earth's ecological balance or that lowers the quality of life .So the method introduced for removal of such pollutants is photocatalysis.

Photocatalysis

Photocatalysis is the amalgamation of photochemistry and catalysis. The prefix photo means light. Catalysis is the process where a substance involves in altering the rate of a chemical transformation of the reactants without being altered in the end. The substance which is known to be a catalyst increases the rate of the reaction by reducing the activation energy. Hence, photocatalysis is a process where light and catalysts are concurrently used to support or speed up a chemical reaction. So, photocatalysis can be defined as "catalysis driven acceleration of a light-induced reaction."

Classification of Photocatalysis

A.) Homogeneous photocatalytic processes mostly are used with metal complexes as catalysts (transition metals complexes like iron, copper, chromium, etc.). In this process, under the photon and thermal condition, the higher oxidation state of metalion complexes generated hydroxyl radicals. Then, these hydroxyl radicals react with organic matter which leads destruction of toxic matters.

B.) Semiconducting materials (TiO 2, ZnO, SnO 2, and CeO2) mainly act as heterogeneous photocatalysts, because of its favorable combination of electronic structures which is characterized by a filled valence band and an empty conduction band, light absorption properties, charge transport characteristics and excited states lifetime.[4] [5] [6]

Adopted process of Photocatalysis in this concept

When compared with other metal oxides, titanium dioxide (3.32 eV) is considered better and also a hopeful candidate for the photocatalytic devastation of harmful pollutants due to its high quantum efficiency, high stability in aqueous media and nontoxic in nature [7] [8] [9] [10]. But unfortunately TiO2 which is being highly evaluated for UV photocatalysis is inactive under visible light due to their wide band gaps. On the other hand, hematite can also be preferred photocatalytic material, because its absorption is in the visible region. While compared with TiO2, hematite shows lower photocatalytic efficiency because of corrosion property or the formation of short-lived metal-to-lig and or lig and-to-metal charge transfer

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states [11]. So, as a result of it co-doping of non-metals (B and N) with Tio2 is done in this concept for the preparation of photocatalytic concrete. Due the B and N co-doping with TiO2, the samples show visible light absorption since the synergetic effect modifying the electronic structure of TiO2 [12]. This heterogenous process of photocatalysis degrade the harmful pollutants emitted from the vehicles under the action of sunlight and convert them into harmless compounds thus forming precipitate which flows or washes away with the surface run-off or rainwater.

Photocatalytic Mechanism

Photocatalytic reaction primarily depends on wavelength or light (photon) energy and the catalyst. In general, semiconducting materials are used as a catalyst which performs as sensitizers for the irradiation of light stimulated redox process due to their electronic structure, which is characterized by a filled valence band and vacant conduction band [13].

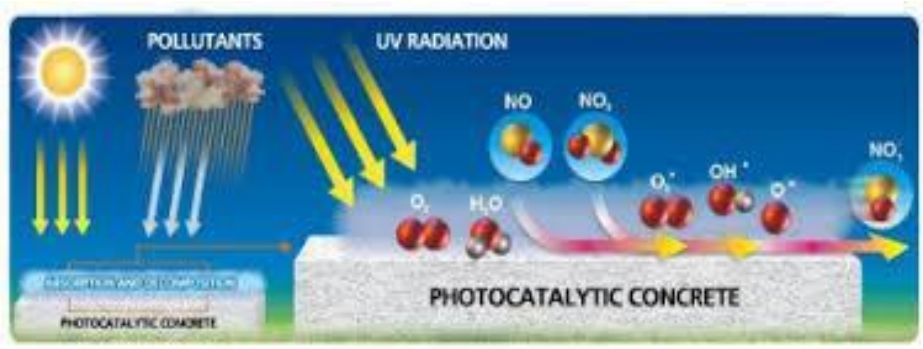


Fig1. Photocatalytic Degradation mechanism under the action of sunlight

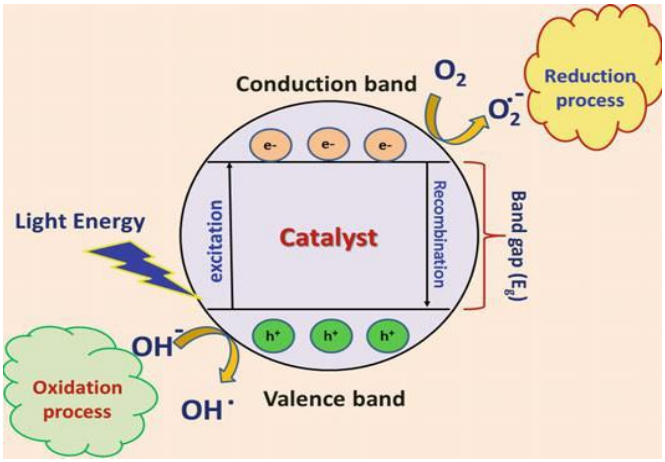


Fig 2 Schematic representation of semiconductor photocatalytic mechanism

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When the light energy in terms of photons fall on the surface of a semiconductor and if the energy of incident ray is equivalent or more than the band gap energy of the semiconductor, the valence band electrons are agitated and move to the conduction band of the semiconductor .Holes would be left in the valence band of the semiconductor. These holes in the valence band can oxidize donor molecules and react with water molecules to generate hydroxyl radicals (The hydroxyl radicals have strong oxidizing power responsible for the degradation of pollutants).The conduction band electrons react with dissolved oxygen species to form superoxide ions. These electrons induce the redox reactions. These holes and electrons could undergo successive oxidation and reduction reactions with any species, which might be adsorbed on the surface of the semiconductor to give the necessary products.

Description of Oxidation Mechanism

The photocatalyst surface contains water, which is mentioned as "absorbed water." This water is oxidized by positive holes created in the valence band due to the electrons shift to the conduction band as a result of light irradiation, thus making way for the formation of hydroxyl (OH·) radicals (agents which have strong oxidative decomposing power). Afterward, these hydroxyl radicals react with organic matter present in the dyes. If oxygen is present when this process happens, the intermediate radicals in the organic compounds along with the oxygen molecules can experience radical chain reactions and consume oxygen in some cases. In such a case, the organic matter finally decomposes ultimately becoming carbon dioxide and water .Under such circumstances, organic compounds can react straightly with the positive holes, resulting in oxidative decomposition[4] [10] [14].

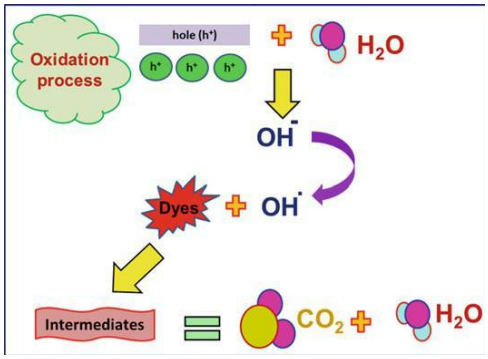


Fig 3 Schematic representation of oxidation mechanism

Description of Reduction Mechanism

The reduction of oxygen contained in the air occurs as a pairing reaction [4] [5]. Reduction of oxygen takes place as an alternative to hydrogen generation due to the fact that oxygen is an easily reducible substance. The conduction band electrons

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react with dissolved oxygen species to form superoxide anions. These superoxide anions attach to the intermediate products in the oxidative reaction, forming peroxide or changing to hydrogen peroxide and then to water. The reduction is likely to occur more easily in organic matter than in water. Therefore, the higher concentration of organic matter tends to increase the number of positive holes. This reduces the carrier recombination and enhances the photocatalytic activity [4] [7] [10].

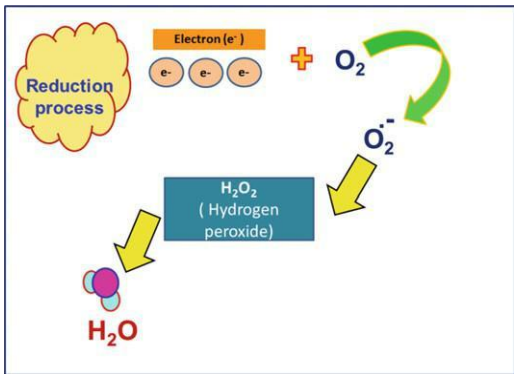


Fig 4 Represents the Reduction Process

Materials

Materials used in the developing cement slurry have the following properties:

a) Cement: Ordinary Portland cement of 53 grades with Specific Gravity 3.15, available in local market.

b) Fine aggregate (FA): Fine aggregate (river sand) obtained from local market was used in this study conforming to the Indian standard. (Zone II). Specific gravity of Fine aggregate was 2.68.

c) Coarse Aggregate [CA]: Coarse aggregate obtained from Local market (Sayla/sevaliya) was used in this study conforming to Indian standards. Specific gravity of coarse aggregate was 2.84.

d) Water: Potable water was used for mixing.

Experiments

Mix design of self – cleaning concrete

Two sets of photocatalytic cement pastes were prepared, one for each of the two commercial TiO2 products. The TiO2 and PPC were dry mixed in the mass ratio 4.0: 97.3. 20g of the mixture was subsequently hydrated with 8g of distilled water (water: solid mixture ratio, w/s = 0.4). A third set (control) was prepared without photocatalyst. After mixing, pastes were cast in 42 mm diameter x 5 mm height moulds and let harden (with no cover) for one day at room temperature and 80.5 % relative humidity. Six cement discs were produced for each set. After one day of curing, all samples were coated with RhB solution. The coating area was approximately 1.2 cm2. All three sets were subsequently irradiated with a UV lamp and reflectance measurements were

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performed after various time intervals using a Stellar Net EPP2000 Spectrometer. Present study involved M-25 grade of concrete with W/C ratio 0.45 (A.M.Neville) [15]. Consider Table 1 for Mix Design. The table represents the value of 6 cubes.

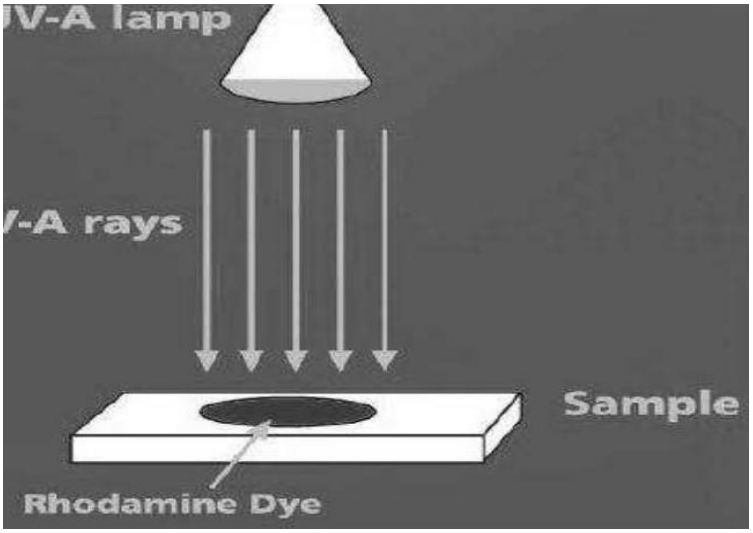


Fig 5 Self – cleaning measurement

Table 1 Mix Design proportion of photocatalytic cement

Cement (kg/m^3)	FA (kg/m^3)	CA (kg/m^3)		Water (kg/m^3)	Tio2 cement
8.0	13.50	14.00	12.50	3.80	4.0 : 97.3

Casting of cubes

Remove moisture from fine and coarse aggregate and mix it for 1min in concrete mixture, then add 1/3 part of water and mix for 30sec. Further add Mix of TiO2 and cement then mix for 30sec then add remaining water again and mix for 3min. Then vibrate for 3min and put in cube and make the surface smooth. All concrete batches were prepared in rotating drum Mixture [16]. First, the aggregates (Fine aggregates and coarse aggregates) are introduced in the mixture and then one - half of the mixing water is added and mixture machine is rotated for approximate two minutes and next cement is introduced with Tio2.150 mm × 150 mm × 150 mm concrete cubes are cast to see the photocatalystic effect . Then all the

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concrete specimens are kept for one day of curing.



Fig 5 Casting of Photocatalytic concrete cubes of known dimensions

Demoulding of concrete cubes

After one day of complete curing, all the concrete cubes are taken out from the curing pond. They are cleaned and dried properly so as to make them suitable for further test parameters. Care should be taken while demoulding of the concrete cubes as there should be no breakage of concrete blocks [16].



Fig 6 Demoulding of concrete cubes

Colorimetric Test

After one day of curing, all samples were coated with RhB (Rhodamine dye) solution on top side. Then these samples are kept exposed to sunlight so as to analyze the degradation efficiency of the photocatalytic concrete. Observations are thus noted on reducing the dye and measured between different specified intervals.

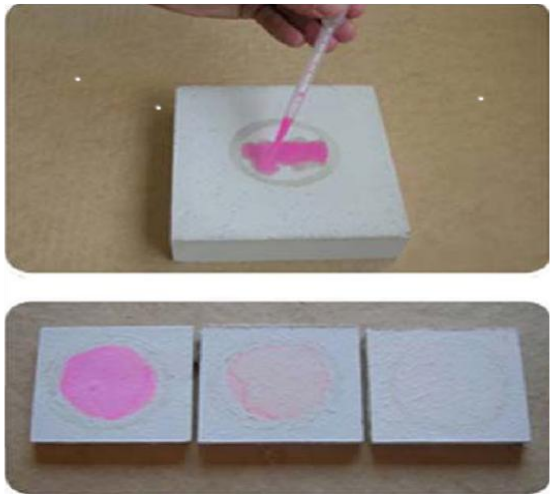


Fig 7 Application of Rhodamine b-dye on the concrete specimen

TEST RESULTS

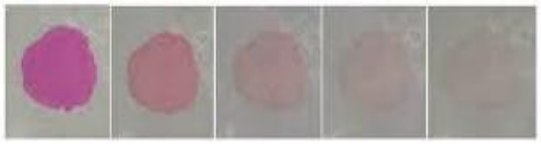


Fig 8

The above figure shows the reduction in Rhodamine b-dye applied on the prepared concrete surfaces under the action of sunlight

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The above experiment shows that the effect of Rhodamine dye is decreasing between different time intervals reduced levels of several environmental pollutants, NOx, SOx, VOC's, CO etc. Continuous oxidizing action results in clean roads for future prospect. So, the photocatalytic concrete containing Tio2 also acts as a self cleaning concrete which keeps its surface clean when exposed to sunlight more environment friendly (no chemical cleanings). Lower lifecycle maintenance costs. Potential for Innovation in Design LEED point credit for using the technology:

A) Exceptional performance in aged reflectance.

B.) Exceptional performance pollution abatement by, the above reduction of the rhodamine b- dye it is seen that photocatalytic degradation process has shown the desirable results and thus been an efficient practice in this concept.

CONCLUSION

The advantage of this concept is that the pollutants emitted from the automotive vehicles which are been increasing day by day are efficiently degraded by this process of heterogeneous photocatalysis. And another advantage is that the harmless compounds which is normally the precipitate formed after the photocatalytic degradation doesn't have any nuisance, odour or harmful reacting chemicals as a result it washes away with the rainwater. Also by implementing this method the human life is been safeguarded. The limitation of this method is that the Titanium Dioxide (tio2) becomes inactive in visible light so for that co-doping of non-metals should be done. Introducing such a new concept in transportation engineering which not only satisfies the basic principle of pavement construction but also keeps in consideration the environmental aspects. So to make the environment pollution free such concepts which enhances air purification should be implemented not only in developed countries but also in developing countries. By such projects we can not only come up to a permanent solution to the vehicle harmful emissions but can also upgrade new methodologies in the fields of photochemistry . This concept is a need of time as due to increase number of vehicles and huge population .Although there may be increased use of electric cars in the upcoming years , but by taking in consideration for nearly the further 30 –

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4 0 years where we will be facing some major environmental problems from the liquefied petroleum vehicles this concept is introduced . Research into photocatalytic technology has been progressing for over three decades. Photocatalytic technology will continue to improve with time and development becoming more efficient and effective. Photocatalytic concrete offers building professionals a unique opportunity to contribute to sustainable development goals while potentially improving the value of their investment.

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